CHEMICAL TECHNOLOGY
OF TEXTILE FIBRES

G. VON GEORGIEVICS

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THEIR ORIGIN, STRUCTURE, PREPARATION, WASHING, BLEACHING, DYEING, PRINTING, AND DRESSING

BY

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PREFACE

In the present volume, dealing with the Chemical Technology of the Textile Fibres (except as concerns the dye-stuffs, which will be treated in a separate work), the author has been obliged to condense the available matter as much as possible, in order to preserve the form of a text-book.

Nevertheless, it seemed necessary, in certain cases, in the interests of the book, to give definite data and an exact description of individual processes. In such instances the details have been gathered exclusively either from the author's personal experience or from reliable sources.

The most important part of the book is the chapter treating of dyeing, whilst, on the other hand, the subject of printing had to be dealt with in a more general fashion, the materials being less suitable for treatment in text-book style.

The author thinks it desirable to point out that in the present work an attempt has been made to completely separate the chemical and mechanical technology of the subject, a standpoint he considers justified by the extensive area occupied by each of these branches. Hence only a few sketches of apparatus have been given; and the methods of dressing the finished goods have been described very briefly, since they almost entirely belong to the domain of mechanical technology.

The author is indebted to Prof. J. Zipser for the whole of the sketches given, and to Mr. C. Schimke, teacher of dyeing at the Royal State Trade School, Bielitz, for much assistance in the production of the book.

GEORG VON GEORGIEVICS

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THE CHEMICAL TECHNOLOGY OF TEXTILE FIBRES

CHAPTER I

THE TEXTILE FIBRES

THE name textile fibres applies to such structures as, in consequence of their physical properties, are capable of being spun and worked up into textile fabrics. These fibres are supplied by all three natural kingdoms, and a few of them are also prepared artificially.

Although nearly a thousand textile fibres are known, only a few of them are of real interest. These are cotton, wool, and silk, followed by flax, jute, ramie and hemp, in a minor degree.

They are divided into four groups:—

1. Artificial fibres.
2. Mineral fibres.
3. Vegetable fibres.
4. Animal fibres.

1. ARTIFICIAL FIBRES.

To this series belong spun glass, metal thread, slag wool, and artificial silk.

Spun Glass.—When a glass rod is heated in the flame until perfectly soft, it can be drawn out in the form of very fine threads, which are used to a small extent in the production of very handsome silky fabrics (cravats, etc.) As spun glass can also be produced from coloured glass, the same method can be applied to the production of coloured fabrics. In consequence, however, of the low elasticity of these products, their practical value is *nil.*

For many chemical purposes, *e.g.* as filtering material for strongly acid liquids, a curly kind of glass wool is produced by drawing out two glass rods of different degrees of hardness to a capillary double thread. On cooling, these curl up in consequence of the different construction of the two constituent threads.

Metallic Threads.—From time immemorial fine golden silver threads, as well as silver gilt and silver threads or copper wires, have been used for decorating particularly rich fabrics. Thus the so-called Cyprian gold thread, so renowned for its beauty and permanence in the Middle Ages, is now produced by covering flax or hemp threads with a gilt skin.

Slag Wool.—Molten slag is run into a pan fitted with a steam injector, which blows the slag into fibre and furnishes a product which is used to a small extent as a packing material.

Artificial Silk.—This product, which is the most interesting of all the artificial fibres, will be described along with Cellulose.

2. Mineral Fibres.

To these belong **Asbestos**. This is a decomposition product of serpentine, and is, chemically speaking, a silicate of magnesium and lime, containing in addition iron and alumina. It is found in Savoy, the Pyrenees, Corsica, Mount St. Gothard, etc., and large deposits have recently been discovered in northern Italy and Canada.

Asbestos forms long, white, glassy fibres; some kinds, however, *e.g.* Canadian, are somewhat curly. Alone it is difficult to spin, and is therefore mixed with a little cotton, which is subsequently got rid of by heating the finished fabric to incandescence. Asbestos fabrics of this kind are generally used where exposure to high temperature is necessary, *e.g.* for packing steam cylinders and hot machine parts, also as a fire-proof material in the manufacture of numerous theatrical requisites, etc. Asbestos is difficult to dye; for this purpose the albumen dyes and substantive dyes are used.

3. Vegetable Fibres.

These are supplied in large numbers by the vegetable kingdom. They are divided into three classes:—(*a*) *Seed hairs.* These comprise cotton, the whole of the cotton tree, vegetable silk, etc. (*b*) *Bast* fibres, forming the cambium layer of dicotyledonous plants, *e.g.* flax, hemp, jute, ramie, Sunn hemp, etc. (*c*) The *vascular bundles* from leaves, stems, or roots of monocotyledonous plants, *e.g.* New Zealand hemp, Pite or Agave fibre, Tillandsia, pineapple fibre, Manila hemp, true aloe fibre, etc. etc. Vegetable fibres contain cellulose as their fundamental substance, in addition to which they are (or at least some of them) more or less lignified. The larger the proportion of woody matter they contain, the greater their brittleness. Finally, they also contain in their cells and interstices so-called encrusting materials (ethereal oils, resins, starch, colouring matter, etc.), and ash.

Cellulose.[1]

As this substance forms the main constituent of all vegetable fibres, a knowledge of its chemical behaviour is of great practical importance. The vegetable fibres, even when in a pure state, do not behave entirely alike towards chemical reagents. Thus, for example, cotton has a greater power of resistance to bleaching powder solution than flax. The name Cellulose must therefore be considered as a generic term applying to several bodies of very similar nature. Cellulose is a colourless, inodorous, and tasteless substance (sp. gr., 1·27 to 1·45), which is insoluble in ordinary solvents. It belongs to the carbohydrates, and its percentage composition is expressed by the formula $C_6H_{10}O_5$, though its true formula is certainly a multiple of this.

Starch is the most closely allied carbohydrate, and may also be regarded as the parent substance of cellulose. Little is definitely known with regard to its actual constitution; it is spoken of as a triatomic alcohol, since when heated with acetic anhydride it furnishes a triacetyl derivative which with potash, soda, lead, oxide, etc. forms loose saline compounds which behave like alcoholates.

More recently, however, a triacetylmonobenzoate and a tetrabenzoate have been formed, from which the presence of four hydroxyl groups may be deduced.

Pure cellulose is almost indestructible and can only be brought into a state of putrefaction in the presence of nitrogenous bodies. When heated it begins to turn brown at about 150° C.; when subjected to dry distillation it decomposes into water, CO_2, methane, ethane, methyl alcohol, acetic acid, pyrocatechin, etc. Furthermore, cellulose is a hygroscopic substance which cannot easily be brought to constant weight by drying. In water it is insoluble and is unchanged even by boiling for several hours; however, at 200° C. it dissolves in water, being itself completely decomposed.

Of greater practical importance is its behaviour towards acids and alkalis.

It resists very dilute mineral acids, but is decomposed and dissolved at ordinary temperatures by concentrated acids, *e.g.* a mixture of 1 part sulphuric acid and 3 parts water.

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[1] A monograph on Cellulose has been published by Cross, Bevan, and Beadle.

By moderately concentrated acids it is modified, the phenomenon being regarded as one of hydration ($mC_6H_{10}O_5 + nH_2O$). The resulting product hydrocellulose, which has the same chemical composition as glucose, is a pulverulent amorphous substance of some practical importance, being the cause of the rotting of acidified vegetable fabrics. On the formation of this substance is also based a method known as carbonising wool, whereby vegetable constituents present in wool are converted by the action of heat and sulphuric acid into hydrocellulose, which latter, being friable, is then easily eliminated by mechanical means. Finally, the same phenomenon (the formation of hydrocellulose) is the basis of the peculiar alteration sustained by paper when treated for a short time with fairly concentrated sulphuric acid, namely, a kind of superficial fusion of the cell walls of the fibre, whereby the paper acquires the same external appearance as animal parchment. This paper is therefore known as vegetable parchment, and can be used for the same purposes as true parchment.

Whereas cellulose is left unstained by iodine, this reagent turns vegetable parchment blue, like hydrocellulose in general.

Organic acids, like oxalic acid, tartaric acid, citric acid, act upon cellulose in the same way as mineral acids, when the cellulose, *e.g.* cotton, is impregnated with the dissolved acid and exposed to a high temperature; acetic acid, being volatilised by heat, has no action. The knowledge of this behaviour of cellulose is important, more particularly in the calico-printing industry.

Zinc chloride acts on cellulose like a mineral acid. The behaviour of cellulose towards nitric acid is important. When boiled with nitric acid of about 60 per cent. strength, cellulose is converted into oxycellulose. This oxidation product has a much greater affinity than cellulose for basic dye-stuffs, and is also of technical importance inasmuch as it is also formed by the action of other oxidising agents on cellulose,—for instance, when bleaching powder is carelessly used in bleaching cotton.

When concentrated nitric acid is allowed to act on cellulose, especially in presence of concentrated sulphuric acid, nitrogenous bodies are formed, which may be regarded as di-, tri-, tetra-, etc. nitrates of hydrocellulose, according to the conditions of the reaction. These substances are insoluble in water and alcohol, but are soluble *e.g.* in a mixture of alcohol and ether; the dissolved nitro groups can be separated again by treatment in various ways (*see* Artificial Silk).

The nitrocelluloses have been put to various interesting technical uses, *e.g.* hexanitrocellulose, which was discovered by Schönbein in 1847, and was by him termed *gun cotton.* Owing to its property of decomposing in an explosive manner when heated—water, nitrogen, carbon monoxide and carbon dioxide being formed—this substance has of late years been employed as an explosive and in the manufacture of smokeless powder. In addition to cotton, nitrocellulose is also prepared from jute and starch, which latter is closely allied to cellulose.

A material known as *celluloid* is prepared from the lower nitro products by dissolving them in molten camphor and pressing the mass while warm. This substance has a horny appearance, and is characterised by hardness, elasticity, transparency, and principally by the fact that when merely dipped in boiling water it acquires sufficient elasticity to enable it to be moulded into any shape under moderate pressure. In consequence of these valuable properties, celluloid is now largely used in the production of a large number of imitation articles, *e.g.* ivory, tortoiseshell, coral, collars, etc.

Finally, octonitrocellulose and other nitrocelluloses can be converted into so-called *artificial silk*, also known as Chardonnet silk, after its inventor. On dissolving nitrocellulose in alcohol-ether, a solution is obtained which has long been known and used under the name of " collodion." If this be forced through capillary tubes it forms very fine threads, to which a handsome silky appearance can be imparted by various mechanical processes. In order to fit this product for use as a textile fibre it must be deprived of its explosive properties, a result obtained by denitration, the threads being treated with various reagents, chiefly ammonium sulphide. This deprives them of a large proportion of their nitrogen, and leaves them not more inflammable than ordinary cotton. The first patent for the manufacture of artificial silk was taken out in 1855, but the material was first made known at the Paris Exhibition of 1889. More recently a company (La France) has been formed in Besançon, with a capital of six million francs, for working the Chardonnet patents. The *modus operandi* is as follows:—Loose wood pulp is disintegrated in a carding machine, so as to form a light and very bulky fleece like that furnished by waste cotton; this is dried by steam at 140° to 160° C., and the hot mass is immersed in a mixture of concentrated nitric and sulphuric acid, the operation being performed in earthenware vessels. The resulting nitrocellulose is centrifugalised, washed until it contains only about 10 per cent. of acid, and is then removed in small trucks, running on wooden rails, to the drying room—which must be at least fifty yards away from the factory—and is there dried at 30° C., great care being taken on account of the danger of explosion. The dried nitrocellulose is placed in iron pans on the same trucks and conveyed to the dissolving vats, containing equal parts of alcohol and ether, the quantity placed in the vats being regulated so as to secure a 20 per cent. solution of nitrocellulose. The resulting collodion is filtered through silk sieves and wadding in closed vessels, and then forced by an air-pump into a spinning apparatus, consisting of two horizontal parallel tubes fitted with a number of nozzles. In the one pipe through which the collodion flows these nozzles are made of glass, with a fine capillary bore through which threads of collodion appear. Each thread is immediately encountered by a very fine stream of water, delivered by a corresponding nozzle of a second or water-pipe, and descends into a water-trough, where it sets hard. From four to twelve of these threads are then united by a so-called collector, whereupon they immediately coalesce, and are then mechanically wound upon bobbins situated about twenty inches above the spinning apparatus. The alcohol of the collodion remains in the cooling water, whilst the ether volatilises, its heavy vapour falling into the water-trough under the spinning apparatus, and having to be removed therefrom by an aspirator. The further treatment of the threads is similar to that employed for natural silk; they are twisted and wound into hanks. Finally, the hanks are denitrated by immersion in a warm (30° C.) solution of ammonium sulphide, which, in about an hour, deprives them of 75 per cent. of their nitrogen; they are then rapidly immersed in a large volume of water, followed by water slightly acidified with nitric acid; finally they are wrung and dried at the ordinary temperature. The denitration process causes the silk to lose 40 per cent. in weight, which, however, can be replaced by impregnation with ammonium phosphate, this treatment also reducing its inflammability.

As may be seen from the preceding brief sketch, the manufacture of artificial silk is dangerous, complicated, and also expensive, nothwithstanding the partial recovery of the alcoholic ether. Strenuous endeavours are, however, being made to perfect the process, and already most of the difficulties, which chiefly reside in the denitrating process, have been overcome.

The La France Company reckons to produce 6 cwt. a day, and hopes to be able to increase this to 24 cwt. before long. The cost of production is said to be about 5s. per cwt., while the trade price is about 11s.

Other processes for the manufacture of artificial silk are those of Vivier, Lehner, Cardaret, and Langhans.

According to Vivier, a mixture of trinitrocellulose, fish glue, and gutta-percha is dissolved in glacial acetic acid; the composition of the solidifying liquid is kept secret. The finished product has a brilliant lustre, and is said to cost only about 1s. 6d. per cwt.

Lehner dissolves purified silk waste in concentrated acetic acid, and mixes therewith a solution of nitrocellulose in wood spirit and ether; turpentine and chloroform are used as the coagulating liquid.

Cardaret nitrates purified cellulose, bleaches it with aluminium hypochlorite, and dissolves it in acetone, ether, alcohol, toluol, glacial acetic acid, and castor oil, the resulting mass being broken down and worked by hot cylinders to make it plastic, and treated at the same time with a solution of gelatine, albumen, or other proteid substance in glacial acetic acid. The plastic silk-like mass is pressed into the spinning apparatus, and is finally treated with tannin to impart elasticity. The cost price is said to be about 2s. 6d. per cwt.

Langhans does not use nitrocellulose at all, but claims rather that cellulose can be so modified by repeated treatment with sulphuric acid of varying strength, that it can be used for the production of silk-like threads.

Artificial silk is deceptively like the natural product, and possesses a beautiful gloss; on the other hand, it lacks the necessary strength and elasticity to enable it to serve as warp. The tensile strength of true silk is twice as great as that of Chardonnet silk. Artificial silk can be dyed just the same as natural silk, but a further bad property of the artificial silk crops up here, namely that it cannot stand a warm bath, this rendering it strawlike, harsh, and inferior in softness to true silk.

Another important matter is the behaviour of cellulose towards alkalis. These, when dilute and in presence of air, act like mineral acids although much weaker, hydrocellulose being produced. When air is excluded their action is very slight indeed, a circumstance that should be taken into consideration in the bleaching of vegetable fibres. Concentrated alkalis produce a chemical change in cellulose, whereby the latter acquires a considerable affinity for dye-stuffs—probably this behaviour is also based on the production of hydrocellulose. This reaction is called "mercerisation" after its discoverer, Mercer; it will be further dealt with under Cotton. Latterly, Cross, Bevan, and Beadle have prepared, by the action of carbon disulphide vapours on mercerised cellulose, a mass which is said to be capable of various industrial applications, *e.g.* according to its consistence it may be used as an agglutinant, a loading agent, or a dressing material. It can also be cast in moulds, and when dry is horny, transparent, and may be cut and polished.

According to a patent taken out by L. Vignon and L. Cassella, the affinity of cellulose for basic dye-stuffs may be increased by amidising it (or the fibres) by treatment with calcium chloride and ammonia at 100° C. The behaviour of cellulose towards ammoniacal copper oxide is also worthy of note. In this solvent it readily dissolves in the cold to a sticky liquid, from which cellulose—partly in the form of hydrocellulose—can be precipitated as colourless flakes by acids. The ammoniacal copper oxide should be pure (free from salts) and concentrated. It is prepared by precipitating a dissolved copper salt by ammonia in the cold and in presence of ammonium chloride, the resulting blue precipitate being thoroughly washed with water, and then dissolved in cold concentrated ammonia to form a saturated solution.

Of the other reactions of cellulose, it should be mentioned that strong sulphuric acid and iodine stain it blue in consequence of the formation of hydrocellulose, whereas zinc iodochloride gives a violet stain. On the other hand, it may be distinguished from lignine in that, unlike the latter, which is stained yellow, it cannot be coloured by means of aniline sulphate.

(1) SEED HAIRS: COTTON TREE WOOL, VEGETABLE SILK.

Cotton.

Origin and Definition.—The name Cotton indicates the downy substance found in the seed capsules of plants of the species *Gossypium* (family *Malvaceæ*). It grows out of the seed, and is therefore a seed hair, consisting of a single cell. The seed is covered with a very coarse, generally yellow, brown or dirty green underwool, whereas the valuable cotton hairs are much longer and for the most part colourless.

For the purpose of cultivation only about five species of *Gossypium* are important, although about twenty are known. They are shrub or tree-like plants, measuring 3 to 24 feet in height, and thriving in all warm countries, their principal habitat being North America and India.

Gathering.—As soon as the cotton fruit is fully ripe, which occurs in August, September, and October, the capsules burst open and the cotton exudes. This is the most favourable moment for the harvest, and the capsules are plucked from the plant, the seeds and cotton being then taken out of the capsules. The cotton is separated from the seeds by means of so-called ginning machines, of which there are two chief systems in use—the roller gin and the saw gin. The former consists of rollers which seize and draw in the cotton fibre, whereas the seeds cannot pass through but are driven back. The saw gin consists of saw plates, which are mounted on rollers, the teeth projecting through a narrow grid through which they draw the cotton fibres, leaving the seeds to fall to the ground on the other side.

The seeds are used for the manufacture of cotton seed oil, whilst the cotton is pressed and sent to market in bales.

Historical.—Cotton has been known and used in Peru and India from the earliest times, and also seems to have been cultivated at a very early period in Persia. Thence it probably found its way to Egypt, where it has been known ever since about the fifth century B.C. At about the same time the Greeks and Romans, who previously had known only wool, began to wear cotton clothes.

The European cotton industry only began to come into importance at about the end of the eighteenth century, and may be considered to date from the year 1772, when the first cotton fabric was produced in England. At that time the supply of cotton was chiefly obtained from the Levant and Macedonia, but, later, America became the chief exporter; and since the North American War, India and Brazil have also successfully competed in the cotton trade. At the present time the demand for cotton is principally covered by North America, India, Egypt, and Brazil. The trade is now mainly centred in England, particularly in Liverpool; and the English cotton trade is the largest in Europe. The yearly consumption of cotton in the whole of Europe is estimated at about one million tons.

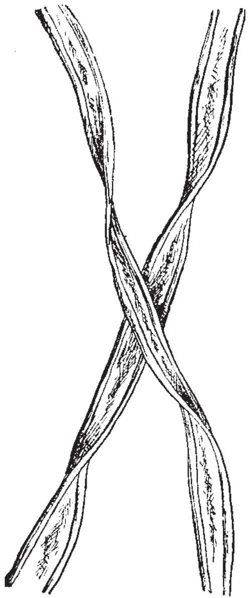


FIG. 1.

Commercial Varieties.—In commerce two principal varieties of cotton are known, namely, "long staple," the fibres of which are 1 to 2 inches long, and "short staple" from $\frac{1}{2}$ to 1 inch. The whiter, cleaner, and more silky the cotton the higher the value, but that consisting of short nepped fibres is inferior. The best and most highly prized of all is Sea Island cotton from *Gossypium Barbadense*, the finest grade of this being also known as "long Georgia," which at present is mainly grown in Florida.

Structure.—The cotton fibre is a single, elongated, conical, epidermal cell, the upper extremity of which is closed, whilst the lower end, which was attached to the seed, is broken off irregularly. Under the microscope the fibre (see Fig. 1) appears as a granular striped band, mostly twisted in the shape of a corkscrew. This is more particularly evident when the fibre has been moistened with water. This highly characteristic feature may nevertheless be absent in places.

The fibres are not cylindrical but flat, though this is sometimes not the case (in parts) in the finer kinds. There is a central cavity known as the *lumen*, which is generally small in proportion to the cell walls. Consequently the latter are often very thick, though in common grades the lumen is three or four times as broad as the cell wall. Occasionally the lumen is absent altogether, and the fibre is then known as dead cotton, being the immature and imperfectly developed hairs; these then take the dye with far greater difficulty than the normal fibres. Viewed under the microscope it appears perfectly transparent, only the edges being visible.

Externally the cotton fibre is surrounded by a fine skin—the cuticle. The substance from which this is formed does not behave exactly like cellulose, and is considered as a conversion product of the latter under the influence of light and air. Whereas cellulose is rightly soluble in ammoniacal copper oxide and concentrated sulphuric acid, the cuticle takes a long time to dissolve in this reagent. On treating the fibre with the first reagent under the microscope, the phenomenon so highly characteristic of cotton is observed: the internal substance, consisting of cotton, turns gummy, swelling up and bursting the cuticle in isolated places. The cuticle appears as though binding the cellulose as with a cord, whilst in other places it hangs in loops. Finally, the cellulose is completely dissolved, and the fragments of torn cuticle float in the solution (Fig. 2).

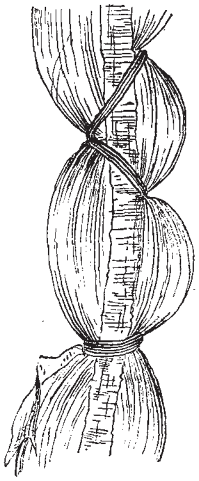


FIG. 2.

As the bast fibres, which will be described later, are devoid of cuticle, they do not exhibit this characteristic behaviour when treated with ammoniacal copper oxide. Consequently this reaction affords a valuable means of differentiation. It must, however, be mentioned that cuticle is not invariably present on all cotton, especially after strong bleaching, since under these circumstances the cuticle is mostly destroyed.

Chemical Composition.—Raw cotton consists of (in round figures) 87 to 91 per cent. cellulose; 7 to 8 per cent. water (cleaned cotton mostly a little over 5 per cent.); 0·4 to 0·5 per cent. wax and fat; 0·5 to 0·7 per cent. of protoplasmal residue and 0·12 per cent. ash; together with a very small quantity of colouring matter. The sp. gr. of air-dried cotton is 1·5.

Chemical behaviour.—Broadly speaking, this is the same as cellulose. However, in the presence of water, cotton fibre behaves somewhat differently from cellulose, inasmuch as it is far less hygroscopic, the reason being that cellulose (precipitated from solution in ammoniacal copper oxide) is in a more finely divided state. Special mention must also be made of mercerisation, *i.e.* the peculiar alteration sustained by cellulose when treated with strong alkalis. Thus, if cotton be treated with 28 to 30° Bé. caustic soda for about a minute at the ordinary temperature, there ensues, in addition to the aforesaid chemical alteration, a modification of structure: the lumen contracts and the fibres become much shorter and thicker. The contraction amounts to about 15 per cent., the increase of tensile strength to 20 per cent.; and the elasticity of the fibre is also augmented. This modification is also produced by far weaker lyes than the foregoing, *e.g.* an 8° Bé. caustic soda will partly bring about the same result. However, it is only cold lyes that act in this manner; hot lyes will not mercerise at all. Since the cotton hereby acquires a great increase in absorptive capacity for dyes, many attempts have been made to render mercerisation technically useful, but, until lately, they failed by reason of the great contraction suffered by the cotton. Recently, however, considerable progress seems to have been made in this direction, and in the process patented by Thomas and Prevost the cotton fibres are stretched whilst they are being mercerised and dried, thus entirely preventing the contraction of the fibre, which, in addition, acquires a powerful silky appearance.

Mercerisation is also employed in calico-printing. In the parts where the lye is brought into contact with the cotton, the fibre contracts and the fabric is therefore caused to assume a crinkled appearance like crepon.

Cotton goods, especially dressed fabrics, have a tendency to become mouldy when damp, the mould appearing in the form of yellowish to dark brown spots. In the early stages of development they can be got rid of by energetic washing; but later on this is no longer possible, and at this stage the cotton fibre or fabric will have become more or less corroded.

Mouldiness can be best prevented by storing the goods in dry, well-ventilated warehouses.

Another kind of spotting, more or less violet in colour, is due to the presence of iron tannate, resulting from the action of ferruginous water or solutions on the residual seed capsules (containing tannin) present in cotton that has not been properly cleaned.

Bombax Cotton from the Cotton Tree.

A kind of cotton similar to that of the cotton plant has, from time immemorial, been collected from the fruit capsules of plants of the Bombax family (allied to the *Malvaceæ*) in the countries of production, and utilised in various ways.

The Bombaceæ thrive in all tropical countries, but are little known in Europe. The cotton is found in commerce under various names, such as—vegetable down, ouate végétale, Edredon vegetal, Pattes de lierre. Bombax cotton is soft, lustrous, and white to yellow brown in colour. Being seed hairs, the fibres are morphologically similar to true cotton, from which, however, they differ in the absence of the spiral twist, the presence of reticulated thickenings of the cell wall, and in the inferior thickness of the latter; consequently they are much weaker than true cotton and cannot compete with it. The fibre is chiefly used for wadding and as an upholstering material, though occasionally it is mixed with cotton and spun. Bombax cotton may be distinguished from true cotton by the pale yellow tinge imparted by iodine and sulphuric acid or aniline sulphate, which indicates a slight degree of lignification.

Vegetable Silk or Asclepias Cotton.

The seeds of a number of *Apocyneæ* and *Asclepiadeæ* (mostly tropical) are provided with a tuft of long fibres possessing a beautiful silky lustre and known as vegetable silk. On account of their beautiful appearance many attempts have been made to spin these fibres, but failed by reason of their brittle character and low tensile strength.

The fibre is readily distinguished from cotton by its lignification, and from Bombax cotton by characteristic thickened strips, revealed in the cell wall under the microscope.

(2) BAST FIBRES: Flax, Jute, Hemp, and Ramie.

Flax.

Definition and Origin.—Flax consists of the bast fibres from plants of the Linum family. The species *Linum usitatissimum* being specially suitable for its production.

The true home of the flax plant is unknown, but it yields, especially in northern countries, a good bast suitable for the preparation of flax. This is the reason why nearly all flax growing countries get their seeds from the Russian Baltic provinces.

Preparation.—In order to obtain a good fibre the plants must be gathered before they are ripe, the proper time being indicated by the change in the colour of the seed capsules from green to brown. The harvest is carried on from June to September, the whole plants being pulled out of the ground, dried on the field, and finally rippled with iron combs to separate the stalks from the leaves, lateral shoots, and seed capsules. The bast fibres amount to about 70 to 75 per cent. of the stalks. These latter are now subjected to a process of retting, a kind of fermentation, the object of which is to decompose and render soluble the glutinous and intracellular substances, which cause the bast fibres to stick together and to the woody matter of the stalk.

This operation is the most important in the entire preparation of flax, influencing, as it does, the final product in the highest degree. It is performed in various ways — water retting, dew retting, mixed retting, warm-water retting, steam retting, and chemical retting. In *water retting* the flax stalks, tied in bundles, are placed in baskets and left for ten to twenty days in running or stagnant water. At first a turbulent acid fermentation is set up, and is followed by a quiescent alkaline fermentation. The stalks are taken out from time to time in order to see whether they are sufficiently retted, which may be recognised by their feeling soft and by the woody parts separating easily from the fibres. When this is accomplished the retting must be stopped immediately, since, if allowed to continue, the fibres would be damaged by over-retting. In *dew retting* the flax stalks are spread out in thin layers on a meadow, and moistened from time to time. This takes much longer than water retting. In *mixed retting* the first part of the fermentation is carried on in water, and the second completed on the grass.

These three methods are also known as "*natural retting*," and the water method being the cheapest is therefore the most in favour, notwithstanding that it does not yield a very handsome product, especially when performed in hard or ferruginous water. Over-retting is also very liable to occur, and an additional drawback arises from the intense putrescent smell given off, in consequence of which water retting must always be carried on at a distance from human habitations.

Natural retting being also greatly dependent on the weather, attempts have been made to supersede it by artificial processes, chief among which is the *warm-water retting* method invented by Schenk. It is similar to ordinary water retting, but is carried on in tanks wherein the water is warmed up by steam to about 35° C. The operation takes from two to three days, and furnishes a product superior both in quality and quantity to that obtained by natural retting; and is, moreover, the most rational method of procedure. Occasionally the bundles are subjected to an alternating treatment of steam and hot water, the process being then termed *steam or hot-water retting.*

Attempts have been made of late to improve existing methods by employing acids and alkalis. Thus an addition of sulphuric acid to the retting water is in so far favourable that it prevents the repulsive smell appearing during the alkaline fermentation. Finally, also a method of retting has been experimentally introduced, the chief feature of which is a treatment with dissolved alkali.

The flax stalks, having been retted by one or other of the foregoing methods, are well rinsed and dried; it is, however, highly advisable to first pass them through rollers, by which means the greater part of the mucinous matters enveloping the fibres are expressed, and the subsequent separation of the fibres from the wooden matter is greatly facilitated. To effect this separation, the dried stalks are subjected to the following mechanical operations:—

1. *Crushing or beating*, which consists in breaking down the woody matter by the aid of mallets or a stamping mill.

2. *Breaking.*—The stalks are passed between the fluted rollers of a flax breaking machine, whereby the woody matter is still further broken down, the greater part being at the same time removed.

3. *Scutching.*—The object of this treatment is the complete removal of the woody matter, and it is effected by beating the vertically suspended flax with blunt wooden knives. The work is done either by hand or in a machine, the fibre suffering less damage in the former case than in the latter.

4. *Hackling.*—The scutched flax stalks are drawn through a series of successively finer steel combs, which separate any fibres that still remain stuck together, and draw them out parallel. This work is also done by hand or machine.

Historical.—Flax is the oldest of all textile fibres, and has been cultivated in China from time immemorial. Linen wraps, some characterised by extreme fineness, have been discovered in lake-dwellers' habitations, and the wraps enveloping Egyptian mummies also consist of flax fibre.

Commercial Varieties and Statistics.—Flax is put on the market in the form of long, soft, lustrous fibres, the colour of the best kinds being a pale blonde. If the flax has been covered with mud whilst retting, it will have a greyish colour, and is particularly soft. Over-retted flax is dull and brittle.

The number of chemical varieties of flax is very large. The best kinds are produced in Ireland and Belgium, though a few French and Dutch varieties may also be included in the first class. The beautiful lustrous Italian flax is also highly prized, but Russian, Prussian, Silesian, and Austrian flax, although long in fibre and strong, are of inferior fineness. Egyptian flax is characterised by its extreme length, which averages about forty inches, whereas Silesian flax, for instance, averages only eleven inches in length. The annual consumption of flax in Europe is estimated at about 300,000 tons. These figures, however, cannot lay claim to any degree of accuracy, since the preparation of flax still remains to a large extent a home industry, and as such escapes the attention of the statistician.

Structure.—Under the microscope the flax fibre appears as a long, straight, transparent cylindrical tube of uniform thickness, either smooth or longitudinally striated, and frequently exhibiting tranverse cracks. In many places it presents nodes and displacements, which cause it to look as though articulated. These nodes, which are specially characteristic of flax fibres, are rendered darker by treatment with zinc iodochloride, and then become very clearly visible.

The natural ends of the fibres are sharp pointed and mostly attenuated; the cell walls are very thick, and the lumen is so narrow that it appears under the microscope as merely a black streak. The cross section of the fibre is also very characteristic, exhibiting a number of polygonal cells, in the centre of which the lumen appears as a yellow dot (in consequence of its yellow protoplasm). Sometimes, however, and especially in fibres taken from the lower part of the stalk, the cells exhibit a rounded shape similar to those of hemp.

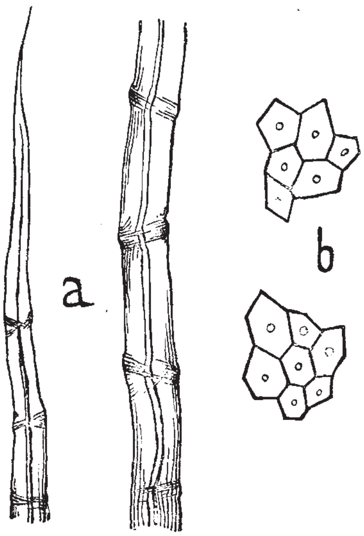


FIG. 3.—Flax Fibres.
a Longitudinal view; *b* Cross section.

Composition.—The purified flax fibre consists of almost pure and quite unlignified cellulose, so that, like cotton, it is stained blue by iodine and sulphuric acid, and is not tinged yellow by aniline sulphate.

In the air-dry condition flax contains about 5½ to over 7 per cent. of water, and various amounts of cellulose, pectin substances, fat, wax, and ash, differing according to the preparation. According to Vignon the specific gravity of flax fibre is 1·5.

Chemical behaviour.—In presence of reagents flax behaves very like cotton, though, mainly owing to the structure, it takes up mordants and dyes less readily than the latter. Moreover, the impurities of crude flax—especially the brown pectin substances—are more difficult to remove than in the case of cotton, and consequently the operation of bleaching flax is harder than with cotton. Flax fibre is more susceptible than cotton to the action of bleaching powder. When treated with ammoniacal copper oxide, it swells up considerably without, however, quite passing into solution.

Hemp.

Definition and Occurrence.—Hemp consists of the bast cells of the hemp plant *Cannabis Sativa*, which, like the flax plant, thrives in moderate subtropical climates. In hot countries, India for example, it yields a defective fibre, though, on the other hand, it produces large quantities of seeds, which are strongly narcotic and therefore used in the preparation of delicacies like *hasheesh*.

Preparation.—This is effected in the same manner as flax, though occasionally the bast is stripped off from the plant whilst still fresh, the product in this case being valued on account of its length and purity.

Historical.—Like flax, hemp belongs to the oldest of the textile fibres. Of all European countries it seems to have been longest cultivated in the South of France.

Commercial Varieties and Statistics.—In commerce a distinction is drawn between clean and stripped hemp. The small waste fibres obtained in hackling are called tow. Since hemp is for the most part coarse and of dark colour, and is very difficult to bleach, none but the very finest qualities are spun, the great bulk of the article being used in the manufacture of string, cord, rope, hawsers, etc., for which its great strength renders it particularly suitable.

The handsomest varieties of hemp come from Italy, and among these Bologna hemp occupies the first place, being fairly white, lustrous, very fine, and flexible. Next to the Italian kind comes Grenoble hemp. The largest quantities are, however, obtained from Russia, whilst other hemp producing countries include North America, Alsace, the south of Baden, Prussia, and Austria. Mention should also be made of the African giant hemp, which, as its name implies, is characterised by great length, the fibres measuring upwards of ten feet long.

About 500,000 tons a year are produced in the whole of Europe, one-fifth of which quantity is grown in Russia.

Structure.—Examined under the microscope the fibre of hemp is very similar to flax, exhibiting displacements, longitudinal fissures, and transverse cracks. On the other hand, the lumen is broad and only contracts to a narrow line near the tip; moreover, the entire fibre is less regular in thickness than flax. The ends of the fibres are highly characteristic, being very thick walled and blunt (see Fig. 4), frequently branching sideways, and thus affording a ready means of distinguishing this fibre from flax when examined under the microscope by a low and high power in succession.

The cross section is also different from that of flax, the cells being mostly in dense groups, with rounded corners, and giving a yellow margin when treated with iodine and sulphuric acid. The lumen, instead of being circular, is elongated, frequently branched, and devoid of contents.

FIG. 4.
Ends of Flax Fibre.

Composition.—In addition to cellulose, hemp fibre contains a not inconsiderable quantity of woody matter, differing in this respect considerably from cotton and flax. According to Vignon, the specific gravity of hackled hemp is 1·48.

Chemical behaviour.—Iodine and sulphuric acid stain hemp fibre green to dirty yellow, the various strata in the cell walls assuming different colours. Unlike the fibres previously described, hemp is stained slightly yellow by concentrated nitric acid. Treated with ammoniacal copper oxide the fibre turns blue to green, swells up in bubbles, without however dissolving, and exhibits delicate longitudinal striations.

Jute.

Definition and Occurrence.—Jute consists of the bast fibres of several varieties of *Chorchorus* indigenous to India. These plants yield such an enormous quantity of fibre that land planted with jute gives a crop from two to tenfold greater than is obtained from flax or hemp.

Preparation.—The jute fibre is obtained from the plant by cold-water retting, and is cleaned by scutching and hackling. Great care, however, is necessary in carrying out the first-named operation owing to the ease with which jute becomes overretted.

The fibre is prepared for spinning by steeping it in an emulsion of oil and soap previous to hackling.

Historical.—Jute has long been the most important fibre produced in India, and has grown in importance in European commerce since 1860, when the Crimean War led to a scarcity of Russian hemp.

Commerce, Statistics, and Uses.—Jute comes on the market as a yellow to French-grey fibre. The coarser kinds are worked up in the production of coarse fabrics, sacks, packing cloths, and the like, whilst the finer kinds, in which the undesirable property of growing darker with age is less apparent, are employed for making carpets, curtains, and heavy plush, for which its high lustre renders it suitable. Jute is also not infrequently used along with animal fibres; and it also serves to mix with hemp, though its low tensile strength militates against it.

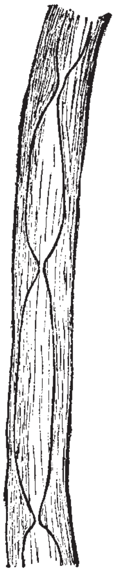


Fig. 5.
Jute Fibre.

Structure.—In microscopic structure jute fibre exhibits a certain similarity to hemp and flax, inasmuch as the cells in the cross section are grouped, polygonal and sharp cornered. On the other hand, the longitudinal view shows neither displacement nor striations, and the lumen is nearly as broad as the cell walls or even more so, besides being strongly constricted at intervals—a special characteristic of jute fibre. In consequence of the irregular thickening of the cell walls, it is advisable before examining jute under the microscope to treat it with alkali or chromic acid, which isolates the individual fibres.

Composition.—Differing from other bast fibres, jute mainly consists of a compound of cellulose with lignine or other similar body, the compound being known as *bastose*. The specific gravity of jute is the same as that of hemp.

Chemical behaviour.—Jute gives the lignine reaction by taking a yellow stain with iodine and sulphuric acid, whilst aniline sulphate colours it dark yellow. When treated with chlorine the principal constituent, bastose, is converted into a compound, which, like cotton containing tannin, is stained a fuchsine red by alkaline sulphites. It may be distinguished from hemp by the red-brown stain produced by concentrated nitric acid. Jute cannot be bleached with chloride of lime since it combines with the chlorine and yields an insoluble compound with the lime. Consequently, sodium hypochlorite must be used for bleaching.

Jute is usually dyed in an acid bath, though alum should be employed on account of the weakening effect produced on the fibre by mineral acids.

Ramie, Rhea, China Grass, Nettle Fibre.

Definition and Occurrence.—For a very long time silky, soft, and extremely strong fibres, known under the above names, have been prepared in China and India from various species of nettle, particular importance attaching to the fibres from *Boehmeria nivea* and allied species. At present ramie and China grass are no longer considered as being distinct fibres.

Preparation.—Although there are numerous species of nettle yielding handsome fibres, only comparatively few are utilised, the stings of many of these plants having a very powerful action on the skin, and consequently rendering their manipulation very difficult.

Ramie fibres are obtained by stripping the fresh bast from the wood. In China, the freshly cut stems of the plant are first scraped to remove the rind, then left exposed to the sun for several days, after which the bast is thoroughly damped with the morning dew and is carefully peeled off, the fibres being then boiled and dried. As the bast will not easily strip except when the stalks are quite fresh, the successful preparation of ramie entails the employment of a very large number of hands in order to be able to treat the whole of the crop at once. To get over this difficulty, Sansone proposed to store the fresh cut stalks in a solution of bisulphite in brickwork pits. Recently a great deal of trouble has been taken, especially in France and North America, over the construction of suitable decorticating machines for stripping the bast from the stalks in a quicker and more rational manner, this forming the most difficult part of the whole process. When ramie is prepared in the form of single isolated cells like cotton, instead of cell bundles like the other bast fibres, it is known as cottonised ramie, and can be spun to very handsome yarn. In Europe, ramie is bleached in the same way as cotton, and thereby acquires dazzling whiteness.

Historical.—Ramie fibre has been prepared in India and China from time immemorial, and has also been found in mummy wraps. In more recent times ramie cultivation has been introduced into Egypt, Algiers, Spain, Italy, France, etc.

Commerce and Statistics.—It is only of late that ramie fibre has attained a certain degree of importance in Europe, and this would be still further increased were the difficulties in the way of its preparation removed.

China alone exports at present about 3500 tons per annum.

Chinese ramie or China grass is generally met with in commerce in the form of slightly yellow or greenish fibres up to about 8 inches long. It is only when the fibre has been bleached that it develops its valuable properties of gloss, whiteness, softness, and strength, which would render this fibre the most perfect of all those of vegetable origin, were it not for one great drawback, namely, that the surface of the fibre, instead of being smooth, is covered with a number of fine projecting fibrils. These greatly diminish the lustre of ramie fabrics, and are also the cause why ramie is not very suitable for the production of body linen.

Ramie is used in conjunction with other fibres; for example, it is spun along with wool, the resulting yarn being used as a weft in woollen-warp fabrics.

Structure.—Ramie fibre chiefly differs from the other vegetable fibres in the great length and breadth of the bast cells, which are up to 8 inches or more in length, and on the average about twice as broad as cotton. The fibre is very irregular longitudinally; in the wide parts it is ribbon-like, flat, and also exhibits frequent displacements and longitudinal and cross fissures. The axial twist noticed in cotton also occurs here. The lumen is broad, the ends of the fibres are thick and rounded, and exhibit a linear lumen similar to that of hemp. In cross section the cells are mostly independent, very large, long and compressed.

Composition.—Ramie fibre consists of almost pure cellulose, without any lignification. The specific gravity is 1·51 to 1·52.

Chemical behaviour.—Iodine and sulphuric acid impart a copper red to pure blue coloration, according to the degree of purification. Ammoniacal copper oxide gives a blue stain, the fibre swelling up greatly at first and finally passing entirely into solution. Aniline sulphate gives no coloration.

The intracellular substance connecting the bast cells has very low powers of resistance against reagents, a circumstance explaining the ease with which ramie fibres can be bleached.

Distinguishing Tests for the Various Fibres.

As may be easily gathered from the foregoing descriptions, there are two modes available for recognising and distinguishing the various vegetable fabrics, viz. the microscope and chemical reactions. In employing the microscope, it should be remembered that the characteristic indications of a fibre are often lacking in places, or less frequently observable in some kinds, one instance of this being the spiral twist in the case of cotton. Consequently the examination of a single fibre is insufficient, and must be extended to several throughout their entire length. Chemical reactions, or rather the characteristic colorations given by the different fibres with various reagents are largely dependent on the concentration of the latter and on the purity of the fibre. Thus, for example, a highly bleached cotton twist often fails to give the characteristic reaction with ammoniacal copper oxide, owing to the fact that the cuticle may have been removed in bleaching.

It is advisable to use reagents of a constant known strength. The usual solutions are prepared in the following manner:—

Iodine Solution.—A 1 per cent. solution of potassium iodide is completely saturated with iodine; this solution must be renewed from time to time.

Sulphuric Acid.—3 parts by volume of concentrated sulphuric acid are mixed with 1 part of water and 2 parts of perfectly pure glycerine; fresh acid must be added from time to time. This solution will then be of the right strength for examining fibres. When a flax fibre is treated therewith it does not swell up, but on the addition of iodine immediately gives a blue coloration, and not merely a pink or violet.

Zinc Iodochloride.—A concentrated aqueous solution of zinc chloride is added to a solution of iodine in potassium iodide, the following proportions being taken—

1 part I.	30 parts $ZnCl_2$.
5 parts KI.	14 parts H_2O.

As to which of these two methods more quickly and readily leads to the desired result, this depends on circumstances. In any event, the microscopical examination is so important that it should not be omitted except in rare cases, the more so because the majority of the colour reactions have to be performed under the microscope. Thus, for example, if a linen fabric has to be tested for cotton—a case of practical importance, inasmuch as linen goods are frequently adulterated with the far weaker fibre cotton—then a simple examination of a few fibres under the microscope will infallibly accomplish our purpose. The loose, flattened, and frequently twisted shape of the cotton fibre is so characteristic as to readily distinguish it from the straight, stiff flax fibres, and in fact all the bast fibres. In this case no colour reaction is needed.

In distinguishing flax from hemp, two important criteria come under consideration—(1) The lignine reaction, hemp being, as a lignified fibre, stained yellow by aniline sulphate, whereas flax is not: (2) The ends of the fibres; these being pointed in the case of flax, but thickened and often forked in hemp. As already mentioned in describing hemp, a low power (20 to 30) should be used first.

Jute is distinguished from flax by the lignine reaction, and from hemp by the nitric acid reaction (jute is stained red-brown, hemp a pale yellow). Under the microscope the chief distinctive characteristic of jute consists in its irregularly thickened cell walls, which cause the lumen to appear strongly constricted in places.

Finally, as regards the differentiation of ramie from other fibres, this presents no difficulty, owing to the great breadth of the ramie fibre.

4. Animal Fibres.

Silk, Wool, Goat Wool, Camel Wool, and Byssus Silk.

General Properties and Differentiation from Vegetable Fibres.—As their name implies, the animal fibres are of animal origin, and consequently do not, like the vegetable fibres, consist of cellulose, but of complex nitrogenous bodies of the protein class. In addition, the animal wools contain sulphur.

For the above reasons their behaviour is therefore very different in presence of the usual reagents and dye-stuffs. This difference is already apparent when they are simply moistened with water, which they take up less readily than the vegetable fibres, and which causes them to swell up to a smaller extent than the latter. The practical consequence of this behaviour is self-evident: the animal fibres, especially sheep's wool and goats' wool, require to be more strongly wetted than the vegetable fibres in the course of preparation for dyeing. Nevertheless, the animal fibres are much more hygroscopic than those of vegetable origin, *i.e.* they take up much more moisture when exposed to damp air.

The two classes of fibres also exhibit very important differences in their behaviour towards acids and alkalis.

The animal fibres, wools in particular, are more resistant than the vegetable fibres towards acids, a property on which the well-known method of separation, termed carbonising (*q.v.*), is based. On the other hand, they are much more susceptible towards alkalis, and on this peculiarity is based the determination of cotton and other vegetable fibres in mixed fabrics and wool substitutes. Consequently special care must be adopted in treating animal fibres with alkaline reagents.

The carbonates of potash and soda should be used at temperatures not exceeding 50° C., even when in a dilute condition. Caustic alkalis, except ammonia, have an injurious action on animal fibres under all circumstances. Considerable difference also exists between the two classes of fibre in dyeing, animal fibres having a greater affinity for the dye-stuffs, especially the acid dyes; the same remarks apply with regard to mordants, a point that will be discussed later on.

In bleaching, the use of chloride of lime is inadmissible for animal fibres, owing to the corrosion produced. Finally, the behaviour of the two classes of fibre when burned is so divergent that this test offers a ready and reliable means of distinguishing between them. On setting light to a vegetable fibre it burns rapidly, and gives off a smell of burnt paper (which itself consists of vegetable fibre), leaving behind a loose white ash. Animal fibres, on the other hand, burn very slowly, give off a smell of burnt horn, and fuse to a small bead of hard porous carbon. Vegetable fibres can be quickly detected in association with animal fibres by warming the sample of fabric with dilute alkali, and examining it under the microscope after washing: the animal fibres will be found considerably swollen and transparent, the vegetable fibres scarcely swollen at all, and sharply defined. Again, if the sample be boiled for about a quarter of an hour in 8° B. soda lye, the animal fibres will dissolve; the residue is then examined for the presence of vegetable fibres, by the combustion test and under the microscope.

Animal wools are distinguished from all other fibres by containing sulphur, and, if boiled along with a solution of lead oxide in soda lye, they will turn black, owing to the formation of lead sulphide.

Silk.

Morphologically, silks are the simplest, and in their other properties the most perfect and the most highly prized, of the textile fibres. The chief difference is in point of structure, since whereas the vegetable fibres are organised, and are products of vegetable growth, and wool also grows as an organised structure out of the skin of the sheep, silk is a solidified secretion of the larvæ of various moths, and consequently is devoid of cellular structure. According as silk is obtained from the larvæ of wild moths or the cultivated silk-worm, it is termed wild or true silk. These two varieties differ in so many respects as to necessitate entirely separate descriptions, the true silk being taken first on account of its far greater value.

True Silk.—The life history of the true silk-worm, *Bombyx mori*, is identical with that of the wild silk-worms, and may be briefly described as follows:—

The perfect insect neither takes nourishment, nor does it produce silk, the sole object of its short existence being the reproduction of the species. From the egg laid by the moth is hatched the sexless form of the insect, the larva, and from this in turn proceeds the pupa or quiescent intermediate form. In order to protect the unharmed pupa from external influences, the larva, before passing into the pupal stage, surrounds itself with a casing or cocoon of silk fibre, which cocoon forms the raw material for the manufacture of silk.

Silk-Worm Breeding.—This pursuit is carried on in establishments known as "magnaneria," and also as a home industry. The first condition for founding an establishment of this kind is the planting of a sufficient number of mulberry trees, the true silk-worm feeding exclusively on mulberry leaves and requiring an abundant supply of these to enable it to produce fine cocoons. A deficient food supply causes the worm to produce either a smaller quantity or inferior quality of silk. 14,000 larvæ, the cocoons of which will eventually yield from 3 to 4½ lb. of silk, will consume during their lifetime about 9 cwt. of leaves, from which figures it can easily be seen that very large mulberry plantations are required for production of silk on a large scale.

When fresh, the eggs of the silk-worm are yellow, dry, whitish grey, and resemble ordinary poppy seeds in form and size, about 16,000 being required to weigh a lb. For hatching, they are spread out on sheets of paper in well ventilated and slightly damp chambers, the temperature of which is gradually raised in ten to twelve days to 60°, 64°, 68°, and 77° Fahrenheit; at this temperature the larvæ, which are very small, motile, and covered with blackish hairs, emerge from the egg, and are transferred without delay to frames covered with white paper. Only those from one hatching are put on the same frame, in order that they may all subsequently spin at the same time. They are now fed with fresh, dry, mulberry leaves cut up, and, in proportion as the larvæ grow, they must be transferred to larger frames. Uniform temperature and moisture, care, cleanliness, and abundance of fresh food are indispensable conditions for obtaining strong healthy worms and good quality silk.

The silk-worm is an extremely voracious animal and grows at a correspondingly rapid rate, until it attains three to four inches in length and weighs about one-sixth of an ounce. At this stage it is of a floury whiteness, or spotted with brown and black, and its body is divided into ten segments, the foremost of which is somewhat enlarged, and carries the head and true legs. It is interesting to note that these legs are of the same colour as the silk that will be subsequently supplied by the worm, *i.e.* white, yellow, or greenish. During its lifetime the silk-worm sheds its skin four times, and is at this period particularly susceptible to external influences. After the fourth shedding, the larva lives another eight or ten days, whereupon it ceases to eat, evacuates the contents of its stomach, and moves restlessly about. It is now transferred to dry mulberry or other twigs, where it at once begins to spin, discharging from its under jaw a thread (silk), with which it first forms a loose network or bed, and then begins to spin the true cocoon. This it does by moving its head to and fro, and winding the exuding silk thread around its body in a very regular manner. In a short time it is completely enclosed, and the cocoon is finished in about four days. Inside the cocoon the larva developes a final skin, and is converted into the pupal state. The shape of the cocoon differs according to the sex of the future insect, the females being oval, whilst the males are a little smaller, more cylindrical, and slightly constricted in the centre. They average about 1·2 inches long, and 0·6 to 0·78 inch across. When fresh they have the following composition—

Water, ...	68·2%
Silk, ...	14·3%
Waste, ...	0·7%
Pupa, ...	16·8%

They are formed of a single, seldom interrupted, double fibre, which is strongest and most uniform at the centre and varies in length from 400 to 3300 yards. The innermost layer of all, surrounding the pupa, resembles a thin skin of parchment. After about ten days the cocoons are collected and sorted. Double cocoons produced by two larvæ spinning themselves in together, or cocoons exhibiting other peculiarities, must be sorted out, being unsuitable for the manufacture of silk in the ordinary manner. Moreover, a certain number of the male and female cocoons are set aside for the purpose of reproduction, all the rest being sent to the reeling house.

The cocoons intended for breeding are placed in a chamber heated to a temperature of 68° F., where, in about twenty days after the completion of the cocoon, the moth, which in the meantime has become perfectly developed, moistens one end of the cocoon with saliva, pushes the threads apart, and crawls out. The wings are kept in constant motion until they have expanded to their full size. The moth is floury white in colour and immediately begins to pair, its life terminating as soon as the eggs have been laid. The eggs are carefully dried and stored until the following spring in a cool, dark, dry place. 1 grm. (15 grains) of eggs will yield over 11,000 larvæ = 3 to 5 lb. of finished cocoons.

Diseases of the Silk-Worm.—Silk-worm breeding is a difficult operation, entailing great care and attention. Moreover, the larvæ are subjected to a number of diseases. At the commencement of the sixties, two highly devastating epidemics made their appearance in the silk-worm industries of southern Europe and India. Their origin was investigated by Pasteur and others, and traced to fungoid growths developing in the bodies of the larvæ.

The Chinese and Japanese breeding establishments are, it is true, unaffected by this disease; but, on the other hand, the Japanese industry suffers another disease caused by a species of ichneumon fly, which bores holes in the young silk-worm and deposits its eggs within the body of the latter.

Silk Manufacture.—The first task consists in killing the pupæ in the cocoons. It is effected in one of two ways, either by heating the cocoons in an oven for two or three hours at 60° to 70° C., or by exposing them for about ten minutes to the action of steam. The cocoons are then sorted, the best and finest being used for the production of so-called organzine, whilst the inferior grades are used for making trame. In weaving silk fabrics, the organzine fibres are used as warps, and trame as wefts. The silk threads forming the cocoons are next reeled, for which purpose they are first steeped in hot water in order to soften the gelatinous matter surrounding the threads, and are placed in a basin of luke-warm water. The attendant who looks after the reeling, then works the cocoons about with a small brush of twigs, in order to find the ends of the threads. Several ends are then united to a single thread and two sets of compound threads of equal thickness are passed separately through perforated agate guides, and, after crossing at one point, are again parted, passed through a second pair of guides and thence on to a reel which is worked at a speed of 800 to 900 revolutions per minute. The mucinous matter, softened by the hot water, causes the loose cocoon threads to stick together and form the simplest class of raw silk thread—grège.

Reeling is a work requiring the greatest attention in order to prevent tearing the silk during the search for the ends, and also to secure uniform thickness in the reeled threads. It is a matter of considerable difficulty, and a good deal of silk gets broken during the former operation.

Recently an automatic silk reeling machine was invented by an American, E. W. Serrell.

Working up Waste Silk.—The silk forming the outer layer of the cocoon, and also that of double cocoons, perforated, burst, or otherwise defective cocoons, and the broken ends in reeling, constitute the so-called waste or florette silk. These cannot be worked up by reeling, but have to be treated by Lister's process—namely, scouring with soda and soap, then combed or carded in suitable machines like cotton, and finally spun. There are two classes of waste silk, namely, florette and bourette; the former consists of the better and longer fibre and is prepared in a manner more similar to worsted, whilst the inferior bourette is worked up in the same way as carded yarn.

At the present time florette spinning forms an important branch of the silk industry; nevertheless it is inferior in value to reeled silk.

Historical.—The historical data on the subject of silk are so comprehensive and interesting as to deserve mention in the present work. China is the home of the silk industry, and it has been known there from time immemorial that certain larvæ contain a secretion from which very durable threads can be produced. At one time these threads were used in making strings for musical instruments, and they are even now employed as fishing lines.

The discovery that fabrics could be prepared from cocoons is attributed to Te-ling-Shi, wife of the Emperor Hoang-te, about 2650 B.C. This monarch is also said to be the first to wear silken garments; and his lady was, after death, raised to the rank of a deity. From that time the Chinese silk industry has been closely connected with the history of the country. It was placed under royal protection, and for a long time formed a monopoly of the monarch and nobility.

The ancient Greeks were also acquainted with Chinese silk and held it in very high estimation. Thus, according to a calculation made by Pariset in the time of the Emperor Aurelianus, one pound of raw silk was worth about £24, and one pound of purple dyed silk four times that amount. This price, however, subsequently fell away to a great extent, so that in the fourth century all classes in Rome wore silken garments. Florette silk from the wild Assyrian moth was also known to the ancients and highly prized, namely, the so-called Bombykia, from which the Coan fabrics were manufactured. In India, Persia, and Japan, the cultivation of silk was introduced from China, though it is undeniable that many of the inhabitants of those countries were already acquainted with and made use of this fibre. In Europe, silk was long regarded as a vegetable product. It was introduced during the first half of the sixth century of our era, and it is recorded that about this period the first silk-worms were brought to Byzantium, concealed in hollow bamboo rods, by two monks. The industry thus founded afterwards spread to Greece, Spain, and Italy.

Commerce and Statistics.—At the present time the cultivation of true silk is carried on (with great care) not only in its Asiatic home, in China, Japan, and India, but in southern Europe, Italy, the south of France, Greece and the Levant. China and Japan are the chief sources of supply of eggs for the European silk-worm industry, the diseases already mentioned having devastated the breeding establishments in southern Europe and India. Nowadays silk culture is making advances in every direction, *e.g.* in Bulgaria, China, and Japan. Although far from equalling European silk in fineness and regularity, the Asiatic silk predominates in point of quantity, and the Chinese production is increasing largely. The early cocoon crop in China is estimated at 270,000 tons, and the total production throughout the world at 460,000 tons of fresh cocoons, equivalent to 28,000 tons of grège silk.

Physical Properties.—Raw silk is usually yellow to white in colour, though occasionally of a faint greenish tinge (Japanese silk), and only after being boiled and subjected to various mechanical operations does it acquire those properties for which it is so highly esteemed.

Scoured silk is distinguished by high lustre, strength, toughness, and elasticity, the tensile strength being almost as great as that of iron wire of equal thickness. The elasticity is also high, a dried silk thread being susceptible of extension by one-seventh to one-fifth of its original length. These two properties mainly reside in the outer glutinous layer and are diminished by about 30 per cent. in scouring. Moreover, immoderate loading (in black dying) deprives the silk of a good deal of its valuable properties. When dried silk is moistened it contracts by about one-seventh, and the same also occurs in dyeing.

Silk is a poor conductor of electricity, and when subjected to friction remains electrified, a circumstance which may cause a deal of mischief in the manufacturing process; this defect, however, can be obviated by keeping the factory atmosphere moist. A property possessed by silk alone of all the textile fibres is that of emitting a crackling sound (scroop) when compressed. This property, however, is not originally present in the silk, but is acquired after immersion in an acid bath. No proper explanation of this phenomenon has yet been discovered, but it is assumed that the acid roughens the surface of the fibre, and that the noise results from the increased friction thereby ensuing when pressure is applied.

Production and Structure of the Silk Fibre.—The silk fibre is produced in two glands along the inside of the body of the silk-worm, which glands are in the shape of convoluted cylindrical threads, and occupy a considerable amount of space in the full-grown larva. The glands consist of three principal portions (Fig. 6):

(1) the part *a*, *b*, where the silk is probably formed; (2) the broader part, *b*, *c*, wherein the silk is probably stored; and finally (3) the capillary tube, *c*, *d*, where a partial hardening of the silk occurs. In this manner two threads are simultaneously formed, which unite at *d*, and issue from the silk-worm's head in the form of a double thread, which only becomes thoroughly hardened on exposure to the air. If the silk gland be cut through at the thickest part, it is found to consist of two distinctly separate parts, an internal transparent layer, and an external stratum which is colourless, greenish, or yellow, according to the breed of the silk-worm, and occupies about one-fourth of the total volume. As in the scouring of raw silk, which dissolves the sericin, an almost identical loss in weight occurs, it is concluded that this is formed simultaneously with the substance of the silk.

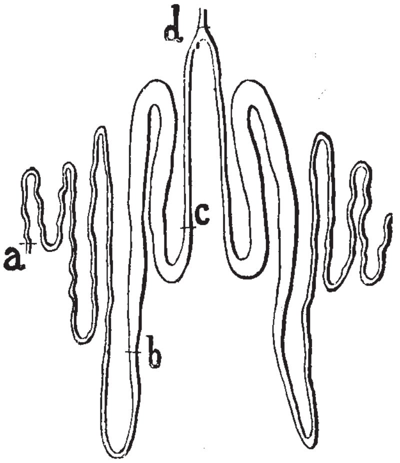


FIG. 6.

In harmony with this method of formation, the silk fibre exhibits under the microscope the appearance of a clear cylindrical double thread, enclosed in a cloudy integument. As is shown in Fig. 7, the two threads stand apart in places; and in scoured silk are entirely separated; consequently, whilst raw silk consists of a double thread, the scoured silk is single.

Florette silk can be recognised by the irregular appearance of the external layer (Fig. 8).

The structure of silk is, however, not so simple as the microscopical picture would lead us to expect; and in fact the fibre is composed of a number of smaller elements or fibrils, connected together by a small quantity of matrix. This can be concluded from the following facts:—

When a silk fibre, exhibiting a slight striation, is treated with chromic acid under the microscope, the striation is rendered more clearly defined. More conclusive evidence is, however, afforded by the behaviour of the fibre in presence of moderately strong sulphuric acid assisted by heat, since if, after impregnation with this acid, the silk be dried and then heated to 80°–100° C., it will be found, on careful examination under the microscope, to be entirely disintegrated into fibrils, separated by the preceding treatment. A similar, and still more decisive, proof is afforded by "lousy" silk (see later, under Decortication).

Chemical Composition.—As already stated, the silk fibre consists of two portions, the outer layer, or *sericin*, and the real substance of the silk, or *fibroïn*, the latter constituting about two-thirds of the total material present in the raw silk.

Sericin is a substance soluble in water and resembling ordinary gelatine, though, when boiled for some time with dilute sulphuric acid, it furnishes decomposition products differing from those yielded by gelatine.

Fibroïn is entirely insoluble in water and is classed along with the proteids. On comparing the empirical formulæ of fibroïn and sericin, the following simple relation is found to exist between them:—

$$\underset{\text{Fibroïn}}{C_{15}H_{23}N_5O_6} + O + H_2O = \underset{\text{Sericin}}{C_{15}H_{25}N_5O_8}$$

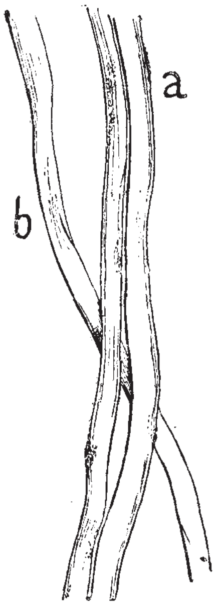


Fig. 7.
(*a*) Raw Silk Thread.
(*b*) Scoured Silk.

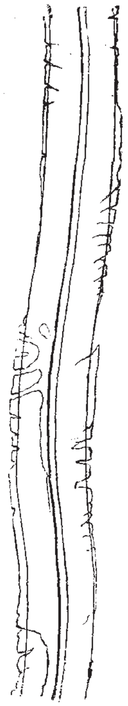


Fig. 8.
Florette Silk.

It is therefore possible that sericin is produced from fibroin, an assumption that would seem to be justified by the fact that when scoured silk, entirely freed from sericin, has been left for some time exposed to damp air, it loses in weight on being subsequently boiled in water.

In addition to the foregoing substances raw silk also contains water, and, in small amounts, fat, wax, and pigmentary matter.

The specific gravity of both raw and scoured silk is 1·34 (Vignon).

Chemical Properties and Absorptive Capacity.—Silk will stand a temperature of 110° C. without undergoing any alteration, but rapidly decomposes on being heated to 170° C. When held in a flame it burns, and, like wool, appears to fuse, without, however, disengaging such an unpleasant smell as is evolved by the latter.

When in the pure state, silk is highly resistant towards putrefactive agencies. It is very hygroscopic, absorbing as much as 30 per cent. of water when exposed to damp air. Owing to this circumstance, and the fact that it is a very expensive material and is sold by weight, it becomes necessary to determine the actual weight of silk in each bale, an operation that is performed in silk-conditioning houses, which establishments will be described later on.

In addition, silk is a very porous substance, and has a high absorptive capacity for all kinds of bodies, *e.g.* alcohol, acetic acid, tannin, sugar, etc. Its capacity for absorbing dye-stuffs is greater than that of any other textile fibre, and is even exhibited at the ordinary temperature. Furthermore, certain salts, used as *mordants*, are absorbed in large quantities by silk, a phenomenon on which is based the operation known as loading or weighting silk.

Warm dilute acids dissolve the sericin, but leave the fibroïn untouched; concentrated acids, however, exert a destructive action. Cold acetic acid dissolves out merely the colouring matter of raw silk, without attacking the sericin, though when heat and pressure are applied the silk dissolves in this acid. Concentrated nitric acid stains silk a beautiful yellow, xanthoproteic acid being formed. This coloration is deepened by alkalis but lightened by acids, and is destroyed by a boiling hot solution of stannous chloride. Formerly this colour was utilised industrially.

Concentrated basic zinc chloride dissolves silk to a viscous solution. A concentrated acid solution of zinc chloride also readily dissolves silk, and the solution can be diluted with water without precipitation being produced. When the liquid is dialysed, to completely remove the acid, an aqueous solution of chemically altered sericin is obtained. This operation, though undoubtedly interesting, does not, however, seem capable of any practical utilisation, inasmuch as the bulk of the sericin is thrown down during dialysis, and in no case is the solution entirely free from zinc, however prolonged the operation may be. On evaporating the solution to dryness, a yellow substance is obtained, which resembles colophony in appearance and is no longer soluble in water.

Dilute alkalis diminish the gloss of the silk, and when moderately concentrated dissolve the material in the warm. Ammonia exerts no appreciable influence in the cold, and soap acts merely as a solvent of sericin, though, after prolonged exposure at boiling heat, the fibroïn also is attacked.

Silk is soluble in both ammoniacal copper oxide and ammoniacal nickel oxide, but differs from cotton in not being reprecipitable by additions of salt, sugar, etc. This solubility in ammoniacal nickel oxide—as also in zinc chloride—can be utilised as a quantitative test for silk in mixed fabrics, the following method being adopted, according to Richardson:—

Twenty-five grms. of crystalline nickel sulphate are treated with caustic soda to throw down the oxide, which is then carefully washed and rinsed by the aid of 125 c.c. of water into a 250 c.c. flask, which is filled up to the mark with ammonia (sp. gr., 0·88), the liquid being then employed for treating the tissue under examination by boiling them together for ten minutes under a reflux condenser. The silk is completely dissolved, and the cotton loses 0·8 per cent. in weight. For silk and cotton goods the following method is, however, preferable:—

A solution is prepared of 1000 parts fused zinc chloride and 40 parts zinc oxide in 850 parts of water; and the fabric, after being boiled in this solution for one minute, is freed from zinc by washing with hydrochloric acid (1 per cent. strength). Under this treatment 0·5 per cent. of the cotton (or 1·5 to 2 per cent. of wool, if present) is also dissolved.

Wild Silk.—In China, Japan, and India, the home of the true silk-worm, there are also found insects belonging to the nocturnal peacock moth family, which not only have the same life history as the true silk-moth, but also furnish a very similar class of silk, though differing therefrom both morphologically and in point of behaviour towards chemical reagents.

Although the manufacture of fabrics from the cocoons of wild silk-moths was practised in the aforesaid countries from the earliest times, it was only about 1860 that, in consequence of the silk-worm disease, the attention of European silk manufacturers was drawn to this material.

The chief reason for this is to be sought in the fact that the wild silk-worm makes several pauses when spinning the cocoon, the consequence of which is that the cocoon is composed of several threads difficult to disentangle and therefore unsuitable for reeling. However, since Lister's method of working up waste silk was applied to wild silk, the cocoons of these wild spinners have become an important factor in the European silk industry, plush and velvet in particular being now made in large quantities from this raw material.

The main advantages of wild silk are—(1) Its greater durability, owing to the greater thickness of the threads, though, in consequence of the method of treatment pursued, the true silk threads are stronger in the finished fabric; (2) Greater cheapness and productivity, inasmuch as the wild silk-worms do not require to be cultivated, but spin their cocoons on trees in the open. Moreover, the cocoons are larger and yield more silk than those of *Bombyx mori*, and many of them bring up several broods in a season (2–8), whilst *Bombyx mori* gives only one crop in the year.

On the other hand, apart from the inferior regularity of the cocoons, the wild silk-worms exhibit the disadvantage of furnishing a silk that is always more or less highly coloured and is very difficult to bleach. For this reason wild silk is mostly spun and woven in an undyed—natural—condition. There is, however, some hope that this difficulty can be surmounted, since, according to the observations of O. N. Witt, wild silk is always colourless when first formed, but is afterwards soiled by the secretion employed by the worm to moisten the spun thread. The coloration thus imparted depends on the plant on which the larva has been fed, and is darker in proportion as the plant is richer in bodies that furnish pigments on exposure to the air. Hence, if the worms during the latter stage of their existence be fed on plants incapable of furnishing such pigments (tannin, etc.), perfectly white silk will be obtained.

On this point practical experiments on a large scale have been successfully carried out, Major Coussmacker having obtained perfectly white cocoons in India by feeding the larvæ of *Antherœa mylitta* in a suitable manner. This result is the easier of attainment in that, unlike the true silk-worm, the larvæ of the wild spinners are not restricted to one source of food supply, but easily stand a change of diet.

The chief wild spinners are—

Antherœa mylitta, which occurs all over India, and yields the most valuable of all wild silks, viz. Tussah silk.

The Eria spinner, *Attacus ricini*, met with in tropical Asia, also in North and South America, yields a very handsome, almost white product, that is daily growing in value. Special mention should be made of one individual of this tribe, viz. *Attacus atlas*, the largest known moth, which produces open cocoons, from which the so-called Fagara silk is obtained.

Antherœa Yamamaï, the Japanese oak moth, furnishes a pale green, very handsome silk, which is the nearest to true silk in character, and is highly esteemed.

Antherœa Pernyi, the North China oak moth, yields a silk that is very largely exported under the erroneous designation of Tussah silk.

Tussur or Tussah Silk.—This, being the most important and best known of all the wild silks, will be described more particularly.

The moth (*Antherœa mylitta*) from which this silk is obtained occurs throughout the whole of India and Southern China, and has been bred regularly in the former country from time immemorial, the industry being carried on by organised castes, and attended with numerous religious ceremonies. According to the Hindoo faith, the Tussah moth is the incorporation of the god Shiva; and the silk-worm breeders must abstain from eating meat, washing, and shaving during the whole time the larvæ are growing and spinning.

The Tussah cocoons are attached by their stems on to twigs, and are reeled, an operation that is very carelessly performed in India. Sometimes the cocoons are brought to Europe; but in that event are not reeled, being spun instead.

Tussah silk exhibits all the aforesaid advantages and defects of the wild silks in general. Chinese Tussah, which is frequently confounded with the Indian variety, is darker in colour and inferior in lustre and beauty.

When examined under the microscope, Tussah exhibits a highly characteristic appearance, differing greatly from that of true silk (see Fig. 9), the fibres showing strong striation, and being apparently much constricted in parts. The very distinct striations are caused by the numerous very fine fibrils of which each fibre is composed. Unlike true silk, the fibre is not of circular cross section, but of elongated quadrilateral form.

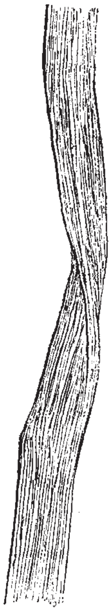


FIG. 9.

In presence of reagents, acids and alkalis in particular, Tussah silk behaves very like true silk. It is, however, much more resistent than the latter, especially towards solvents, so that the two kinds of silk can be separated in a fairly accurate quantitative manner.

The other wild silks behave very much the same as Tussah silk.

Byssus Silk.—This fibre, which morphologically and chemically is nearly allied to true silk, is the product of certain mussels which are found in Sicily, Sardinia, and Corsica, and spin a long silky thread, for the purpose of attaching themselves to the rocks at the bottom of the sea.

This fibre is golden brown in colour, lustrous, soft, and elastic. In former times it was extensively collected, and employed in the manufacture of the highly prized Byssus garments; but at the present time it is not much used, its collection being attended with considerable difficulty. From a chemical point of view, it differs from other silks in that it merely swells up when treated with acids, alkalis, or ammoniacal copper oxide, without passing into solution.

ANIMAL HAIRS.

The skins of all warm-blooded animals are covered with a protective coating of horny cellular structures, which, in the case of mammals, assume the form of hair, and constitute the feathers of birds.

These structures are elaborated in special glands in the skin, and protrude through the epidermis in proportion as they increase in length in consequence of cell multiplication.

Animal hairs are the most complex, morphologically, of all textile fibres, and, after silk, are the most perfect. In point of chemical behaviour and conduct in presence of reagents, they closely resemble silk, and therefore may be classed along with the latter in one group—that of the animal fibres as contrasted with the fibres of vegetable origin.

Chief in importance among the animal fibres is—

Sheep's Wool.

Wool is the name given to the fibrous substance secreted by the skin of the sheep, and forming the hairy covering or fleece of the animal. This covering is composed of several similar elements, whose anatomical structure exhibits different degrees of development.

In the main the fleece of the sheep consists of body hairs and true wool hairs, the latter being thin, soft, and curly, and possessing the valuable property of felting, whilst the body hairs are thicker, darker in colour, and, for the outer third of their length at least, stiffer and sharply tapered.

In a few parts of the body, on the legs and head, of the animal there occurs a third kind of hair, viz. bristles, least of all endowed with the valuable properties of sheep's wool.

The fine wools of commerce are chiefly composed of only one of the above classes of hairs, viz. either body hairs alone or solely of true wool hairs; whilst common grades, on the other hand, form mixtures of both.

It is more than likely that the article we now regard as typical wool is not a really natural product, but one that has been gradually evolved in the course of many centuries of selection. Even at the present time there still exist two breeds of sheep, the Corsican moufflon and the argali, found in Asia and America, in whose hairy coats the valuable properties of sheep's wool are merely suggested. Moreover, it can be clearly observed in the domestic sheep that improvements in the breed by suitable selection produce a corresponding improvement in the wool. Consequently the wools of the highest breeds consist almost exclusively of true wool hairs; though even in the finest wools may be found body hairs, which must be ascribed to atavism, *i.e.* a reversion to the original type of hairy covering.

The circumstances influencing the quality of wool and the percentage of body hairs therein are exceedingly numerous, chief among them being race and climatic conditions. Thus, for instance, in the hot, dry countries of Central Africa the proportion of wool hairs, in even the best breeds of sheep, steadily diminishes, and that of the body hairs as regularly increases. Conversely, the climate of Australia is so excellently adapted for wool-growing that even the poorest breed of sheep will produce a good wool in a few years time there.

Again, the fodder supplied to the sheep has a great influence on the quality of the wool. Grass from chalky soils produces a coarse wool; whilst that from rich, loamy soils gives fine silky fibres. Finally, the quality is influenced by the age and health of the sheep, and also depends on the part of the body on which it grows.

It is worthy of mention that the sheep producing the finest wool yield poor mutton.

Collection.—The wool of the sheep is mostly obtained from the living animal by shearing—an annual operation. The amount of wool furnished by an individual sheep, of course, varies considerably, and depends mainly on the breed and sex, the male merino yielding about 8 lb. at a shearing, the female only about 5 lb. Taking the general average, the yield per head varies from 3½ lb. to 13 lb., though this is exceeded by some breeds—the Argentine ram, for example, occasionally producing a fleece weighing 40 lb. and upwards.

Wool that is cut from carcases or separated from the fells by liming, is known as tanners' wool, and is always inferior to the shorn fleece, especially when obtained by liming.

Historical, Commerce, and Statistics.—In Western countries wool has been used from very early times, whereas in Asia, the conditions being less favourable for sheep-breeding, the article has always played a less important part, though the hair of certain goats, distinguished for its special lustre, has been there woven into fine fabrics from time immemorial.

The home of the sheep-breeding industry in Europe is Spain, where the indigenous merino sheep has been bred for its wool from very early times. In the Middle Ages the Spanish woollen industry was in a thriving condition, and the Moors devoted special care to the breeding of merinos. Subsequently the industry languished, but has recently revived. At first the Spaniards protected the breeding industry with extreme jealousy, and the exportation of a live merino sheep was prohibited under pain of death. This attitude, however, could not be maintained permanently, and, since the year 1723, merinos have been repeatedly exported to other countries with beneficial results in every instance. Specially important for the breeding of sheep in Europe was the introduction of the merino into Saxony in 1765, the Saxon Electoral breed now furnishing the thinnest and finest known grade of wool.

The introduction of sheep-breeding into Australia and New Zealand has been attended with the most successful results. Australia possesses no native breed of sheep, and it was only towards the end of the eighteenth century that the first sheep were sent over. The originally coarse, useless hair of these animals soon developed into good wool under the favourable influence of the Australian climate, and subsequent crossings of the breed with good English sheep brought about additional improvement, which was still further heightened by repeated crossing with merinos, so that at the present time the Australian sheep furnishes a wool ranking with the very best merino.

In South America, also—especially in Chili and the La Plata States—sheep-breeding has long been pursued on a large scale; and in North America the cultivation of wool has latterly made great strides, and will probably ere long attain considerable importance.

About fifty commercial grades of wool are known, chiefly divided into two principal classes—long and short staple, according to the length of the component fibres. To the latter class belong all wools measuring 1 to 1½ inch in length, those between 3½ and 6 inches being classed as long staple. The latter are treated by the combing process, and are used for making worsted fabrics; whilst the short wools are carded for spinning in the production of woollens.

With regard to the wool production of the various countries, it must be admitted that, notwithstanding the increased activity in the woollen industry in Europe, the output of wool in that continent is on the down-grade, owing to the more favourable natural conditions prevailing in extra-European lands; and consequently the import of wool into Europe is constantly increasing. About half the total output of raw wool produced in Europe is grown in Russia.

The trade in extra-European wool is almost entirely in English hands, though latterly a share of the trade has been acquired by Belgium. Accurate statistics of production in the several wool-growing countries are difficult to obtain, European wools being occasionally brought into the market in a partly cleaned condition, whereas the extra-European article is always sent over in the grease (unwashed). The total production for the whole world may, however, be estimated at about 1,000,000 tons per annum.

As regards the woollen manufacturing industry, in this respect

Europe is far ahead of any other countries, and the chief place of all is occupied by Great Britain.

Composition of the Fleece.—The term fleece is applied to the entire hairy coating of the sheep, including all impurities. It is composed as follows:—

Fibres	15–72 per cent.
Yolk (wool fat)	12–47 „
Water	4–24 „
Dirt	3–24 „

In addition to the hairs already mentioned, the fibres contain shorn hairs, recognisable by their clipped extremities when viewed under the microscope.

Structure. — Wool has the most complex and interesting structure of any of the textile fibres hitherto mentioned.

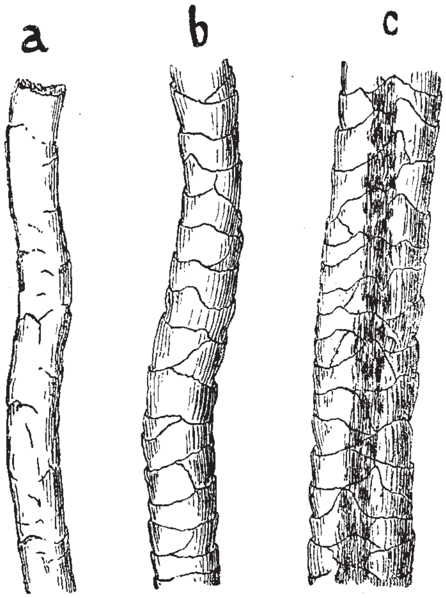


Fig. 10.

When a fibre of wool is examined under the microscope it is seen to consist of three parts, distinguished respectively as the scaly epidermis, the cortex, and the medulla or pith. The outer scaly epidermis is composed of thin horny scales lying one above another like the tiles on a roof. In the finer qualities of wool a single scale is generally sufficient to entirely surround the wool hair, so that the latter seems to be formed of a number of cups set one within another (Fig. 10, *b*), the upper edge of each scale being also generally projecting, ragged, and serrated. These scales form the chief external characteristic of sheep's wool, and render its detection under the microscope an easy task. They are, however, not always so well developed as the specimen given in Fig. 10, *b*; being in many instances less clearly visible, and in some merely present as faint broken lines (see Fig. 10, *a*). In other cases they may even be entirely absent in places, as, for example, in the wool of several breeds of country sheep where the scales are invisible for some distance from the tip of the fibre, or in wool taken from a piece of cloth which has been put through a finishing process that has stripped the scales off to a greater or smaller extent; and, even in some of the finest wools, the scales are occasionally very imperfectly developed near the tips. In the case of body hairs the scales are far smaller, and in no instance does a single scale surround the entire hair (Fig. 10, *c*).

On the structure of these scales depends one of the most valuable properties of wool, viz. the felting or shrinking power. This is due to the circumstance that, when the wool is soaked in certain solutions (*e.g.* soap), and subjected to pressure and friction, the individual scales engage one in another so that they can no longer be separated without breaking. On this behaviour is based the operation of fulling or milling woollen cloth. This explanation of felting property is in perfect harmony with the fact that body hairs, and, indeed, all other hairs with less fully developed scales, are harder to full than wool.

Two other properties of wool also depend on the nature and arrangement of the scales, namely, the lustre of the fibre and the degree of facility with which it will absorb water and dye-stuffs. Wool, with scales that either lie down flat or project only very slightly, always has more lustre than that wherein the converse conditions prevail. Some common grades of wool have very hard scales, which tightly encompass the hair and greatly retard the penetration of water and dye; such wools must therefore be well wetted before dyeing.

The second or cortical layer of the wool fibre consists of small spindle-shaped cells which give the wool its strength. These cells are visible, when viewed longitudinally under the microscope, as long striations, especially when the wool has passed through the finishing process.

Finally, the third or central layer, the medulla, is of far less importance than the other two, since it is entirely absent in the very best kinds of wool (merino). In fact, the dimensions of this medulla afford an indication of quality, since while the coarse body hairs have a broad medulla, and can thus be distinguished from the fine wool hairs under the microscope, the quality of the true wool hairs varies inversely with the amount of medulla they contain. The presence of this pith is a cause of weakness in the fibre, and therefore it gradually disappears in proportion as the wool is improved.

Microscopical examination plays an important practical part in the case of sheep's wool, since it forms the best means of distinguishing between the different kinds of wool, and also of differentiating between body hairs and true wool, the former being readily recognised by their well-developed medullary layer and small scales. Tanners' wool that has been removed from the pelt by liming can be detected by the presence of hair-root sacs, which are never found in the shorn fleece. Moreover, the microscope forms the best means of detecting the peculiar malady known as "stocks," and probably due to mouldy growths, which infests wool or woollen cloth that has been stored for some time in warm, badly ventilated rooms whilst in a damp state, especially if this dampness be due to alkaline liquids or contact with decaying wood. The malady is most frequently encountered in woollens dyed with indigo, and generally takes the form of small light-coloured spots distributed over the surface of the goods. The view that the mould eats away the dye is, however, erroneous, and it is really the fibre that is attacked and rendered brittle, the result being that it drops away and leaves a spotty mark. When the corrosion has proceeded sufficiently far, its effects on the fibre are clearly visible to the naked eye; and if a portion be examined under the microscope, a very peculiar and characteristic appearance will be detected (see Fig. 11), viz. that the scales on some parts of the hairs, and especially at the tips, have disappeared, leaving the spindle-shaped cells of the cortical layer protruding like the hairs of a brush, whilst some of them have become detached altogether and can be seen lying upon and between the wool hairs. In other places they stick out from the side of the wool hairs like so many tufts.

Fig. 11.

Some skill is, however, required in detecting this characteristic appearance, especially when the malady is only in the incipient stage, since shoddy and other wool substitutes present a similar picture under the microscope, though what is really seen in this case is the broken ends of fibres, and not the separate spindle cells.

The malady in question plays an important and much dreaded part in the woollen industry, since the affected pieces can neither be properly dyed nor milled, and, besides, the goods are weakened.

An equally characteristic appearance is exhibited under the microscope by wool corroded by alkalis, the wool being curled up in horseshoe form when the reaction has been very strong (see Fig. 12), or merely turned round in the form of a crosier at the ends when a less powerful reaction has occurred. A similar corrosion of the fibre is often met with after the carbonising process, and, in the subsequent dyeing, gives rise to what is known as "soda spotting."

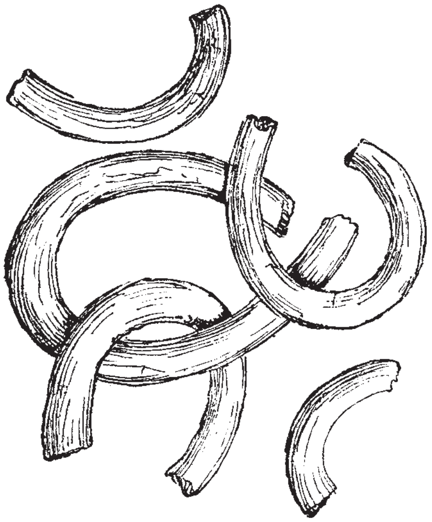


FIG. 12.

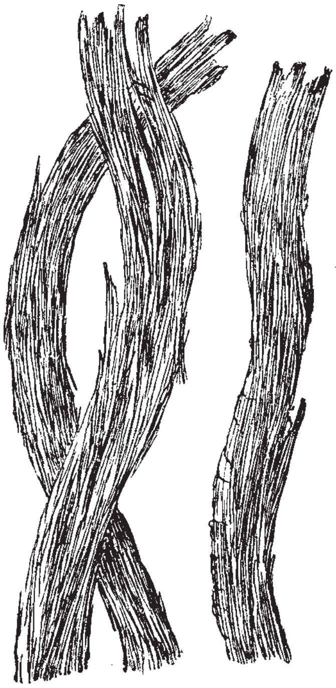


FIG. 13.

Finally, it is also occasionally possible to detect acid corrosion in wool by the aid of the microscope, the fibre being in such case more than usually striated, and in some places, the ends particularly, looks as though hacked to pieces. Unfortunately, the microscopic picture furnished by such wool is not very characteristic, and for this reason the formation of "acid spotting" due to carbonisation cannot always be detected by the microscope test alone, although when the wool has been strongly corroded by acid the microscopic picture is characteristic enough (Fig. 13).

Physical Properties.—Wool is a very hygroscopic substance, and can absorb a large proportion of water without becoming appreciably wet. This property is utilised by certain fraudulent dealers, inasmuch as they leave the wool in a damp place, or else sprinkle it with water, in order to increase the weight. For this reason it has become necessary to condition all parcels of wool. The toughest wool generally contains the largest percentage of water; in the case of unwashed wool, the amount of moisture is inversely proportional to the fat content. Although so hygroscopic, wool absorbs moisture in large quantities far less rapidly than the other textile fibres, and therefore requires to be well wetted before dyeing, one to two hours' boiling in water being necessary.

In warm water wool fibre swells up, becomes soft, and, like all horny substances, plastic—*i.e.* retains the shape into which it has been moulded. Several important operations in the finishing process for woollen goods are based on this property of the fibre, as well as on its high elasticity and felting power.

The lustre of wool varies considerably, the straight, smooth wools being mostly superior in this respect to the curly merino wools. Such wools, however, as have a glassy lustre are generally very hard and horny, and are difficult to dye, on which account they must be particularly well wetted.

The colour also varies greatly in the different grades, the best kinds being white, the others yellowish, red, brown, and black. The dark-coloured wools are almost impossible to bleach, and are worked up in their natural shade to dark goods.

Wool greedily absorbs acids, metallic hydroxides, and dye-stuffs, more especially in the warm. This interesting feature will be fully dealt with in treating of mordanting and dyeing.

Chemical Composition.—In the unwashed state wool consists of three parts—fibre, wool fat, and suint or yolk.

The thoroughly cleansed fibre has the same chemical composition as horn and feathers—viz. the substance known as keratin, which is classed with the proteids. It consists of carbon, hydrogen, oxygen, nitrogen, and sulphur.

The percentage values obtained for the constituents of keratin by ultimate analysis are worthless, since it is impossible to dry wool thoroughly without decomposition. It is, moreover, almost certain that what we regard as pure wool is not a uniform substance, since if even the purest wool be boiled in water, one or perhaps more organic substances and sulphur pass into solution. The organic matter thus dissolved gives precipitates with silver and lead salts, and is therefore probably of an acid character.

If this boiling be repeated with fresh quantities of water, a point is at length reached when no further extraction occurs.

With regard to the part played by sulphur in the substance of wool, nothing definite is known. A portion of this sulphur can be extracted by solvents, and even, as already stated, by boiling with water, without altering the structure of the wool or its behaviour towards reagents; and it also appears to be in part contained in the soluble matter just referred to. Nevertheless, the whole of the sulphur cannot be extracted without producing structural modifications. These considerations also explain the highly conflicting analytical reports on the percentage of sulphur in wool, the figures ranging from 0·8 to 3·8 per cent.

The presence of sulphur distinguishes animal wools from all other fibres, and may be employed as a means of differentiation between them, a black coloration being produced when wool is boiled with sodium plumbate.

Wool Fat.—This, the fatty matter found in wool, is an accidental constituent of wool fibre, but cannot be entirely removed without spoiling the softness of the wool.

Its composition is complex, and has been only partially investigated. It consists of cholesterin and isocholesterin, both in a free state and in combination with oleic acid, stearic acid, hyænic acid, etc. Free higher fatty acids, and other still unidentified substances, also appear to be present. Wool fat is therefore not a true fat, since it contains no glycerides.

Suint or Yolk.—Under this name are comprised all the bodies that are eliminated from raw wool in the washing process, though, scientifically speaking, the term "suint" applies only to the fluid secretion of the skin of the sheep. The amount varies in different wools, and it is an accepted axiom that the larger the proportion of suint the better the quality of the wool.

The extracted and dried suint contains 60 per cent. of organic matters and 40 per cent. of mineral substances. It consists chiefly of the potash salts of oleic acid and stearic acid, probably also of other volatile fatty acids; and, in addition, contains potassium chloride and the phosphates, sulphates, and silicates of calcium, potassium, iron, and magnesium, together with nitrogen in the form of ammonia salts and in the organic compounds.

Both wool fat and suint are recovered from the waste waters of wool-washing establishments, and are utilised in various ways. (See Wool-Washing.)

Chemical behaviour of Wool Fibre.—In the pure state wool fibre consists of keratin, which is classed with the proteids and has the character of an amido-acid, *i.e.* is both acid and basic. The presence of amido groups in wool has been proved by diazotisation.

Even when stored in the damp, sheep's wool is less subject to mould than vegetable fibres. On being heated in the dry state, wool undergoes slight decomposition, even at 120–125° C., attended with liberation of ammonia and slight yellowing; when heated to 140–150° C., it also loses part of its sulphur, which is liberated in the form of sulphuretted hydrogen.

The behaviour of wool on combustion and towards water has already been described, and it only remains to state that wool is far more resistent towards water than silk, though unnecessarily prolonged boiling should be avoided, since this roughens the wool and lowers its tensile strength. It suffers far less when boiled in acidified water, the reason apparently being that pure water behaves like a weak alkali, and therefore dissolves out a (probably acid) constituent of the fibre. When heated with water to 200° C., under pressure, complete decomposition and solution occur.

The effect of alkalis on wool has already been mentioned in part. Ammonia in the cold does not attack wool to any appreciable extent, though some loss of substance occurs even when the ammonia is very dilute and the period of exposure brief.

Ammonium carbonate has but very little effect on wool, and is for this reason the best detergent for this material.

Lime acts less powerfully than the caustic alkalis, but extracts sulphur and renders the wool hard and brittle, besides making it more difficult to full. It is for this reason that tanners' wool is such an inferior material.

By the energetic action of barium hydroxide, a substance known as lanugic acid, possessing the general properties of wool, has been isolated from the fibre.

Wool has a greater power of resisting dilute acids than is exhibited by any of the other textile fibres already mentioned, but suffers more or less corrosion when treated with concentrated acids. Thus, if carbonised wool be left for several weeks without neutralising the residual sulphuric acid from the carbonising process, it will be found to have sustained considerable alteration, evidenced by the abnormal loss in weight experienced on boiling it with water. Such wool also behaves in a peculiar manner when dyed, inasmuch as it will then readily absorb Methylene Green, for example, which is not the case with normal wool. Concentrated acids will dissolve wool completely.

Concentrated nitric acid stains wool yellow, xanthoproteic acid being formed. This property is frequently utilised for producing false yellow selvedges in cloth.

Chlorine or hypochlorous acid has a very powerful effect on wool, the latter absorbing up to 33 per cent. of the reagent, and suffering an entire change of character, being stained brown, losing its felting properties, acquiring a hard feel, and in many cases assuming a silky appearance, inasmuch as it scroops when compressed, and exhibits a greater affinity for dye-stuffs.

However, an entirely favourable modification is produced in wool by the moderated action of hypochlorous acid; and practical use is made of this circumstance—for example, in securing better development of the so-called steam dyes in the printing of woollen piece goods. Latterly this reaction has also been employed in the production of the so-called "silk wool," a product exhibiting the above-mentioned properties of silk, and obtained by treating wool with an acidified solution of bleaching powder. (Full particulars of the method are given in the directions published by the Badische Anilin- und Sodafabrik.)

Finally, it may be mentioned that true wool hair is dissolved by ammoniacal copper oxide in the warm, whereas body hairs, and hairs in general, are destroyed but not dissolved by this reagent.

Goat Wool and Camel Wool.

In morphological and chemical character these textile fibres are closely allied to sheep's wool, and the particulars given with regard to that substance apply to them also.

Mohair is the silky hair of the Angora goat, indigenous to Asia Minor, the climate of which country seems favourable to the growth of long silky hair, since the dogs, cats, and rabbits there found are all covered with hair of this kind. Latterly it has been found possible to acclimatise the Angora goat in Cape Colony also.

On account of its stiffness, mohair is used for making plush, and, by reason of its handsome lustre, it is also employed in fine fabrics, for decorating cloth, and for fancy yarns in place of silk.

Under the microscope, mohair is distinguishable by remarkably broad and regularly distributed striations; the scales are thin and serrated.

Cashmere, or Thibet wool, is the soft down of the Cashmere goat (*Capra hircus laniger*), indigenous to Thibet. It forms the material for the justly renowned Indian shawls, and, on account of its great softness, is also used in the European woollen industry, mainly for producing a nap on winter clothings.

It is worthy of remark that this wool is more difficult to dye than that of the sheep.

Alpaca, Vicuna, and Llama.—These fibres are furnished by camel-goats, of the Auchenia family, inhabiting the mountains of Peru and Chili. They are mostly of a red-brown to black colour, but are of only minor importance to the European textile industry.

It should be noted that the commercial product known as vicuna or vigogne is not obtained from the vicuna, but is a mixture of wool and cotton; further, that an artificial wool, or wool substitute, is met with in commerce under the name of alpaca.

These exotic wools are frequently infested with a micro-organism (*Bacillus anthracis*), which produces the disease known as anthrax (wool-sorter's disease) in man, and engenders a species of typhus in cattle and horses. Consequently the rooms where these wools are sorted should be well ventilated, and the sorters should wear respirators.

Camel Wool.—On account of its strength and softness, camel wool has latterly been largely used for making bedcovers and winter clothings. As it cannot be bleached, it is used either in the natural colour, or dyed dark brown or black.

Cow Hair.—This fibre being cheap, and possessing a certain—though not considerable—amount of felting power, is now somewhat largely used in the manufacture of coarse blankets and bedcovers.

Artificial Wool (Wool Substitutes).

The first experiments on converting woollen rags into fibre suitable for spinning were made in England in 1845, the product being put on the market under the name of shoddy. This industry has increased to a very considerable extent, and, according to an old estimate made by Grothe, about 33 per cent. of the total wool manufactured consists of wool substitutes; in fact, of all the samples of woollens examined by him, only 15 per cent. were free from such admixture. At the present time, the quantity of wool substitutes manufactured and used is far greater. Shoddy factories now exist in nearly every country in Europe, and it is therefore natural that all cheap woollen goods should contain wool substitutes; in fact, many low-priced cloths consist of 70 per cent., and more, of such materials. On the other hand, they can only be used for the under wefts of worsted fabrics.

There are several varieties of wool substitutes, the value of which stands in direct relation to the quality of the waste from which they are produced. The chief members of the series are the following:—

Shoddy.—This is made of waste or rags from pure unmilled woollens, flannels, bedcovers, curtains, and also from knitted and twisted goods. The resulting fibres are about an inch long, and are sorted according to colour and fineness, vegetable fibres being eliminated by carbonising.

Mungo is obtained from milled woollen rags, and being of much shorter staple than shoddy ($\frac{1}{4}$–$\frac{3}{4}$ inch) is therefore of less value than the latter.

Alpaca, or extract wool, is a long staple substitute from fine unmilled cloth waste, and generally contains a good deal of vegetable fibres. The crux of the process, therefore, resides in the operation of carbonising.

Thibet Wool substitute is recovered from light cloth waste.

Cosmos Fibre.—This contains no sheep's wool at all, being made of waste from flax, jute, and hemp fabrics; it also frequently contains fragments of hopbine, nettle fibre, etc. Belgium and North America are the sole centres of production.

In addition to the foregoing adjuncts, use is made in the woollen industry of the short fibre obtained as a waste product in the shearing or cropping of cloth. This material is milled in, to the extent of about 20 per cent., on the under side of cloth, the operation being known as "impregnating." It can be detected under the microscope by the shortness of the fibres and by their truncated ends.

Testing Wool Substitutes.—In most cases all that is requisite is to determine the amount of cotton present; but in a complete analysis the percentage of water and fat (the latter being usually added to facilitate spinning) must also be determined, and a qualitative test made for silk.

Water is ascertained by drying a 5–10 grm. sample at a little over 100° C.

The fat is estimated by extracting a dried sample with petroleum ether.

The percentage of cotton is found by digesting a fat-free sample —of at least 10 grms.—for a quarter of an hour at boiling temperature in 8° B. caustic soda. This dissolves out the wool, leaving the cotton behind for weighing after filtration through a linen cloth, washing out all the alkali with boiling water, and drying.

Silk, which is occasionally present, need only be tested for qualitatively. This should never be omitted, since, unlike cotton, silk is not removed by carbonising, but remains behind in the wool, and will, by reason of its different affinity for dye-stuffs, cause irregularities in dyeing. The test is performed as follows:—A sample of the substance is dyed with logwood, which stains only the wool, leaving the cotton and silk almost unaffected and easily recognised by their lighter shade. A sample is then examined for silk under the microscope.

Examining Fabrics for the Presence of Wool Substitutes.—With this object, a few fibres are cut from the fabric by the aid of a sharp knife and placed under the microscope, whereupon the wool substitutes will be recognisable by their shape and colour. That the form of these fibres will be different from ordinary wool can be readily understood when it is remembered that, in addition to the tearing process they have to undergo (in the case of shoddy and mungo, at least), the wool substitutes have been through the finishing process twice over. Hence these fibres exhibit ragged ends, owing to the loss of the scales, and they are frequently also partly broken in the middle. As, however, wool hairs attacked by mould also exhibit a similar appearance, care is necessary to prevent confusion.

Variety of colour is the best indication of the presence of artificial wool, since, although the different colours are sorted out in the making, this cannot be done with perfect accuracy, and therefore the fibres of wool substitutes are usually many-coloured, unless, which rarely happens, the material is all white. Thus, in examining a red cloth, for example, if it be found to contain blue and green fibres as well, the presence of wool substitutes may be justifiably assumed. In the case of very dark coloured materials the colour should be first partly removed by boiling with a weak alkali or dilute acid before making the examination.

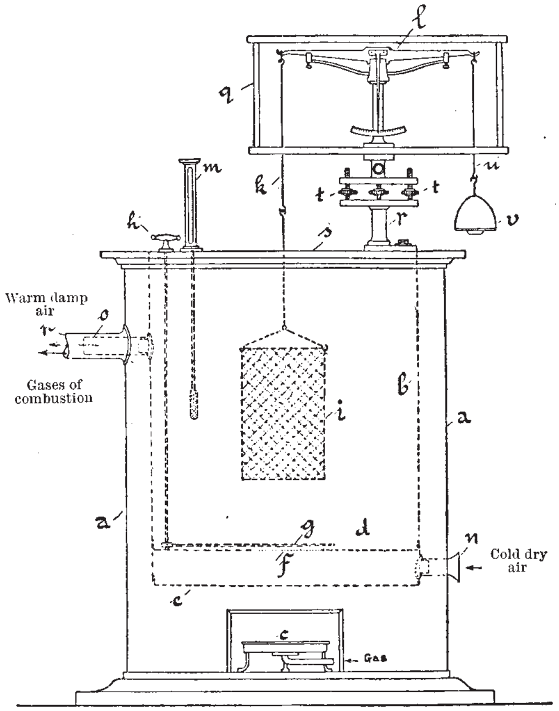


FIG. 14.

Of course, in the case of coloured mixture fabrics, hairs of more than one colour (usually two or three) may be expected. To prevent deception it is also advisable to examine the colour of the selvedge; blue cloths, for instance, generally have a yellow selvedge, and it may happen that a few hairs—almost invisible to the naked eye—from this selvedge will come off on to the cloth, which will then seem to contain yellow fibres in the microscope sample. In any event, the examination should not be confined to a single sample.

Sometimes the presence of wool substitutes can be indirectly determined by a qualitative examination of the ash left by the material on combustion. Thus, if the sample have been dyed with a Ponceau dye, and chrome be found in the ash, the presence of artificial wool is indicated, since these dyes are never fixed with chrome salts, and therefore the latter must have been introduced in a wool substitute.

Conditioning.—As already stated, silk, being an expensive and also hygroscopic substance, has to have its actual weight determined when sold. This operation is performed in official institutions, known as "conditioning houses," the *modus operandi* being as follows:—

The parcel of silk is first weighed, after which samples are drawn, to the extent of about 1500 grms., from different parts of the whole. The sample is divided into three parts, two of them being weighed to ½ grm. and then placed in the apparatus shown in Fig. 14, where they are dried, until of constant weight, by a current of air heated to 110° C. If the resulting weights agree to within ½ per cent., the average is taken, but when a greater difference exists the third part of the sample is dried in the same way, and the mean of the three determinations is adopted. The standard commercial weight is found by adding 11 per cent. to the dry weight. In the case of mixed yarns of silk and wool the standard of permissible moisture is 16 per cent. of the dry weight of the material.

Conditioning houses of this kind exist in London, Paris, Lyons, Vienna, Crefeld, Zurich, Basle, Turin, Milan, Verviers, etc.

Latterly the custom has arisen of conditioning both wool and cotton as well as silk, the work being done in just the same manner. The officially permitted percentages of moisture are as follow:—

For worsted and worsted yarn	18¼ per cent.
For unwashed wool, woollen waste, combings, and carded yarn	17 ,,
For cotton and cotton yarns	8½ ,,

CHAPTER II

WASHING, BLEACHING, AND CARBONISING

Washing and Bleaching

BROADLY considered, any operation performed with the object of cleansing a textile fibre at any stage of manufacture or improvement may be included in this category; but, in their more restricted sense, washing and bleaching are terms confined to the cleansing of the textile fibres in their crude state in order to prepare them for the subsequent operations of dyeing, dressing, etc. Thus, in speaking of wool-washing, the first process of purification to which the wool is subjected before spinning is meant, and not the rinsing of dyed wool, for example.

Corresponding operations are not always described by the same names in different branches of the textile industry; and, conversely, the same term is differently applied. Thus the term "cotton bleaching" comprises the entire set of operations employed to free the cellulose from all natural and other impurities, whereas, in the case of silk and wool, the term "bleaching" implies only the more restricted sense of the word, being confined to the operations effecting the actual decoloration of the fibre. Again, the first cleansing process applied to raw silk is not called "washing," as in the case of wool, but is termed "scouring," or "removing the bast."

The means or reagents employed for cleansing the fibres also differ considerably, according to the nature of the fibres in question, the stage of manufacture, and the nature of the impurities to be removed. For instance, one would not attempt to cleanse animal fibres with caustic alkalis, and raw fibre must be cleansed in a different manner to that employed for the same fibre when dyed. Thus, raw silk is freed from sericin by washing with soap and soda, whereas dyed silk is merely rinsed with water alone, if at all.

Raw wool is also washed with soap and soda; the same materials are likewise used, though in a different way, to free the yarn from the oil applied in the spinning process, whilst the dyed pieces are merely rinsed with water or cleansed with soap or fuller's earth. Raw cotton is freed from natural impurities by energetic treatment with caustic alkalis, soda, alkaline earths, etc., sometimes also with acids to remove size. When dyed, however, it is mostly washed with water alone, whilst printed goods are treated with soap, malt, etc.

The present chapter deals solely with the purification of the raw fibres in their undyed state, the various washings subsequent to dyeing and printing being postponed to a more suitable part of the book.

The reagents employed may be divided into two classes—detergents and bleaching agents — the former comprising water, soda lye, ammonia, sodium carbonate, ammonium carbonate, quicklime, magnesia, hydrochloric acid, sulphuric acid, soap, resin lyes, benzine, oil of turpentine, etc.

The author takes it for granted that the reader is acquainted with the properties and examination of these materials, and will therefore confine himself to dealing with water, and that, too, merely from a textile point of view.

Water plays an important part, not only in washing and bleaching, but also in the operations of dyeing and printing fabrics. Of the various substances that may be present in water, the following alone are of interest to us, viz.—

1. Solid matters in suspension;
2. Salts of lime and magnesia, which produce "hardness";
3. Other less common impurities, such as iron, humus acids, alkali carbonates, and sulphuretted hydrogen.

Turbid water containing matters in suspension must be clarified before use, by filtration or settling. Another method of clarifying impure water is to boil it with bran and skim off the frothy scum.

From the washer's and dyer's point of view, the most important defect in water is hardness, since hard water is unsuitable for either washing or dyeing. If such water be used for, say, washing textile fibres, the lime and magnesia present will be thrown down as insoluble soaps of these metals, and thus, not only is there a considerable waste of soap, but the precipitated compounds adhere to the fibre and are liable to cause spotting. Therefore, to render hard water fit for use, it must first be treated with soda, to throw down a large portion of the alkaline earths. A more economical plan, however, especially when the water is to be used for scouring silk, is to first throw down the bicarbonates of lime and magnesia by simple boiling, and then add the soda. In this manner a saving of soda is effected and the water is more effectually softened than by the first-named method.

For dyeing, only the so-called temporary hardness of water produced by the bicarbonates of lime and magnesia is injurious, except where the dyeing of silk in a bast soap bath is in question, in which event the soap may also precipitate the lime and magnesia compounds, producing permanent hardness.

Temporary hardness may cause the precipitation of basic dye-stuffs and mordant dyes, the colour base being thrown down in the first case, and the lime or magnesia salt of the dye-stuff in the other; *i.e.* with basic dyes the alkaline earth carbonates act by the alkaline reaction they impart to the dye bath, and in the other case by the formation of insoluble salts. In either event the use of hard water is attended with a loss of dye; this is specially noticeable in the case of dyeing with logwood and various alizarine dyes.

Hardness in the water does not matter when acid dyes are used, or in mordanting wool, since in these cases acid baths are used; only when mordanting with cream of tartar does the water require to be corrected beforehand, since otherwise a portion of the tartar would be precipitated as calcium tartrate and lost. No harm is caused by hard water in mordanting cotton and silk; in fact, hard water is preferable to soft for fixing the mordant on silk.

In order to fit hard water for dyeing, it is "corrected" by neutralising the contained carbonates with an acid, the amount required being ascertained by titrating a small sample—about 2 litres—in a porcelain basin, with decinormal hydrochloric acid, using methyl orange as indicator. In practice, the acids used are acetic acid or sulphuric acid; oxalic acid cannot be recommended, since, though it precipitates all the salts of lime and magnesia in an almost complete manner, the pulverulent oxalates are liable to be deposited on the fibre, and are then difficult to wash off.

It should be an invariable rule to use none but corrected water for dyeing, though when an acid dye bath is employed the correction of the water is effected at the same time as the acidification of the bath.

When the water has been corrected no precipitation of the dye-stuff will ensue from the alkaline earths, these being now in the state of acetates or sulphates, of a more strongly acid character than the mordant dye-stuffs themselves.

Water containing iron or sulphuretted hydrogen cannot be used for dyeing except under special circumstances; and ferruginous water is altogether unsuitable for bleaching. Water of this kind has a deadening effect on many bright colours, such as alizarine red, cochineal scarlet, etc.

Water containing sulphuretted hydrogen may exert an injurious influence when used in mordanting with metallic oxides which give insoluble coloured sulphides.

Water exhibiting an acid or alkaline reaction, from the presence of humus acids or alkaline carbonates respectively, can be fitted for use by careful neutralisation.

Purifying Waste Water from Dyeing and Bleaching Works.—This is too wide a subject to be exhaustively dealt with here, though a brief mention cannot be omitted. The best method to adopt in dyeworks is to run all the various bath liquors into a large collecting tank. Here the different mordants and dyes precipitate each other, the reaction being completed by an addition of lime. Ferrous sulphate may also be used for the same purpose in virtue of its precipitating and reducing action.

For decolorising purposes, an addition of aluminium hypochlorite—a clarified mixture of alum and bleaching powder—is advisable, any excess of this reagent being rendered innocuous by adding ferrous sulphate.

Bleaching Agents.

By the term bleaching we understand destruction of colour, in the present case the natural yellow-brown colour of the textile fibres in their crude state.

The requirements exacted of bleaching agents in practice are threefold—(1) they must really bleach, *i.e.* convert the yellow colour of the crude fibre into a pure white; (2) they must not corrode the fibre; and (3) they must be cheap.

Only two chief bleaching agents are known, and these at the same time may serve to represent the two groups into which these agents are divided: the first is oxygen, the other sulphurous acid. In the former case the bleaching effect is the result of a destruction of the colouring matter by oxidation; but in the second group the process cannot be expressed by a single word, and, moreover, has not yet been fully elucidated. However, to distinguish these bleaching agents from the others, they may be termed reducing agents.

Finally, there are various other substances which impart a bluish white tinge to textile fibres; these, however, are not bleaching agents but colorants, their action being to mask the natural yellow colour of the fibre. Their description will therefore be postponed.

(*a*) **The Oxidising Bleaching Agents.**—This class includes oxygen itself, ozone, chlorine, bromine, hypochlorites, peroxides, chromic acid in the form of potassium bichromate, permanganic acid as potassium permanganate, and potassium ferricyanide. Whichever of these substances be employed, their action is invariably attributable to nascent oxygen.

Chlorine acts only in the presence of water, perfectly dry chlorine having no bleaching action. The reaction is based on the decomposition of water and liberation of oxygen—

$$Cl_2 + H_2O = 2HCl + O.$$

Bromine acts in a similar manner.

The hypochlorites act by the decomposition of the liberated hypochlorous acid into hydrochloric acid and oxygen—

$$HClO = HCl + O,$$

whence it follows that the activity of these salts can be increased by an acid setting the hypochlorous acid at liberty.

The peroxides, and also potassium bichromate and potassium permanganate, when brought into contact with readily oxidisable bodies, undergo decomposition and liberate oxygen, which then acts as a bleach—

$$H_2O_2 = H_2O + O \; ; \; BaO_2 = BaO + O, \text{ etc.}$$
$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + O_3.$$
$$K_2Mn_2O_8 = K_2O + 2MnO + 5O.$$

All these bleaching agents act more energetically than oxygen itself, because the oxygen they liberate is in the nascent state. In all cases the presence of water or moisture is indispensable for the performance of the bleaching reaction, perfectly dry oxygen having no oxidising power.

Atmospheric Oxygen and Ozone.—The oxygen of the air is the oldest bleaching agent known, and is the active ingredient in the process of grass bleaching, which was formerly employed for cotton and linen, but is now almost entirely confined to the latter class of goods. Whether in this process the oxygen acts partly in the condition of ozone has not been definitely ascertained.

The decolorising or discharging of dyed colours is also nothing else than a process of oxygen bleaching.

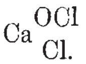
In recent patented processes by Siemens and Halske, atmospheric oxygen is ozonised by an electric current, and in this form is used for bleaching fibres, principally linen. The operation is performed in a closed illuminated glass chamber, and is claimed to occupy only one-third the time consumed in the ordinary grass bleach.

Some oils possess the property of absorbing atmospheric oxygen and, under the influence of light, converting it into ozone. Oil of turpentine is one of these, and, in addition, exercises a cleansing effect on textiles, especially in presence of water and an alkali; in fact, a mixture of ozonised turpentine and alkali has been recommended as a bleaching agent by Depierre and Georgievics. The new product "ozonin" is prepared by allowing light to act for three days or so on a mixture of resin, turpentine, alkali, and hydrogen peroxide. It is claimed to bleach well even when diluted to 1 part per mil.

Chlorine was formerly used for bleaching cotton, but the method never attained any practical importance. Latterly, this reagent has again been advocated by several, Breinl and Karrer having recommended it for bleaching cotton on the bobbin, and Leykham of Josefsthal for jute. The Brin's Oxygen Company employs a mixture of chlorine and oxygen for bleaching. Finally, it may be mentioned that proposals have been made to intensify the bleaching action of chlorine by the influence of the electric current as applied to oxygen by the Siemens and Halske method.

Bromine has been recommended for bleaching Tussah silk, the excess of reagent being afterwards removed by the aid of a sulphite, which, in turn, is eliminated by an acid bath.

Bleaching powder, or "chloride of lime," is one of the oldest and most important of the bleaching agents. When dissolved in water, it has the normal composition of a hypochlorite, corresponding to the formula $Ca(ClO)_2$. In the solid state it is credited with the formula



$\mathrm{Ca}\begin{smallmatrix}\mathrm{OCl}\\ \mathrm{Cl}\end{smallmatrix}$.

Bleaching powder is the main bleaching agent used for all the vegetable textile fibres except jute; but, like chlorine or other hypochlorites, is unsuitable for animal fibres. It must be stored in well-closed vessels, in a cool place, since otherwise it undergoes rapid decomposition.

Particular care is necessary in dissolving this reagent in water, it being essential to avoid heat, or decomposition will ensue. The solution should be perfectly clear and free from particles in suspension, since these would be deposited on the fibre to be bleached and produce "super oxidation," *i.e.* not only destroy the colouring matter of the fibre, but convert the cellulose into oxycellulose. As the latter has a greater affinity than the former for dye-stuffs, the result would be to form dark spots impossible to eliminate. In cotton-printing these oxycellulose spots turn brown when steamed, and the fibre exhibits more or less corrosion. If bleaching powder be treated with too much water at first it forms lumps that cannot be afterwards reduced. Consequently the powder, after being passed through a crushing mill, is first carefully mixed to a paste with a small quantity of water, and then treated with enough water to form the solution. It is advisable to use two stone tanks for this operation, the solution being prepared in the one and poured, when clear, into the second, where it is reduced to the proper strength. The common practice of recording the strength of bleaching powder solutions in degrees of the Beaumé hydrometer is irrational, since whilst the useless substances present, such as calcium hydroxide, calcium chloride, etc., increase the density of the solution, the active free chlorine has the contrary effect. Hence the density is no criterion at all of the real strength of the solution. In fact, this can only be ascertained by chemical means, *e.g.* titration with potassium iodide, sodium hyposulphite, and starch paste. The proper strength of solution to use for bleaching depends mainly on the nature of the fibres under treatment, their capacity for resisting the action of bleaching powder varying. Cotton is the least susceptible of all; nevertheless care is required even in this case. The "chemicking," as the bleaching with chloride of lime is called, is the most risky operation of the whole bleaching process, because here the corrosion of the fibre is most likely to occur. In practice the strength of solution used varies from $0{\cdot}2^\circ$ to $2\frac{1}{2}^\circ$ B.

When a fibrous material impregnated with dissolved bleaching powder is exposed to the air the bleaching effect is increased in comparison with the action produced when the same is merely left immersed in the liquid, the reason for this being that the hypochlorous acid is liberated by the carbon dioxide in the air. Fabrics impregnated with such a solution must not be exposed to direct sunlight, or the oxidising action of the bleach will be so strong as to corrode the fibre and reduce its strength.

Moreover, it must be remembered that simple washing with water is insufficient to entirely remove the bleaching powder solution from the fibre, and consequently the material must be afterwards soured in an acid bath, or, in the case of household linens, treated with an "antichlor," since otherwise the fibre will be more or less weakened in course of time.

Finally, bleaching powder can be used in the manufacture of other hypochlorites; aluminium hypochlorite, for example, being prepared by treating bleaching powder solution with alum.

Sodium Hypochlorite.—This compound is prepared for bleaching purposes by acting on bleaching powder with sodium carbonate—

$$Ca(ClO)_2 + Na_2CO_3 = 2NaClO + CaCO_3.$$

This salt is gentler in its action than the lime compound, probably because the latter—owing to the less ready solubility of calcium carbonate—is more easily decomposed by atmospheric carbon dioxide, and the liberated hypochlorous acid comes into action more energetically than in the case of sodium hypochlorite. For this reason no weakening of the fibre occurs in bleaching with the sodium salt, though almost inevitable when bleaching powder is used. Another advantage of the former is that the acid bath, after bleaching, is dispensed with, the reagent being easily removed by a simple rinsing in water.

Again, the bleaching process goes on better by simple immersion in the sodium hypochlorite solution than in the usual method practised when bleaching powder is used. Not only does sodium hypochlorite form the most important bleaching agent for jute, but its use for cottons has grown more and more in favour of late—an extension that may be expected to continue to the entire suppression of bleaching powder, owing to the ease with which the sodium salt can be prepared by electrolytic methods, the product being cheaper (provided motive power be available at a reasonable cost) and always obtainable of constant strength.

Of the various methods for preparing "electrolytic chlorine," only the process of Dr. Kellner will be described here. This inventor produces a cheap bleach by the aid of his special brush electrodes, which consist of a number of ebonite plates, fitted in a special manner with brush-like wires of platinum, which at the two end plates are connected to two common contacts leading to the pole of a dynamo. The apparatus is enclosed in a prismatic box of ebonite, the lower part of which is shaped like a hopper and is fitted with the inlets for admitting the sodium chloride to be decomposed. The solution of the latter ascends between the several plates, forming the electrodes, and is split up into sodium and chlorine, the former acting on the water, and forming sodium hydroxide (caustic soda), with liberation of hydrogen, and then combining with the free chlorine to form sodium hypochlorite. There also occur certain subsidiary reactions, of both an oxidising and a reducing character, chiefly concerned with the formation of a chlorate and the re-decomposition of hypochlorite to chloride.

In consequence of the chemical reaction produced, the solution issuing from the lateral outlets of the apparatus, and already containing active chlorine, has sustained an increase of temperature, and must, in order to prevent decomposition, be passed through a cooling coil to restore it to the original temperature, whereupon it is returned to the electrolyser. This process is repeated until the solution contains 1 per cent. of active chlorine, at which stage it is ready for use in bleaching.

Ammonium hypochlorite has been proposed for bleaching Tussah silk; and aluminium hypochlorite and magnesium hypochlorite have also been recommended as bleaching agents.

Hydrogen peroxide is the best bleaching agent, and can be recommended for all kinds of fibre, as well as for removing stains, and for bleaching the hair. It possesses the great advantage over all its competitors, that it does not attack the fibre in any way; but it is too expensive for general use. Up to the present its chief application has been in the bleaching of wool, and here it exhibits the decided advantage of producing permanent decoloration, which was hitherto unattainable by the use of sulphur. Nevertheless, hydrogen peroxide alone is incapable of furnishing a perfectly pure white.

Hydrogen peroxide is met with in commerce as an aqueous solution, containing 1·5 per cent. of active oxygen, the solution being of 12 per cent. (vol.) strength. It is rather unstable, and must therefore be stored in the dark; an addition of glycerine, however, is said to increase its stability. The strength of the solution is ascertained by titration with potassium permanganate, or with potassium iodide and sodium hypochlorite. It should be as pure as possible, since impurities like alumina, baryta, magnesia, etc., may exert a catalytic decomposing action. For this reason it cannot be stored in metallic vessels.

Alkaline solutions of this reagent are particularly unstable, and consequently these alone are employed in bleaching, the oxidising action being otherwise too slow. The *modus operandi* is as follows:—The commercial solution of peroxide is diluted with two to ten volumes of water, and, before use, receives an addition of 20 grms. of ammonia per litre (of peroxide). The strength depends on the nature of the material under treatment, the concentration being the greater in proportion as the latter is the more difficult to bleach. According to Prudhomme and Koechlin, an addition of magnesia, instead of ammonia, to the bleaching bath, is very favourable, because in such case heat may be applied owing to the formation of magnesium peroxide, which is difficult to decompose. The material to be bleached is either left in the liquid for about ten hours, or is merely impregnated therewith, the excess being wrung out, and the stuff left exposed to the air for some time. This treatment is repeated as often as necessary.

The following method has of late been largely used for bleaching woollens, especially for mousselines that are to be afterwards printed:—The suitably cleaned goods are entered, full width, in a bath of hydrogen peroxide (diluted with two to ten parts of water, and containing an addition of ammonia), after leaving which it is rolled on a wooden roller and left for twenty-four hours, covered up with damp nettles. It is next washed, passed through a bath of 35° B. (diluted with two to ten times its volume of water, according to requirements, as determined by experiment for each class of material), then rolled up and left as long as before. On unrolling the fabric, it is dried, passed through a weak acid bath (1° B. hydrochloric acid), and finally washed. This method furnishes an excellent white.

Attention must once more be drawn to the fact that solutions of hydrogen peroxide undergo decomposition when brought into contact with metallic vessels, and that such must therefore be avoided when this bleaching agent is used. If the goods are to be drained in the hydro-extractor, that vessel must therefore be lined with some material to prevent contact and the resultant spotting.

Some years ago H. Koechlin devised a process for bleaching cotton with hydrogen peroxide.

Sodium Peroxide.—This, the newest bleaching agent, is manufactured by the Aluminium Company, of London, and is prepared by passing air—freed from carbon dioxide—at a temperature of 300° C. over metallic sodium contained in aluminium vessels.

The commercial product contains 20 per cent. of active oxygen, and is only recommended for bleaching animal fibres. Some precaution is necessary in its application, since it hisses and disengages considerable heat when dissolved in water; and if brought suddenly into contact with a large quantity of that liquid is liable to produce an explosion.

The best method of procedure is as follows:—The sodium peroxide is added by degrees, and with constant stirring, to the requisite quantity of water, and is then treated with sufficient sulphuric acid to neutralise the bath, which condition may be ascertained by the aid of litmus paper. This neutralisation is necessary to prevent corrosion of the animal fibre by the strongly alkaline sodium peroxide. Finally, the warmed bath receives an addition of 1 to 2 lb. of a 45° B. solution of sodium silicate to each pound of peroxide.

The bath temperature and the duration of bleaching depend on the material. Silk should be bleached at 85–100° C.; wool at 50–60° C., in one and a half to three hours, or even longer. The concentration of the bath liquor must be ascertained by experiment; though, for wool and silk, an average of 10 to 15 per cent. of peroxide, calculated on the weight of the material, may be used; and for Tussah silk, 20 to 30 per cent.

Barium peroxide serves for bleaching Tussah silk, and was also recommended by Mullerus for bleaching cotton. In using this substance, however, the fact that it contains barium hydroxide—a strong alkali capable of corroding animal fibres—must not be forgotten; and it should therefore be washed with water before use. The commercial product contains 8 per cent. of active oxygen.

Potassium Permanganate.—This substance is a very powerful oxidising agent, and is frequently used for this purpose in the laboratory. It must be kept in closed vessels, away from the light, and its solutions are readily decomposed.

Bleachers make use of this salt for treating wool, jute, straw, leather, etc., the mode of application being as follows:—The material to be bleached is first treated with a dilute solution of lukewarm permanganate, until the colour turns to brown (formation of potassium manganate). In bleaching animal fibres this solution receives an addition of magnesium sulphate, which, by forming magnesium hydroxide (insoluble) and potassium sulphate, prevents the corrosion of the fibre otherwise resulting from the formation of caustic potash. To remove the brown coloration the material is next treated with a cold dilute solution of bisulphite, or a similar solution of sulphurous acid and borax (prepared by saturating dissolved borax with sulphur dioxide), and finally washing in slightly acid water, followed by pure water.

Owing to its cheapness this method is largely used for woollens, but far less frequently than the sulphur process described below The permanganate method is very serviceable where stained woollen goods are to be treated with a view to render them fit for sale, if only as inferior goods. It is also useful in bleaching jute, and is actually employed for that purpose.

Potassium Bichromate, in conjunction with sulphuric acid, has a very powerful oxidising effect, and is used for bleaching oils, straw, etc., though not for textile fibres. It has been recommended for jute, but is unsuitable, as it attacks the fibre.

Owing to its property of destroying the colour of indigo, it is used as a discharge in blue printing (*q.v.*).

Potassium Ferricyanide has been proposed by Kassner as a bleach for textiles, and, as a matter of fact, its bleaching action is very powerful in alkaline solutions, potassium ferrocyanide being formed. Nevertheless, the only use made of this property at present is in discharging indigo.

(*b*) **The Reducing Bleaching Agents.**—This class comprises free sulphurous acid, bisulphite, and hyposulphurous acid.

The bleaching action of these substances is not yet fully elucidated, but is assumed to consist in a reduction of the pigmentary matter to its leuco compound, and in the combination of this latter to form a colourless substance. This hypothesis is apparently favoured by the fact that animal substances bleached with sulphurous acid have a tendency to revert to a yellow shade, especially after being treated with alkalis, thus showing that the colour was not really destroyed in the first place, but converted into a colourless compound, which in time has become decomposed and allowed the original colour to reappear.

This phenomenon is most clearly shown in the case of goods that have been bleached with free sulphurous acid. In addition to animal fibres, jute is often bleached by this class of reagent.

Sulphurous Acid is used in three forms—as a gas, an aqueous solution, and as liquid sulphurous acid. The gaseous form is the one most in use, whilst the aqueous solution is the least adapted for bleaching, being always contaminated with sulphuric acid; the liquid (condensed) form is almost entirely free from this impurity, and has been successfully employed in bleaching.

Wool and silk are generally bleached with gaseous sulphurous acid in so-called "sulphur chambers," which are spacious brickwork chambers, fitted with peep-holes for inspecting the goods, the latter being hung on supports inside. The sulphur is placed in iron pots, or in sunken brick pans, which can be fed from the outside. To begin bleaching, the sulphur is ignited, the doors, etc., are closed, and the goods left exposed to the sulphurous fumes.

The quantity of sulphur used must bear a certain proportion to the size of the chamber, in order that a sufficient supply of oxygen for the combustion of the sulphur may be available. The volume of oxygen at disposal for this purpose can be readily calculated from the cubical capacity of the chamber, and a considerable margin in excess of the actual requirements must be allowed for in practice. Should the oxygen be insufficient for complete combustion, the sulphur ceases to burn, and sublimation readily ensues, with the result that the goods get stained with yellow patches that cannot be afterwards eliminated. To prevent this evil the wooden grid over the sulphur pans should be covered with lead and felt.

The average consumption of sulphur required to bleach woollens is 6 to 8 per cent., or for silk 5 per cent., of the weight of material treated. The operation generally takes six to eight hours, but must be repeated three or four times, according to requirements.

To prevent condensation and the consequent spotting of the goods by droppings, a number of heating-plates or steam-pipes are arranged under the ceiling of the chamber, and a chimney with a good draught is provided for carrying off the sulphur fumes after the bleaching is finished.

The sulphur chamber should be entirely free from iron fittings, since the sulphur trioxide invariably produced when sulphur is burned unites with the moisture present, thus forming sulphuric acid, which would rust the iron.

Like all other bleaching agents, sulphurous acid requires the presence of water in order that the reaction may occur at all; consequently the goods must be introduced in a damp state into the chamber.

Light goods, especially those for printing, are bleached by the continuous process, the apparatus used being of the same type as the first steamer employed in calico-printing. In large works two sets of apparatus are mounted side by side; the goods are entered damp and are carried onward over rollers fitted with hardened lead pins. The passage through the chamber occupies ten minutes; and light goods are put through twice, heavy articles three times.

In addition to the more serious defect of the sulphur bleaching process, viz. yellowing, it is also attended with the following disadvantages:—The sulphuric acid, always formed, retards the bleaching action of the sulphurous acid, and may also be a source of danger to cotton in mixed fabrics; and the process makes the wool harsh, though this can be remedied by a treatment with warm soap and water afterwards. Nevertheless, owing to its cheapness and the beautiful white it produces, the sulphur method is still the one most largely used in bleaching animal fibres.

Sodium Bisulphite ($NaHSO_3$) is more generally used for bleaching on a small scale. There are two methods of procedure—either the goods are immersed in a solution of the bisulphite and hydrochloric acid, or else they are treated with the bisulphite first and the acid after. The first is the one most practised, and, as a matter of fact, is equivalent to bleaching with an aqueous solution of sulphurous acid. The goods are left to soak for several hours in a weak solution of bisulphite, containing a corresponding quantity of hydrochloric acid, and are then washed, the process being repeated if necessary. When the bisulphite and acid are used separately, the goods are steeped for some time, *e.g.* overnight, in a fairly strong (about 20° B.) solution of bisulphite, after which they are passed through very dilute hydrochloric acid, and are finally washed with water.

Hyposulphurous Acid.—This compound, which was first recommended for bleaching by Kallab, can be used in the same way as bisulphite, except that acetic acid replaces hydrochloric acid in acidifying the bath.

In this case the goods may be blued at the same time as they are bleached, for which purpose they are immersed in water containing indigo in suspension, and are then transferred to the bleaching bath. After remaining in the latter for several hours, they are exposed to the air for a short time, and then washed with a weak solution of soda, followed with pure water.

Further particulars on the production of the hyposulphites will be given in the section on indigo-dyeing.

Cotton-Bleaching.

In the bleaching of cotton goods, the first question arising is the class of impurities present, and to what extent these are to be eradicated. In addition to the natural impurities, those artificially introduced—in the dressing process, for example—have also to be considered. A piece of cotton fabric coming direct from the loom will always be cleaner and differently bleached than one that has been used as a backing in calico-printing, and therefore contains mordants, dye-stuffs, etc., besides the natural impurities of the fibre. Again, goods that are to be dyed in dark shades will require different treatment to those intended for pink, light blue, or white.

Finally, there arises the question whether the bleached material shall merely *appear* to be clean and white, or shall really be so. In the former event, the actual bleaching process may be dispensed with, the suitably prepared goods being blued, to mask the yellow colour of the raw cotton and turn the same into a fine, slightly bluish white. On the other hand, cottons to be afterwards printed must be bleached and cleaned in the most thorough manner possible, any residual impurities preventing the production of a first-class printed article.

Another point that must be borne in mind in carrying out the various manipulations the goods have to undergo is the nature of the fabrics themselves. For example, curtains, lace goods, and similar light fabrics must not be subjected to any tension or rigid pressure in the machines, and for this reason they must be handled tenderly, boiled as little as possible, washed loose, drained by squeezing between rubber rollers in the wringer, and so on. This also applies to raised goods, in which materials the lay of the nap has likewise to be considered, *i.e.* the goods must always pass through the machines in one direction, that of the pile, and never the other way about. In bleaching these goods, the operation of liming may be omitted, the lime having a hardening effect on the fibre, and impeding the subsequent operation of raising.

Formerly the bleaching of cotton was performed in such a manner that the goods, after a treatment with potash lye (from wood ashes) were decolorised by the action of atmospheric oxygen ("grass bleaching"), these two operations being several times repeated, and supplemented by a process of souring by immersion in sour milk. The bleaching process, under these conditions, lasted one and a half to three months in the case of cotton, and twice as long for linen goods.

This primitive method contained the germ of the modern processes of bleaching, all of which, however highly developed, comprise the three main operations of treatment with alkaline reagents (the so-called "bowking"), the actual bleach, and the employment of acids.

The substances to be removed from the fibre by bleaching are the natural and the adventitious impurities, the former comprising incrustating substances, fat, wax, yellow pigment, etc.; whilst the others include the dressing materials applied to impart greater stiffness to the fibre, and so facilitate the operations of spinning and weaving—these are mostly mineral substances—and also mordants, dye-stuffs, etc., in the case of piece goods that have been used as backing in calico-printing.

It was quickly recognised that the first-named substances could be got rid of by boiling with alkaline reagents, and that the pigmentary matter of the raw cotton could be destroyed by means of bleaching powder, provided the greater portion of the mineral impurities had been previously removed. Consequently dressed cottons are either first steeped for some time in water, or, preferably, freed from the dressing by treatment with acids.

By boiling with lime the organic impurities can be converted into compounds that can then be readily dissolved and removed by boiling with soda and resin soap, the action of lime therefore being merely preparatory, and not actually one of cleansing: as a matter of fact, the goods are far darker in colour after liming than they were at first. The chemistry of this operation is still involved in some obscurity; probably the lime decomposes the pre-existing fats to form a lime soap, and converts the other organic matters into saccharine compounds or aldehydes, this view being countenanced by the discovery of Thies, who found that cotton treated with alkaline earth acquired strongly reducing properties. The acidifying ("souring") process after liming certainly decomposes the organic lime compounds, and enables the liberated fatty acids and other organic bodies to be brought into solution by the subsequent boiling with soda and resin lyes. At this stage the goods are already almost perfectly clean, and their faint yellow colour can now be destroyed by a treatment with bleaching powder, the latter being then eliminated by the aid of an acid bath, followed by washing with water.

The foregoing is a brief sketch of the modern bleaching process, which therefore consists of the following operations:—(1) Boiling with lime; (2) souring; (3) boiling with soda and resin soap; (4) bleaching with chloride of lime; (5) souring.

That each of the operations is succeeded by a rinsing in water, goes without saying.

Latterly it has been found that the operations of boiling with lime and soda-resin soap can be advantageously replaced by boiling with soda lye. Many difficulties were, however, encountered in introducing this alteration. In the first place, the lye must be weak, because strong lye mercerises and also weakens the fibre. Kœchlin proposed to aid the action of weak alkali by steaming the steeped goods, but this method damaged the fibre, and the proposal was therefore devoid of practical value.

Nevertheless, it is possible to cleanse cotton in an excellent manner, without the slightest injury, by the use of strong soda lye. The credit of uniting the various factors here concerned into a technically practicable method belongs to H. Thies and E. Herbig, who found that impregnation with alkaline earths protected the cotton from mercerisation during subsequent boiling with strong soda lye, provided the treatment were performed in the absence of air, both in the kier and in the material.

The cleansing action of strong lye is so complete that the Thies-Herbig process must be characterised as the most important improvement made in the bleaching of cottons. Its value is further increased by the fact that it is also applicable to other kinds of vegetable fibres.

In connection with modifications of the bowking process, it may be mentioned a sulphide is employed in France, and that the commercial product sold as "*sel de soude antiseptique*" seems to be a preparation of this kind.

The proposal to add benzine and other detergent substances to the bowking liquor has not yet been adopted in practice.

The actual operation of bleaching has not suffered any important alterations, notwithstanding the numerous proposals made from time to time; and, for the most part, bleaching powder continues to be used, the method of application being that already described. It is, however, in many cases replaced with advantage by a purer form of sodium hypochlorite.

To turn now to the details of the bleaching process, it may be premised that cotton is bleached, almost exclusively, in the condition of yarn or cloth, the only exceptions being the bleaching of loose cotton for surgical wadding and jewellers' wadding—the last named being usually dyed some delicate shade. The boilings necessary in bleaching would result in the entanglement and balling of the fibres if applied to the loose material, and the operation is therefore performed in the following manner:—The material is first cleansed by a short boiling in a weak alkali, *e.g.* a 3 per cent.

solution of sodium silicate (water glass), and then bleached, if necessary, with hydrogen peroxide. When required for medicinal purposes, the cotton must be very slightly moistened with water, an object attained by very gradually drying the bleached material.

Bleaching Cotton Piece Goods.

The preparatory operations in this process consist of marking, sewing, gassing, and raising. Each piece is marked with a number, etc., so that it can be recognised after bleaching, the marking colour —generally coal-tar—being of a kind capable of resisting the bleaching agents used. Then the pieces are sewn together, end to end, so as to make the entire batch of goods into one long piece or band. Next follows gassing, the object of which is to singe off the nap fibres standing up above the surface, since these would otherwise give the bleached material a woolly appearance, and also cause inconvenience in printing. The pieces may be gassed one or more times, and on either or both sides, by passing them rapidly over red-hot plates or cylinders, or over a row of non-illuminating gas flames.

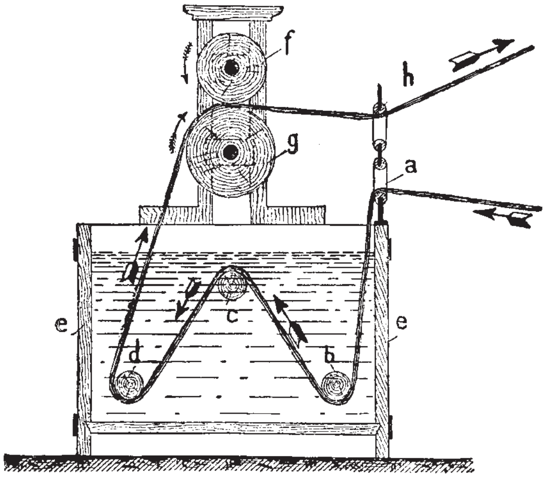


Fig. 15.

In the case of plates, there is a difficulty in keeping them at uniform temperature throughout, owing to the cooling action of the cloth. This inconvenience is reduced in the cylinder machines, but the naked flame method is the best, especially for light goods.

Occasionally, as in the case of flannels, mollinos, etc., the goods are raised before bleaching; this is generally confined to the underside of the fabric though sometimes both sides are raised.

Full Bleach with Lime and Resin Soap for Piece Goods.

(100 Pieces of 65 yards.)

1. **Steeping.**—The goods are steeped in water for twelve hours, or even longer; this softens the dressing and other impurities

present, and facilitates their solution afterwards. This preliminary steeping is, however, frequently omitted, especially when the goods are fairly clean already. On the other hand, if the pieces contain much dressing, or have been used in calico-printing—in which event they will generally be strongly contaminated with alumina—they will need steeping for some time in a weak solution of hydrochloric acid or sulphuric acid.

2. **Lime Boiling.**—A milk of lime is prepared by mixing about ½ cwt. of quicklime with 100 gallons of water, and passing the mixture through a sieve. Through this mixture the goods are passed, and are then transferred to the bowking kier (Fig. 15), an iron vessel fitted with a wooden grating as false bottom, which is covered with a layer of sacking and then with the band of goods, the latter being packed together as closely as possible, in order to prevent them from being displaced in the course of boiling, and also to guard against the formation of cavities or hollow spaces between the layers, since otherwise the goods are liable to local overheating or scorching. The whole is next covered with wrappering, tamped down with rods, and covered with water, which is then raised to boiling heat, and maintained at that temperature for six to fifteen hours, the kier being closed, and the pressure kept up to three or four atmospheres. The duration of this lime boiling varies according to the class of goods and the pressure employed, light pieces being finished sooner than heavy ones, and high-pressure accelerating the operation.

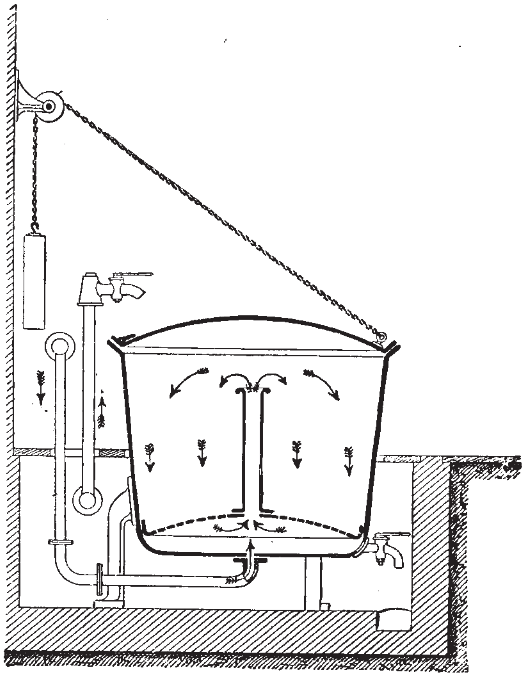


Fig. 16.

Apart from the various forms given to bowking kiers, they all contain, as a matter of principle, some arrangement for ensuring a continuous circulation of the bowking liquor (see Fig. 16).

When the operation is finished, the lime liquor is run off, the pieces being then swilled with water and transferred to a washing-machine (Fig. 17). The lime must not be allowed to dry on the goods, or it will become very difficult to remove.

The washing machine used consists mainly of two wringer rollers, *e*, *d*, mounted on a strong frame, *a*, and driven by the pulleys, *b*, *c*; also of the roller, *h*, which revolves in the water, the grating, *l* (separating the hanks in the case of yarn), and the two porcelain orifices, *i*, *k*, for the ingress and egress of the goods.

3. **Souring.**—The goods are passed through a vat containing 2° B. hydrochloric acid—sulphuric acid, though occasionally used, is less suitable, the insoluble calcium sulphate then formed being more difficult to eliminate than the soluble chloride—and is then left, covered up so as to exclude the light, in a wooden vat for about half an hour; or else the pieces are steeped for four to five hours in very weak (about $\frac{1}{2}$° B.) acid. After this they are washed.

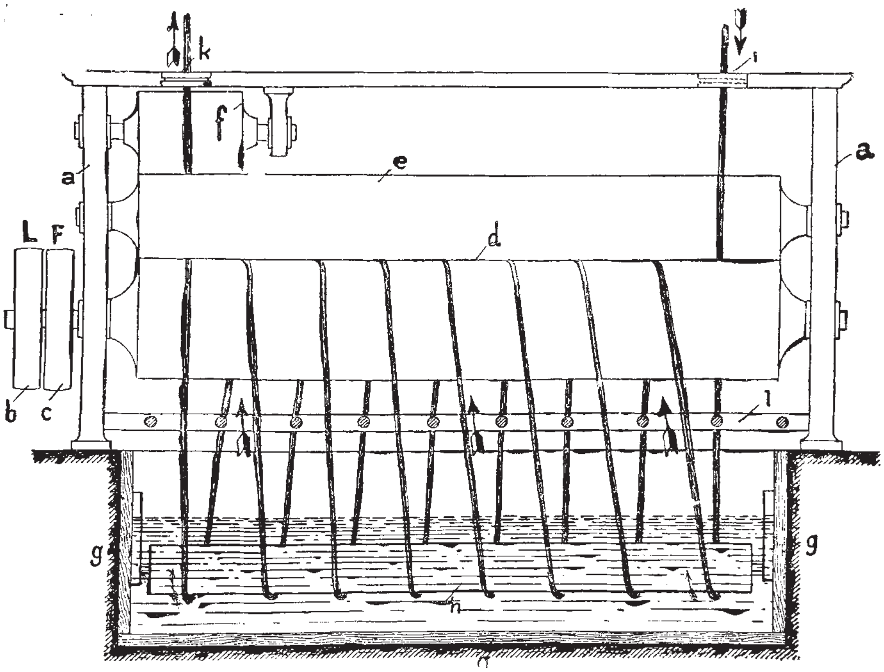


FIG. 17.

4. **Boiling with Resin Lye.**—This operation is performed in the same manner as in lime boiling, and in similar kiers. The liquor is prepared by boiling 10 lb. of colophony with 30–40 lb. of soda and 20 gallons of water for about six hours. This

preparation is then diluted with about eight times its own volume of water, and the goods are boiled therein for about twelve hours, under a pressure of three atmospheres. After running off the liquor the goods are boiled with water, to remove the resin, and are finally well washed in the machine. If the goods were to be treated with cold water immediately after the resin boiling, the residual resin would adhere to the material and be difficult to remove.

5. **Bleaching** ("**Chemicking**").—The goods are impregnated with a clear, freshly made $\frac{3}{4}^\circ$ B. solution of bleaching powder, and then left alone in a dark place for half an hour or an hour; or they are steeped for six hours in a 0·3° B. solution of the same reagent. In either case the treatment is followed by a good washing.

6. **Souring.**—To eliminate the rest of the bleaching powder, which would render the goods friable in time, they are next passed through dilute (1° B.) hydrochloric acid, and left exposed to the air for half an hour; or they are steeped for several hours in a more dilute acid. Washing follows in either event.

Full Bleach for Piece Goods in Soda Lye.

1. The goods are steeped in water for at least twelve hours.
2. They are next boiled for fourteen hours in $2-2\frac{1}{2}^\circ$ B. soda lye, without pressure, to prevent the impurities being fixed in the material. Washing follows.
3. Souring, by immersion for four or five hours in $\frac{1}{2}^\circ$ B. hydrochloric acid, succeeded by washing.
4. Second lye boiling, with lye of the same strength as before, for sixteen hours, but under pressure; washing.
5. Souring as before; washing.
6. Chemicking. The goods are steeped for six hours in clear, freshly prepared 0·3° B. bleach liquor, and afterwards washed.
7. Souring as before, followed by washing.

If the goods are to be dyed with alizarine rose-red, they must be bowked with lime previous to the first lye boiling.

The Thies and Herzig Full Bleach for Piece Goods.

(30 cwt. of Cotton.)

1. Souring, partly for removing the mineral impurities, partly for separating them from their organic combinations. An original feature in this method is the addition of a small quantity of hydrofluoric acid, which increases the effect of the other acids and removes any silica present. The acid bath contains 10 grms. (1 per cent.) of 60 per cent. sulphuric acid, or 16 grms. of 30 per cent. hydro-

chloric acid, and 0·5 grm. of 75 per cent. hydrofluoric acid per litre. The cotton is steeped for four hours in its own weight of this solution, and is then exposed to the action of steam in a small steamer for about half a minute, and washed. When the goods are clean this preliminary treatment may be omitted.

2. The goods are steeped all night in a ½ per cent. soda lye at 50° C., to remove adherent matter, dried sap, etc. If the stuff is very unclean this operation is repeated.

3. The next process is washing in water containing an alkaline earth salt, which facilitates the removal of the alkali and deposits insoluble alkaline earth in and upon the fibres. Fifty grms. of 25 per cent. magnesium chloride are taken per 1000 litres of water—*i.e.* 0·0005 per cent.—or correspondingly less in the case of hard water. The pieces are then put through a wringer, so as to leave in the material only about its own weight of water.

4. Bowking in the kier by steam heat, at a temperature of over 100° C. This takes up to two and a half hours, according to the size of the kier, and is performed as a preparation for the following boiling in strong soda lye. The latter being introduced in a hot state, the mercerisation of the goods is prevented, and the steam expels the air which would otherwise enable the strong alkali to corrode the fibre.

Moreover, the conjoint action of the alkaline earth and heat on the impurities in the cotton results in the formation of reducing bodies, which are easily removed in the subsequent lye boiling, and besides counteract the oxidising action of the latter.

5. The goods are suffused with hot lye, at a temperature exceeding 100° C. This solution is prepared from 1 cwt. of 98–99 per cent. soda, causticised with lime and diluted to 110–120 gals., 20 lb. of resin being then boiled therein. This gives a lye of about 5–7 per cent. strength. The specified weight of cotton occupying a space of about 140 cub. ft., this quantity of lye will only be just sufficient to thoroughly impregnate the material. In the older methods the use of strong lyes was prohibited for economical reasons, since to cover the goods requires about 2–3 times their own weight of lye.

The circulation of the lye and steam is maintained by the pump, *d* (Fig. 18), which draws and delivers them into the vessel, *c*, thence into the heated vessel, *b*, from which they return to the kier, *a*, where the goods are situated. The vessel, *c*, contains a perforated pipe, *e*, through which a part of the steam escapes into the open air at *f*, thus compensating for the dilution produced by the saponification process within the vessel, and maintaining the uniform strength of the lye.

At the end of about three hours, the goods are washed with boiling water in the kier.

6. **Chemicking.**—This operation is performed with bleaching powder as usual, or with pure sodium hypochlorite, the only difference being that the liquors are merely one-third the ordinary strength.

7. Souring, as in the first operation.

The principal advantages of the Thies-Herzig process consist in a saving of about 40 per cent., as compared with the ordinary method (lime and resin soap), more rapid performance, absolute purification and unimpaired strength of the bleached goods. Indigo blue can be more readily discharged than usual when the goods have been bleached by this method.

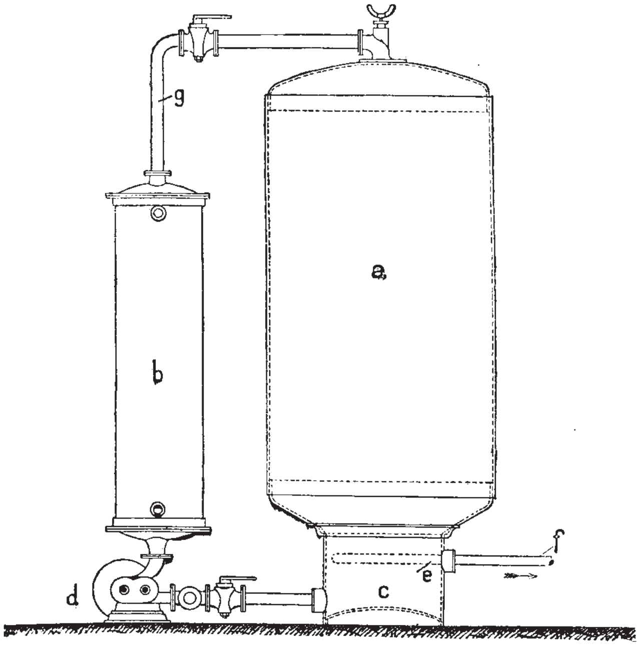


FIG. 18.

Whichever method of bleaching has been employed the goods are afterwards loosened in a machine, then spread out and hot-calendered, or tentered, if necessary, after which they are sorted and shorn. The latter operation is performed in order to remove the nap from the surface of the cloth, the short hairs composing same being first raised by brushing and then cut off by revolving cutters. A final brushing completes the process. Of course this operation is omitted in the case of goods in which the pile constitutes an essential feature of the weave.

Bleaching causes the goods to lose 8–14 per cent. in weight, and even a loss of 20 per cent. is not extraordinary

In order to obtain perfect results, every stage of the bleaching process must be supervised with extreme care, the more so because a batch represents a considerable sum of money. The progress of the operations is checked by taking samples at intervals and dyeing them with alizarine, this test revealing any spotting produced by lime, resin, or bleach. The latter, due to the formation of oxy-cellulose, can be also detected by dyeing with methylene blue.

The bleached goods are washed out in separate machines and stored away from possibility of contact with chemicked or soured pieces. Great care must be taken to avoid rust stains, these forming the most unwelcome of all the bleacher has to fear. With this object the kiers must be kept perfectly clean; no accumulations of liquids must be allowed to collect in the steam and water-pipes, etc. Should they occur, these stains may be taken out with oxalic acid. Dye stains, such as the alizarine red on backing pieces from the calico-printers, can be discharged by bleaching with potassium permanganate.

Full Lye Bleach for Yarns.

1. The goods are steeped in water for about ten hours, but if the yarn be fairly clean this may be omitted.
2. They are next boiled for fourteen to sixteen hours in lye of 2–2½° B. strength, followed by washing.
3. The next stage is souring, by several hours' immersion in ½° B. hydrochloric acid, succeeded by washing.
4. Chemicking. The goods are steeped for about five hours in a 0·15–0·2° B. solution of bleaching powder, and then washed
5. Second chemicking in the same way.
6. Second souring, as before.
7. The yarn is softened by steeping for some time in a hot solution of soap, and is then washed once more.

This method is very similar to that employed for piece goods. Modifications of the process are practised in some places, and occasionally the other methods described are applied to yarns.

Partial Bleaching.

As already stated, it is not always necessary to fully bleach cottons, this being done only when the goods are to be dyed in light shades or printed, whereas for dark shades of dyed goods bleaching would in many instances be a superfluous operation, and one likely to injure the colour in the case of Turkey-red dyeing.

Cottons for half bleaching are bowked with lime or soda, soured, and washed. Yarns are boiled, without pressure, in a very weak soda lye, and then boiled off and rinsed; occasionally a simple boiling in water is sufficient. Goods to be dyed with aniline black do not require any cleansing at all.

White goods are first boiled with alkali, then chemicked, and blued with ultramarine. In the case of piece goods, this is done in the dressing process, but with yarns the ultramarine is applied in suspension in a warm soap bath. Latterly, however, owing to the ease with which irregularities occur in blueing with ultramarine, this pigment has frequently been replaced by methyl violet applied in an alum bath.

Out of the many methods proposed for bleaching cottons, the following may be mentioned:—

G. Hertel's Bleaching Process (German patent 75,435, 30/3/93).—The material to be bleached is impregnated with a $\frac{1}{4}$–10 per cent. solution of Turkey-red oil (according to the desired effect), the excess being removed by wringing or draining in the hydro-extractor, and the goods boiled with 1·5–2 per cent. of caustic soda for six hours under pressure, after which they are rinsed, slightly soured, washed, lightly soaped, rinsed, and dried.

This method is claimed to be specially suitable for yarns to be dyed rose-red by the Erban and Specht process, and also for Mako cotton, which hitherto could not be bleached except by the aid of very strong chemicking baths.

In France (Rouen, for example) such cottons as are to be dyed in delicate shades are cleansed by boiling with lye and a sulpholeate. A product of this kind is sold under the name "Fankhausine," and is possessed of certain advantageous properties in that it readily moistens the cotton; the duration of boiling is reduced to one to four hours, and the bath may be allowed to cool down while in use —a condition impossible with the ordinary process. For goods that are to be dyed with basic dyes, the Fankhausine treatment can be applied at the same time as the tannin.

The Mather and Thompson Continuous Bleaching Process. —The characteristic features of this process are that, after certain preparatory treatment, such as lye boiling, souring, etc., the goods are passed continuously over a series of rollers, and also through a chamber filled with gaseous carbon dioxide for the purpose of liberating hypochlorous acid and thereby increasing the activity of the bleaching powder. The goods are passed in succession through warm water, bleaching powder solution, the carbon dioxide chamber, cold water, warm soda solution, water, a second chemicking bath, carbon dioxide gas, water, dilute hydrochloric acid, and, finally, water.

Electrolytic Bleaching Process.—The method is usually associated with the name of Hermite, who was the first to propose the preparation of a bleaching liquor by the electrolytic decomposition of magnesium chloride. The most important features of the process have already been described in dealing with sodium hypochlorite.

Linen-Bleaching.

The bleaching of linens is conducted on the same principles as in the case of cottons, the impurities being removed by boiling with lime or soda, and the colouring matter by the aid of bleaching powder.

The fibres are, however, more difficult to decolorise than those of cotton, owing to the larger quantities of impurities present, the amount and quality of which depend on the method of retting pursued. Consequently, this last-named process should be performed with special care.

Moreover, flax fibre is more susceptible than cotton, and on this account the various reagents must be used in a weaker condition and applied over and over again. The chief cause of the difficulty in bleaching flax resides in the brown substances, known as pectin bodies, contained in the fibre, since they cannot be destroyed by the unaided action of bleaching powder, but require the assistance of the grass bleaching process. Apparently these bodies are not destroyed by the bleaching agent, but are merely converted into a form more soluble in alkalis. A single vigorous treatment with bleaching powder does not suffice to remove the pectin bodies; neither is this treatment advisable, as it would certainly attenuate the fibre. The conversion of the pectin bodies into a soluble form is therefore a matter of repeated attacks with bleach, assisted by interposed treatments with alkaline baths, and supplemented by grassing.

Apart from the repetition of the various operations and the recourse to grassing, the process of linen-bleaching differs from that for cotton in that the goods are kept in motion during the treatment in the chemicking bath, and are subjected to friction between two fluted boards in order to get rid of particles of the adherent brown matter.

Flax is bleached either as yarn, twist, or in the piece, and the process is divided into four classes—quarter, half, three-quarters, and ull bleach, according to the degree of purification produced. The loss in weight ranges up to as much as 18 per cent., or occasionally as high as 25 per cent., and ends at the half-bleach stage. The entire operation takes about three to six weeks.

The boiling is effected in open and in low-pressure keirs; the chemicking and souring are performed in a special manner, viz. in a series of (usually) three stone or wooden tanks containing respectively dissolved bleaching powder, water, and dilute hydrochloric acid. The yarn is suspended on pegs, which are mounted on a frame running on rails over the top of the tanks. Sometimes the pegs supporting the yarn are fitted with cog-wheels which engage in one another and cause the yarn to turn round and round in the bath liquor.

After a short time the entire frame is lifted out of the bath and transferred to the next tank, where the yarns are washed. In the same manner they are conveyed to the third tank, where they are soured, and are finally washed in a fourth vessel, or returned to the second tank for that purpose.

Piece goods are first moved about in the chemicking liquor for some time, and then left to steep therein, though more usually the movement is continued and extended over a longer time.

For grassing, the yarns and piece goods are spread on the grass in summer, and turned at intervals; in winter they are hung on sticks or frames. Naturally, the bleaching action is stronger in the summer, and becomes apparent after the lapse of only a few hours. Begemann proposed to expedite grass bleaching by first slightly blueing the goods with indigo, in order to ensure the absorption of the more active blue light rays as well as the yellow ones.

Well bleached linens should be white all through, and should not stain when treated with an alkali, such discoloration indicating imperfect removal of the pectin bodies.

The details of linen-bleaching naturally vary in different localities. The following description applies to the method as pursued in Silesia:—

Full Bleach—

1. Boil for nine to ten hours, or longer, according to quality, with 10 per cent. of soda, under gentle pressure.

2. Chemick with a bleaching powder solution, containing 4 per cent. of active chlorine; wash and sour.

3. Treat in hot (50° C.) soda solution in an open kier; wash.

4. Grass for two to three days (in summer), turning once.

5. Chemick for several hours in a weak solution of bleaching powder, evolving only an almost imperceptible odour of chlorine.

6, 7, 8. Repetition of 3, 4, and 5.

9. Weak soaping in circular vat, the soap solution being

admitted automatically, flowing through the yarn, collecting underneath, and returning to the goods after passing through an upcast pipe.

For quarter-bleach the operations are restricted to Nos. 1 and 2, in addition to a boiling with soda.

Piece goods are treated in the same manner, except that the operation commences with a lime bowking.

It should, however, be borne in mind that working on any invariable lines is an impossible matter in linen-bleaching, the method of treatment being wholly dependent on the quality of the goods and on the effect to be obtained.

Jute-Bleaching.

Almost every known bleaching agent has been tried on jute, from which circumstance it will be evident that a perfectly satisfactory method of bleaching this fibre has still to be discovered.

As a rule, the work is confined to a bleaching in the restricted sense of the term, sodium hypochlorite being chiefly used. Under these conditions a supplementary treatment with dilute bisulphite will prove beneficial.

The method of bleaching jute by alternate treatment with potassium permanganate and bisulphite, though rather expensive, furnishes good results, and the loss in weight is small.

Jute, being very susceptible to the action of alkalis, should only be treated with such as are of a very mild character, like sodium silicate, borax, etc.

However, this fibre is generally used in an unbleached condition, either in its natural colour, printed, or dyed (or both).

Hemp-Bleaching.

Great difficulty is experienced in bleaching hemp in a thorough manner, and the fibre is generally used in the unbleached state; in fact, only the yarns intended for making up into string are bleached, the operation being effected by the aid of bleaching powder after a preliminary cleaning with sodium silicate.

Ramie-Bleaching.

As already mentioned, the process used in Europe for bleaching ramie is almost identical with that employed for cotton; only, in the chemicking especially, greater care is necessary to ensure the protection of the fibre.

Scouring and Bleaching Silk.

The purification of silk consists in removing the sericin and colouring matter present in the raw material. As, however, these mainly reside in the bast layer, all that is necessary in most cases is to get rid of this latter by the operation known as scouring, or decorticating.

The bast layer gives the silk a hard, rough character, which prohibits its use in a raw state, except in very few instances. As a rule, silk is desired to exhibit all its valued properties, such as softness, lustre, etc., and on this account must be freed from the bast, the more so because raw silk cannot be dyed so permanently as when scoured, the reason for this being that the dyes are then absorbed by the bast, which afterwards yields them up more readily when washed.

Removing the bast entails considerable loss in weight, amounting to 18–22 per cent. in the case of Chinese and Japanese silks, and 25–30 per cent. in European silks. On this account it is often customary to only scour the silk to such an extent that the loss amounts to about 6–8 per cent., the endeavour being at the same time to impart to the product a portion at least of the valuable properties of scoured silk. The resulting product is known as "souple" silk, and is used as a weft. In treating this article, the fact that it will not stand warm soap or alkaline baths must be borne in mind; in fact, if only left to lie in a moist condition, it sheds part of its bast layer spontaneously, this effect being recognised by the formation of lustrous spots. It must therefore be either dried at once, or else dyed and dried; should immediate dyeing be impracticable, the silk must be left in water.

The silk is scoured in hank form, as grège silk, or also after weaving, the operation being performed by the aid of soap and soda. True, soap alone is best, and that too of good quality, devoid of free alkali or smell, and being readily soluble so that it can be afterwards easily washed out of the silk. Potash soap is better than soda soap for this purpose; and, in fact, soda does not form a good addition to the scouring bath, owing to its tendency to make the silk harsh. However, for the sake of cheapness, a mixture of soap and soda is frequently used, and the cheaper souple silks are even scoured with soda alone.

For better qualities it is essential to employ nothing but soap, an addition of soda being inadmissible, except for the purpose of softening the bath water, since the lime soap, otherwise formed, would be deposited on the fibre and dirty it, or at least spoil its sheen. It is therefore necessary in scouring silk to entirely prevent any deposition of lime or magnesia soap on the fibre. Should the raw silk not be entirely free from mineral matters (*e.g.* dust) it is advisable to wash it, first in slightly acid water and then in pure water, before scouring. The same consideration must also be borne in mind in washing the silk after scouring.

Two scouring baths are generally required: the one containing 25 to 30 per cent. of soap, the second 20 per cent., calculated on the weight of raw silk treated.[1] The grège is treated in the first bath for about ten minutes or longer, according to the quality, at a temperature rather below 100° C. The bast swells up, making the silk sticky, and then dissolves, leaving the lustrous internal thread of the silk exposed. A sojourn in the second soap bath then completes the removal of the bast. Silk that is to be dyed in delicate shades is passed through a third soap bath, and finally rinsed with fresh water.

The first bath can be used seven times over, but will then be so full of sericin as no longer to be applicable for this purpose, though suitable for use as "bast soap" in silk-dyeing. The second bath, which contains a smaller proportion of sericin, is advanced to the dignity of first bath, a fresh solution being prepared in its place.

Of course it is not feasible to treat all kinds of silk in exactly the same way, some being more easily freed from bast than others; and in point of their ability to stand the action of the scouring baths considerable differences exist, Milanese trame silk being particularly ticklish to handle. In fact, this silk must not be left in the bath more than ten minutes, and, should the bath liquor contain any pre-existing sericin, the silk will be rendered "lousy." Such silk exhibits, when dyed, numerous light patches, due to disintegration of the silk thread; the appearance may, however, be improved by treatment, first with soap and afterwards with weak hydrochloric acid.

In the case of *loaded* silk, the removal of the bast is almost impossible to effect in a satisfactory manner, owing to the inevitable formation of metallic soaps. Before proceeding to the scouring process a portion of the loading materials has therefore to be eliminated by treatment with acid.

After the silk has been scoured it is stretched, chevilled (smoothed), lustred, bleached, loaded, and dyed. The first three

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[1] The following recipe from a practical source may be cited as an example of other methods of scouring silk. The silk is treated for three to four hours at 70–80° C. in a bath containing 6 parts, by weight, of Marseilles soap and 1 part of soda per 1000 parts of water—the latter previously softened—after which the material is washed, soured with weak hydrochloric acid, and rinsed.

operations are performed with the object of rendering the silk as soft and lustrous as possible. Stretching consists in repeatedly pulling back the silk threads when stretched taut between two rods, and is effected either by hand or in a machine.

Smoothing is effected by winding the silk upon itself, by hand or in a machine, whereby the separate threads are smoothed by mutual friction. (Machines for this purpose are illustrated in Knecht, Rawson, and Loewenthal's *Handbook of Dyeing*.)

Lustring or glossing consists in imparting the maximum lustre to the silk by a combined process of stretching and steaming.

Bleaching is only practised when the silk is required to be white, or to be dyed in very light shades. Sulphurous acid is the agent employed, and the method has been already described in dealing with that reagent.

Loading.—In the case of white or very light-coloured silks, a dressing of tin chloride (*see* Chap. III.) is applied before dyeing, but dark-coloured silks are loaded in the dyeing process or afterwards, by the aid of tannic acid.

Scouring silk in the piece is a method increasing in favour on account of the advantages resulting from weaving the threads in an unscoured state. For example, raw silk is better able to stand friction, and is more elastic than when scoured, so that it is less liable to break in the loom; and again, the almost inevitable dirtying to which the threads are exposed in weaving is merely superficial in raw silk, and is readily removed in the subsequent scouring.

The operation is performed in a continuous manner by passing the pieces, full width, over rollers and through vats containing hot solutions of soap and soda (*e.g.* 6 parts of soap and 1 part of soda per 1000 parts of water); they are heated first to 70–80° C., then to 100° C. The operation takes a half to three-quarters of an hour, or sometimes longer.

Half-silk goods are scoured in the piece exclusively, and must be gassed beforehand. Half-silks to be dyed dark shades contain raw (unbleached) cotton, and therefore, except when the proportion of this is very small, the goods must be put through a strong scouring bath (containing 3–5 per cent. of soda, calculated on the weight of the goods), the operation in this case lasting one and a half to two hours.

Half-Scoured or Souple Silk.

To prepare half-scoured or souple silk, the silk is first cleansed by treatment in a weak, luke-warm soap bath, which at the same time softens the bast. After this it is immersed in a 10 per cent. bath of potassium nitrite, strongly acidified with sulphuric acid for an hour, or for about a quarter of an hour in warm dilute *aqua regia* (nitro-hydrochloric acid); in the first case, the colour turns grey, in the second green. Then, after being treated in a bath of soap, plus a large proportion of soda, it is sulphured three times, six hours each time, in a damp state, the hanks being turned after each treatment. The next stage is rinsing in water acidified with sulphurous acid, followed by the actual process of softening, the hanks being steeped in a hot (90–100° C.) 5 per cent. solution of potassium bitartrate, and an aqueous solution of sulphurous acid —the condensed droppings from the sulphuring chamber—until the threads are exposed, though this is not perfectly visible until they have been drained. According to the quality of the silk, the treatment lasts an hour or more.

Some dyers use a bath of bitartrate and hydrochloric acid, or magnesium sulphate, in which latter event the loading of the silk is effected at the same time; the feel of the silk is, however, best when sulphurous acid has been used. When the silk is to be dyed in dark shades the softening process may be performed with tannic acid in the dye bath.

Bleaching and Scouring Tussah Silk.—Attempts have been made to bleach Tussah silk by almost every known bleaching agent. The operation is a difficult one, and is therefore omitted except when the silk is to be dyed in light shades. For the most part it is woven in its natural colour.

The best bleaching agents for this fibre are the peroxides, the material being treated for an hour or so in a bath containing 50–100 per cent. of barium peroxide at about 90° C.; or else with hydrogen peroxide in the manner prescribed for that reagent.

Scouring is also a more difficult process with Tussah than with true silk, and entails more time and the use of stronger soda baths.

Washing and Bleaching Wool.

Whereas the entire series of operations concerned in the purification of cotton are comprised in the term "bleaching," a distinction is made, in the case of wool, between the actual bleaching process and the preparatory cleansing operations, the latter being termed "washing."

As it comes from the sheep, wool is contaminated with so many impurities that washing is the first treatment necessary, it being impossible to spin unwashed wool, though raw cotton can be spun without question.

Woollen yarns and piece goods, though freed from the natural impurities of the fleece, nevertheless contain impurities consisting of the fatty matters added to the wool to facilitate spinning and weaving, in addition to dirt acquired by contact with dirty machinery, dust, and the workmen's hands. Consequently the washing of these goods is performed in a different manner to that employed for the raw wool.

Bleaching, as applied to wool, is restricted to yarn and piece goods, and plays a far less important part than in the case of cotton, the great bulk of manufactured wool never being bleached at all.

Though in this country it is a common practice to wash the sheep before shearing, this is rarely done in the case of foreign wool, and when practised has always to be supplemented by the usual wool-washing process, except for low-grade wools such as Hallina. This supplementary washing should be performed as soon as possible after shearing, since delay only increases the difficulty —as experience has shown in the case of fleece-washed foreign wools.

The washing to which the wool is subjected in wool-washing establishments is a far more important operation than fleece-washing, its object being to secure the removal of all the impurities comprised in the term "grease." For this purpose use is made of alkaline substances—soda, potash, soap, Quillaya bark (*Quillaya saponaria*), ammonium carbonate, and stale urine. Caustic alkalis, however, must be carefully avoided, owing to their known corrosive action on wool fibre.

The oldest known detergent for wool-washing is stale (putrescent) urine, which, when diluted with about five times its own bulk of water and used at medium temperatures, cleanses the wool very well. The real active ingredient is ammonium carbonate, liberated by the decomposition of the urea. Despite its unpleasant smell, this detergent is still used in many small works.

Ammonium carbonate itself is an excellent detergent for wool, but is still too dear for practical use, the field being left almost exclusively open to soap and soda (or potash). Usually a mixture of the two is employed, the proportions being regulated according to the quality of the wool and the hardness of the water. The coarser the wool the larger the proportion of soda, and it will be readily apparent that hard water requires more soda than soft water, it being necessary to throw down the lime and magnesia as carbonates, in order to prevent their deposition, in the form of fatty acid compounds (soaps), on the wool. The carbonates of these alkaline earths come down in the form of powder and can then be easily washed out of the wool, which is not the case with lime and magnesia soaps; moreover, the formation of the latter entails a certain waste of soap.

Wool of low quality, such as is used for making coarse fabrics, rough blankets, etc., is washed with soda alone, for the sake of cheapness; but worsted wools are washed solely with soap. Wools for carding are washed with a variable mixture of soap and soda, averaging 4 to 5 parts of ammonia-soda and $1\frac{3}{4}$–2 parts of soap per 1000 parts of water. Soda soon roughens wool, and the temperature should not be allowed to exceed about 50° C. when this alkali is used. Its employment is nevertheless essential for fine carding wools, since fine wools are more difficult to cleanse than the coarser kinds, and a larger proportion of soap would cause the fibre to shrink and thus unfavourably influence the wool for the purpose in view.

The exact proportions of soap and soda can only be determined by practical experience, since each kind of wool behaves differently in the washing. Hence care should be taken never to wash different sorts of wool together; and the sorting of wool previous to washing must be performed with great caution.

Other proposed adjuncts to the above-named detergents are—common salt, sal ammoniac, olein (as an emulsifier), etc., but none of them have made any headway in practice. Patented detergents of undisclosed composition, sold under fancy names for wool-washing, should be avoided in any case, since they are either worthless, or could be prepared by the washer himself at a much lower cost. For the most part they consist of a large proportion of soda and a very little soap, and are therefore generally recommended for washing with hard water.

Of late, experiments have been tried with the solvents used for extracting fats, such as carbon disulphide, benzine, etc., but the practice has been discontinued in nearly every case, the process having the disadvantage of requiring very complicated plant, and, in addition, the risk of fire is high and the fatty matters are too thoroughly removed, the wool thereby losing much of the suppleness so desirable in the subsequent treatment.

The Washing Process.—The wool is first carefully sorted and freed from burrs, which latter would injure the fibre if not removed. It is then put in the washing machine, the so-called "leviathan," shown in Figs. 19 and 20, which consists of a series of tanks (generally four or five), the first of them containing the detergent solution, the others filled with warm clean water. The actual cleansing of the wool therefore takes place in the first tank, the temperature of which is kept at about 50° C., whilst the others serve for rinsing the purified charge. Each tank is fitted with cranked rakes, which move the wool onwards, and between each two adjoining tanks is mounted a pair of heavy wringer rollers, which take the wool from the elevator and, after expressing the superfluous liquor, deliver it to the next tank. The best type of leviathan washer is that of A. Déru shown in Fig. 19, the chief advantage of this type residing in the excellent elevator and wringers, which latter work under a pressure of about eighteen tons. By this means the wool is wrung in a very thorough manner and the transference of dirty scouring liquor into the rinsing tanks is reduced to a minimum.

Fig. 19 shows the elevator and the submerging roller of the second tank of the Déru machine, the former consisting of two toothed wheels *a*, rotating about a shaft *b*, mounted at *d*. Bearings *c* support the pins *f*, which carry the paddles *g*, and the attached zinc forks *h*. The movement of the forks which carry the wool is effected by the sliding of the rollers *i*, *k*, on the tracks *l*, *m*, and the wool is delivered between the rollers *o*, *p*, whence it passes at *q* into the wheel *r*.

Fig. 20 shows the manner in which the wool is worked in the Demeuse machine by the crank rakes *b*, *c*, to the elevator *d*, and from the latter to the wringer rollers *f*, and thence to the creeper *h*.

The scouring liquor in the first tank will, of course, remove the bulk of the impurities, and will have to be drawn off after a certain time. In order to utilise the liquors to the utmost, that from the second tank is then run into the first one, its place being taken by that from the third tank. This transfer is effected by means of an injector.

When properly washed, wool still contains about 1 per cent. of fat. In some washing mills a larger proportion is designedly left in the wool, but this is not advantageous to the purchaser.

When washing worsted wool, it is sometimes the practice to incorporate combings, as a cheap and pure adjunct which unites well with the wool and cannot afterwards be detected therein.

The spent liquor from the washing machines is run into a collecting tank, through a vertical iron grating which keeps back any accompanying wool fibres. These latter, though very dirty, can be washed and sold as inferior wool. The liquors are then passed through a series of settling tanks, where the bulk of the suspended impurities is deposited, after which the liquid portion is either run off or treated with sulphuric acid or lime for the recovery of the contained fatty acids. When acid is used, the fatty acids are obtained in a free state, but when lime is employed they are in the condition of lime soaps, which must then be decomposed by an acid. The former method is most in use, and is best performed in the warm. The recovered fatty acids are purified by pressing, smelting, and bleaching.

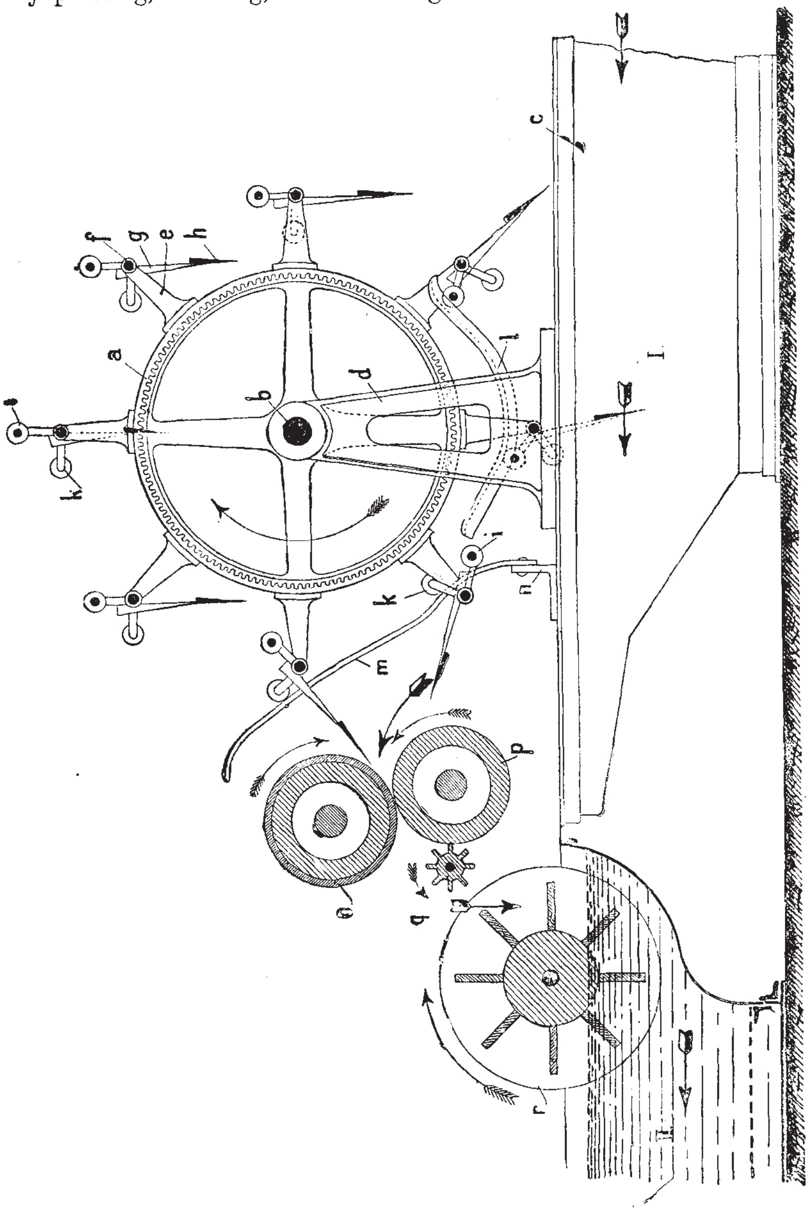

Fig. 19.

This recovery of fatty acids pays only in the case of large establishments, and even in such works the acids are sold in their crude state to the soapmaker.

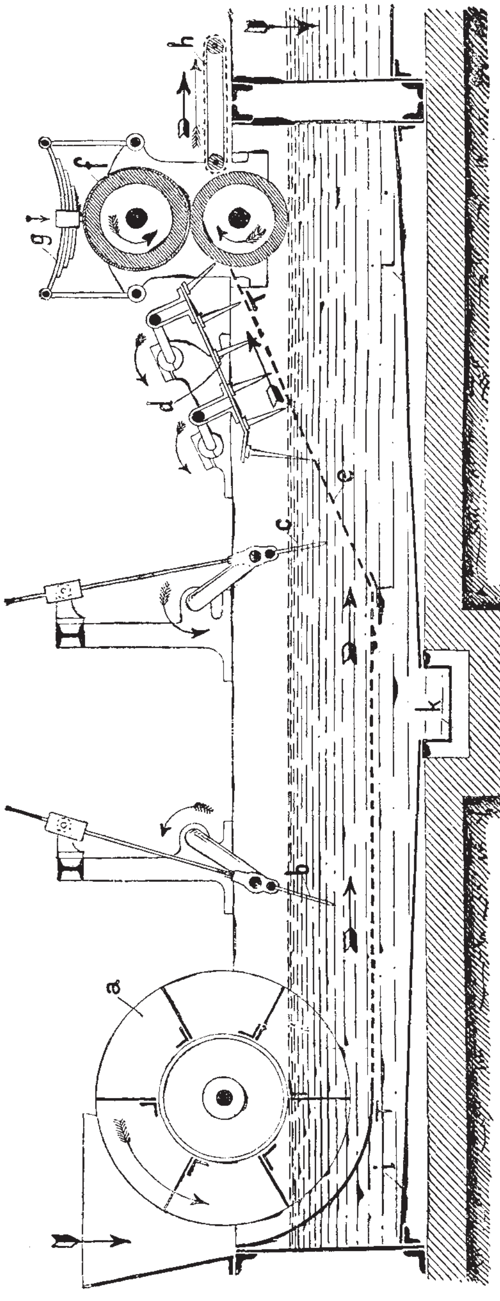

Fig. 20.

Latterly the recovery of wool fat from the washing liquors is practised, the liquor being treated in a centrifugal extractor, which retains this fat. The latter is then purified by repeated meltings, boiled with water, and kneaded with water to form the commercial product lanolin, which is largely used as a salve, owing to its capacity for penetrating the skin. Liebreich was the first to recommend it for this purpose.

The soapy water left in the recovery of wool fat can be used over again as scouring liquor.

Finally, the potash in the yolk of the wool can be recovered if the wool, before washing, be systematically lixiviated in a series of tanks by the aid of water at a temperature of about 45° C. in order to obtain a concentrated solution of the yolk. To this end the solution containing the highest percentage of yolk is employed for treating the fresh wool, whilst the nearly exhausted wool is treated with fresh water. In this manner a solution of about 10° B. is obtained, which can be converted into crude potash by concentration and calcination. According to Havrez, the concentrated extract may also be worked up into potassium ferrocyanide if treated with an addition of nitrogenous materials.

Washing Woollen Yarn.—Woollen yarns cannot be thoroughly purified unless the raw wool has been washed perfectly clean. All that the present operation has to effect is the removal of the oil added before spinning; and the method of treatment and composition of the washing liquor depend entirely on the degree in which the oil used is capable of saponification and emulsification. The yarn is treated in a solution of soap or soda (or both) at a temperature of about 40° C. until it ceases to feel greasy, which generally takes about half an hour. The wool is then rinsed in warm water, in order to prevent the residual fatty particles solidifying and sticking to the wool. It is therefore impossible to wash all yarns on a rigidly fixed plan, though generally a solution containing 4 per cent. of soap and 3 per cent. of soda, calculated on the weight of the yarn, will be strong enough. Worsted yarns are always washed with soap only.

Washing Woollen Piece Goods.—As in the case of yarns, woollen goods made from carded yarn are washed with soap and soda; worsteds with the former alone. The operation is performed in the following manner:—44 lb. of soap curd are dissolved by boiling in a 2° solution of soda, to form 66 gals. of washing liquor, which must be used warm, since it sets when cold. The piece is thoroughly steeped with this liquor in the machine, and is left in soak for a half to three-quarters of an hour, after which it is rinsed by adding fresh water until the effluent runs away clear. Should the goods still feel greasy, the operation is repeated.

Woollens are occasionally washed with soda alone, for the sake of cheapness, but this is inadvisable as it makes the fibre harsh.

Worsteds are preferably washed twice, half an hour each time, in a 5° solution of olein (soft) soap.

Blueing or White Dyeing.

As already stated, the yellow tinge of imperfectly bleached fibres is often converted into a more or less pure white shade by the aid of blue dyes.

Cotton yarns, for example, are blued after bleaching by treating them with ultramarine in a soap bath, whilst cotton piece goods are treated with the same pigment in the dressing process.

White silk is blued in a lukewarm soap bath containing a very small quantity of some blue or violet dye, the various blue methyl violet marks being most frequently used for this purpose.

This blueing process is of far greater importance in the case of woollens intended for parti-coloured or fancy articles. In this case a wide range of white shades is required, and, as in the case of silk, is usually obtained with methyl violet blues in a lukewarm soap bath.

The chief difficulty in blueing resides in the accurate matching of the required tint. Of particular importance when methyl violet is employed is the amount of soap taken for the bath, since, if an excess be used, an insufficient quantity of the dye will be absorbed, whilst in the contrary event the dyeing is liable to become irregular. The blued yarn has then to be sulphured, so that, in dyeing, the alteration sustained by the colour in this operation has also to be taken into consideration.

A white, capable of resisting fulling, is in many cases produced on loose wool by dyeing with archil and indigo-carmine.

So-called "pure white" is best obtained by first blueing the goods very slightly in a hyposulphite bath, and then shading off with fast acid violet, A2R (*Höchst Farbwerk*), which is a fast and readily distributable dye, in a fresh bath.

It is still customary in some places to dye woollens white by treating them with some insoluble alkaline earth salt, such as calcium carbonate, barium sulphate, etc., held in suspension in water; or by precipitating these substances direct on the fibre by passing the piece through a solution of sodium sulphate, and then immersing it in dissolved barium chloride.

Carbonising.

In addition to other impurities, sheep's wool contains burrs and other vegetable fragments, which adhere to the fleece and cannot be removed by washing. When such wool is dyed, the cellulose of the vegetable matter absorbs the dye less readily than the wool fibre, and then becomes apparent in the material as light-coloured spots or "nops." Formerly these were removed by cutting with a nopping tool, or hidden by staining with nop tinctures, but this procedure had many drawbacks, the cutters being liable to damage the cloth, whilst the staining was of a merely superficial character, and far from permanent.

At the present time this method has been superseded by carbonising, an operation whereby the vegetable matters in the wool are eliminated by the aid of acid and heat, which converts the cellulose into hydrocellulose, the latter being easily removed by mechanical means. The operation derives its name from the carbonised appearance assumed by the vegetable matter under the treatment applied.

The reagents employed are sulphuric and hydrochloric acids, the former in a free state, the latter in combination as aluminium chloride or magnesium chloride, both of which split up into oxychlorides and free hydrochloric acid when heated. (The statement that these chlorides are converted into oxides and hydrochloric acid at the temperature employed in the carbonising process is incorrect.)

The woollen material to be carbonised must be clean, and, in particular, free from fatty matter. If the wool contain any soap residue, the carbonising process fixes the fatty acids upon the fibre in such a manner that their subsequent removal by washing is well-nigh impossible, and they will then show up as patches when the wool is dyed.

Carbonising is applied only to loose wool or piece goods; and even the latter alternative is attended with numerous drawbacks, owing to the formation of acid spots, soda spots, and other spots arising from impurities in the goods, these defects for the most part only becoming visible after the material has been dyed. On the other hand, these inconveniences are practically non-existent when the wool is carbonised loose, and for this reason the practice of carbonising in the piece has been discontinued at Verviers and many other places. Where still in vogue the process is applied to piece goods at various stages of manufacture, either just before or just after milling, or after dyeing. This refers only to woollens, worsted fabrics being seldom carbonised at all, since if not more than ten nops are found in a hundred-yard piece they are taken out by means of a nopping tool, and carbonisation is therefore superfluous.

The process is divided into three principal stages—impregnating the material with the carbonising reagent; the actual carbonising; and the removal of the residual reagent.

Impregnation consists in steeping the material for several hours in the reagent. In the case of sulphuric acid, the operation is performed in lead-lined tanks. To ensure thorough impregnation, piece goods must be drawn through the steeping liquor, the excess of the latter being squeezed out by means of rollers and removed by the hydro-extractor (which for this purpose must be lined with coarse cloth to prevent contact with the metal). They are then dried at a gentle heat, generally in a moderately heated drying chamber; though sometimes this preliminary drying is omitted, and the goods are carbonised in their wet state. In such event, however, it must not be forgotten that the action of the reagent is far more energetic.

Care is necessary to see that the impregnation is performed in a perfectly uniform manner, and that no irregularity occurs in the drying, and consequently in the distribution of the carbonising reagent, since this will certainly result in the production of spots in dyeing. This is especially the case in carbonising piece goods, and the latter should therefore be carefully drained in the hydro-extractor and carbonised as soon as possible, being stored in the meantime away from contact with light and air.

The actual carbonising is effected by passing the impregnated material through a carbonising stove, such as the one illustrated in Figs. 21 and 22.

Fig. 21 represents a wool-drying stove also used for carbonising. The wool is introduced at *a*, and passes through the chamber *b*, falling from one set of conveyors to the others in succession until it is discharged at *c* into the box *d*.

Fig. 22 shows the excellent wool-drying and carbonising machine made by Déru. The wool is introduced at *a*, and rests on the hinged gratings *b*, which, when turned through a quarter revolution, as at *c*, allow the charge to fall from storey to storey until it arrives at *d*. The drying is effected by hot air blown in through the heater *f* by the fan *e*; *i*, *i*, are dust cages, and *k* is a grid for retaining any fibres that may be carried away.

Piece goods are carbonised in an apparatus similar to Fig. 21, the pieces being led over rollers up and down through the chamber. Heat is imparted by iron steam-pipes led through the chamber, but, in order to prevent rust spots, all the pipe connections must be situated outside the chamber.

The temperature and the duration of the process depend on the reagent, and, to a smaller extent, on the quantity of impurities to be eliminated, as well as on the thickness of the material in the case of piece goods. Full particulars will be found below in dealing with the various reagents used.

After carbonising, the loose wool is willowed—piece goods being beaten—at once to remove the burrs, etc., whilst still dry and brittle.

Finally, the residual reagent must be got rid of. When magnesium- or aluminium-chloride has been used, this is effected by a vigorous washing in water, but in the case of sulphuric acid the excess has to be neutralised by treating the wool with a lukewarm solution of soda (about 2° B.) for half an hour or an hour. The elimination of the acid must be complete, since any allowed to remain would concentrate in the subsequent drying, and corrode the wool fibres, the result being the production of acid stains in dyeing. However, when the goods are to be dyed with acid dyes the neutralisation may be omitted, the removal of the acid being then unnecessary. This happens, for instance, in the dyeing of fezzes.

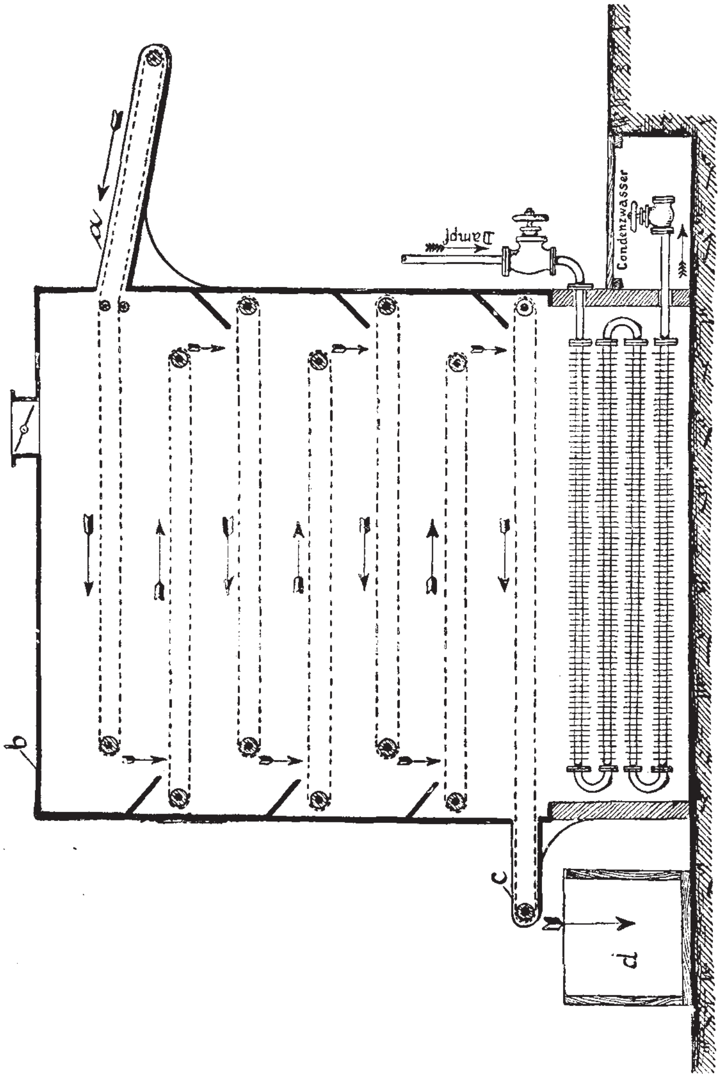

Fig. 21.

After neutralisation is finished the soda in turn must be thoroughly got rid of by washing, since otherwise the concentration of the alkali in drying would result in the formation of soda spots on the dyed goods being subsequently exposed to a high temperature (as in the dressing process).

At Verviers and other places the neutralising operation is performed with soap and soda in small (three-tank) leviathans, the soap being used for correcting the harshness produced in the fibre by carbonising.

Carbonising Agents.—The most important and most largely used of these is sulphuric acid, which is only replaced by magnesium- or aluminium-chloride, when the operation has to be performed on woollen fabrics dyed with colours unable to resist the acid, otherwise dyed cloth can be carbonised with this acid. Both the above-named chlorides are milder in their action than the acid in question, and have less effect on the fibre or colour of the material under treatment. This is due to several causes. In the first place, sulphuric acid is a stronger acid than hydrochloric

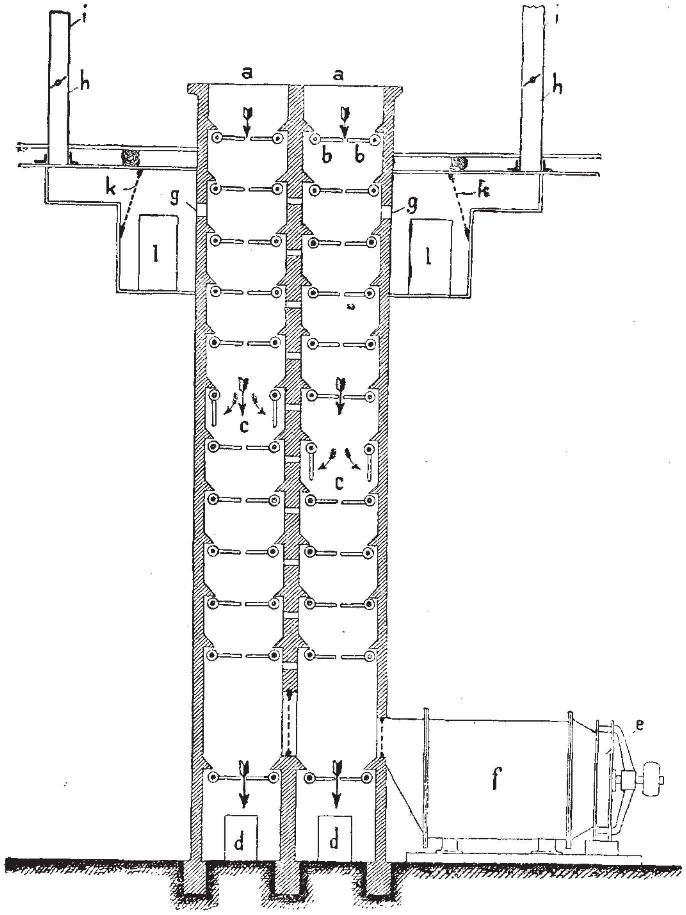

Fig. 22.

acid, the more so that it is not volatile at the temperature of the carbonising process, and therefore remains in the fabric. Secondly, in using the said chlorides, the temperature is such that ammonia is liberated from the wool and neutralises the freed hydrochloric acid to some extent, so that the latter only exerts its full power in such places where vegetable matters occur. Finally, the action of the hydrochloric acid is weakened by the oxychlorides formed.

The main defect of the chloride process of carbonisation resides in the high temperature required for the decomposition of the reagents, the consequence being that, especially with magnesium chloride, the wool is always faintly tinged with yellow, thus impairing the purity of the more delicate colours, especially blues. This defect is less apparent with aluminium chloride; this salt nevertheless being ever less and less used, on account of its higher price. Generally speaking, therefore, only two carbonising agents —sulphuric acid and magnesium chloride—are in current use.

Carbonising with Sulphuric Acid.—The usual procedure is to employ 4° B. acid, the temperature of the operation being 70–80° C., and the duration about twenty minutes. The practice, however, varies in different establishments, the concentration ranging from 2–6° B. The more dilute the acid the higher the temperature required, and *vice versâ.* Thus, acid of 2° B. strength must be applied at a temperature of about 100° C., whereas 6° B. acid can be used at about 60° C. It is always preferable to work with weaker acid and employ a higher temperature than under converse conditions.

Where the fabric to be carbonised has cotton selvedges, the latter must be protected from attack by coating them over with a solution of soda, thickened with fullers' earth and gum. This practice may, however, prove a source of inconvenience, inasmuch as by using an excess of the said solution the wool bordering the selvedges is liable to corrosion from the soda, and soda spots will form in dyeing. The defect may be obviated by using sodium acetate instead of soda.

Carbonising with Magnesium Chloride (A. Frank, 1877).—The fabric is impregnated with a 15° B. (or weaker) solution of magnesium chloride, and carbonised for thirty to forty-five minutes, at 140–150° C. According, however, to Breinl and Hanofsky a 9° B. solution is strong enough.

If magnesium chloride be heated by itself to 140–150° C. for some time, only about one-half of the contained chlorine will be liberated as hydrochloric acid, an oxychloride with a strongly alkaline reaction being left; and the same result apparently ensues when a fabric is carbonised with this salt. Accordingly the fabric so treated gives a stongly alkaline reaction afterwards, and this reaction may be occasionally so pronounced that the fibre is attacked, and assumes under the microscope the same appearance as when corroded by soda (see Fig. 12). To prevent this, it is necessary to thoroughly dry the material after impregnation and to keep the carbonising chamber perfectly dry. From the foregoing, it also follows that dye-stuffs sensitive to the action of alkalis will suffer more or less when carbonised with magnesium chloride. For the most part, however, the defect can be corrected by after-treatment with dilute acid.

When the piece to be carbonised is one with cotton selvedges, the latter must not be coated over with soda, since the resulting alkaline magnesium carbonate would corrode the wool. Consequently, in such event, the carbonising must be performed with sulphuric acid; or the selvedges could be dressed with sodium acetate.

In carbonising with magnesium chloride, care must be taken that no magnesia soaps are formed in the material, since these render the fibre harsh and cannot be removed by washing.

Carbonising with Aluminium Chloride (R. Joly, 1874).—The fabric is steeped in a 7° B. solution of aluminium chloride (as neutral as possible), then well dried, carbonised at 120–130° C. for one hour, and well washed.

When aluminium chloride is heated by itself at 120° C., about four-fifths of its chlorine is driven off as hydrochloric acid. Here, also, an oxychloride is formed, which, however, differs from that of magnesium by having an acid reaction.

As in the case of magnesium chloride, care should be taken to prevent the formation of a soap of the metal on the fabric; and, finally, it may be mentioned that a variety of carbonisation effects may be produced on mixed cotton and wool fabrics by printing with aluminium chloride. Owing, however, to the cost of this reagent and its lack of advantages, its use in carbonising is now practically abandoned.

Carbonising with free hydrochloric acid was practised, but only for a short time, in Belgium. The hydrochloric acid gas, produced by the action of sulphuric acid on common salt in retorts, was conducted by means of a current of air over the wool spread out on frames; or a solution of the acid was sprayed over the wool by a revolving brush, the material being afterwards exposed to a high temperature. The disadvantages of the method consisted in the corrosion of all the metallic fittings of the apparatus, and in the difficulty experienced in regulating the strength of the reagent.

The defects of manufacture liable to be produced by the operation of carbonising are, as already mentioned, the stains developed in the subsequent dyeing, and which are due to either acid or alkali.

Soda stains may result from neutralisation or from carelessness in carbonising with magnesium chloride, or, finally, from dressing the cotton selvedges with soda. They frequently appear as dark patches in the dyed cloth, and can almost invariably be recognised by microscopical examination.

Acid stains occur solely after carbonisation with sulphuric acid, and show up as light patches in the dyed cloth (sometimes also before dyeing). If the action of the acid in these places has been strong, they will be found to damp more readily in water than the other parts of the material. These stains require a very experienced eye to detect under the microscope.

However great the care bestowed on the sulphuric acid carbonisation process, the presence of impurities is liable to cause acid stains; hence, in the case of such wools, it is better to carbonise with magnesium chloride.

CHAPTER III

MORDANTS AND MORDANTING

Mordants.

IN the operations of dyeing and printing fabrics a number of metallic salts are employed to fix the mordant dyes, in the form of lakes, on the fibre. The lakes are compounds of the dye-stuffs with metallic hydroxides. They are insoluble and very resistent towards reagents, and the usual method of bringing them on the fibre is to first precipitate the hydroxide, from a metallic salt, on the fibre and then dye with a suitable dye-stuff. The metallic salts, or hydroxides, used for this purpose are termed "mordants," and the operation of precipitating the hydroxides in and upon the fibre is known as "mordanting."

To be of practical utility, a mordant must fulfil the following requirements:—Cheapness; easy precipitation of the hydroxide; insolubility in water on the part of the hydroxide, coupled with a certain affinity for the fibre; the resulting colour lakes must be of good colour and as "fast" as possible, *i.e.* capable of withstanding the influence of light, acids, alkalis, etc. These conditions, however, are fulfilled by only comparatively few metallic salts, and, in fact, the only mordants in practical use are the alumina, iron, chrome, tin, and copper mordants. The alkalis are not mordants, both their hydroxides and the compounds of these with dye-stuffs being soluble in water, and though the alkaline earths give insoluble colour lakes, the colour of these is poor, and they have no affinity for the fibres. As regards the remaining metals, not all of these have been examined as to their capacity for forming lakes. Some of them furnish good colour lakes, which, however, are too dear for practical application (*e.g.* nickel), whilst others, though cheap, give lakes deficient in stability (*e.g.* zinc).

Some dye-stuffs yield faster lakes when other metallic salts—chiefly those of lime, zinc, or magnesia—are allowed to take part in the formation of the lake. Such salts are termed supplementary mordants, and are used in calico-printing with steam dyes. A combination of two or more fast mordants will also frequently produce more stable lakes (*e.g.* alizarine red on wool). One peculiar and hitherto unexplained feature is the behaviour of the alumina and iron mordants in presence of certain dyes, it being impossible to dye with alizarine (*see* Turkey-Red) a fabric that has been mordanted with alumina or iron, unless lime salts be present.

One and the same dye-stuff will furnish colour lakes of divergent shade and fastness with different mordants. The lightest and brightest are the tin and alumina lakes, the copper and iron lakes being the darkest, whilst the chrome lakes occupy an intermediate position in this respect. In point of stability, it is a difficult matter to generalise, but, as a rule, the copper and iron colour lakes are the fastest under the influence of light.

The behaviour of the various textile fibres towards mordants is mainly dependent on their nature, and, in a secondary degree, on the metallic salt of which the mordant is composed. A general description of the behaviour of the fibres towards mordants, and the operation of mordanting, will therefore be given first, after which the special applications of the separate mordants will be briefly considered.

Mordanting Wool.

The high absorptive capacity of wool finds expression in an interesting manner in the mordanting process, for when wool is immersed in a solution dilute of some mordant, it absorbs a portion of the contained metallic hydroxide, leaving the remainder in solution, *i.e.* only a small proportion of the acid in the metallic salt present is taken up. This absorption goes on at the ordinary temperature, more rapidly in the warm, and most quickly and completely at boiling-heat. The usual manner of explaining this peculiarity is by saying that the wool has a power of decomposing salts and takes up a strongly basic salt, leaving behind a strongly acid salt in solution. If, however, the mordanting be performed in a more concentrated solution, it will be found that the proportion of acid taken up in comparison with the base increases with the strength of the bath, and when a certain degree of concentration is attained more acid is taken up than base. Consequently wool possesses an absorptive capacity for both acids and bases, each class of substance being taken up from the mordanting salt as though it alone were present, the absorption being chiefly dependent on the concentration and temperature of the mordanting bath. Wool is also able to absorb a portion of a free acid from solution, but its behaviour towards the mordanting hydroxides cannot be determined by direct experiment owing to their insolubility in water.

For the above reasons the assumption that a basic salt is taken up in the mordanting process is untenable; and equally arbitrary is the hypothesis that the salts are decomposed by the wool, the dissociation being effected at the moment of their solution in water by the action of that solvent.

From the foregoing it is evident that dilute solutions are necessary in the practical performance of the mordanting process, the object of the operation being solely to deposit a metallic hydroxide on the fibre; whilst the amount of acid absorbed should be as small as possible, owing to its unfavourable action on the formation of a lake and on the shade of the colour in the subsequent operation of dyeing.

It has also been noticed that in the event of too rapid absorption the hydroxide is generally fixed in an imperfect manner, being more superficial and often causing uneven dyeing. The mordanting should therefore be carried on slowly and gradually, on which account salts that are easily dissociated, like the acetates and basic salts, cannot be used for mordanting wool. The most suitable mordants are—of the alumina mordants, alum and aluminium sulphate; of the iron mordants, ferrous sulphate; of the copper mordants, copper sulphate (blue vitriol); of the tin mordants, stannous chloride (tin salt); and of the chrome mordants, potassium and sodium bichromates, and chromium fluoride. Even when these are used the operation will go on too fast if the wool be immersed in the boiling hot mordant liquor; and the process must therefore be pursued in the following manner:—The wool is first thoroughly wetted by boiling in water for half an hour to one hour, after which it is entered in the bath of lukewarm mordant, to which a small quantity of an acid substance has been added (see below). The temperature of the bath is then slowly raised to 100° C. (in about an hour) and boiling is continued for an hour to an hour and a half longer. Loose wool and yarn must be thoroughly worked about in the bath to ensure uniform mordanting of the whole of the fibre, and piece goods are kept in motion by winding.

After mordanting, the goods are generally merely cooled down and the excess of liquid removed, rinsing being omitted. Loose wool is spread on the floor, yarn being unwound and hung up, and piece goods alternately folded and opened out again, and finally hung on a wooden frame to allow the excess of bath liquor to drain away. The hydro-extractor is, however, a better means of draining the goods.

Before drying, the mordanted wool must be dyed, since otherwise it would have to be re-wetted for dyeing—a difficult operation when alumina mordants have been used. The usual custom is to leave the wool overnight after mordanting, the reason given for this procedure being, that unless allowed to stand for some time the wool takes more dye-stuff to dye it than otherwise. The real purpose of the delay, however, is apparently to give the excess of mordant time to drain off, since the larger the amount of this liquor introduced into the dye bath the greater the loss of dye through useless precipitation as insoluble colour lake. It is therefore more rational to wash the mordanted woollen material previous to dyeing, but it should first be allowed to get quite cold, or part of the fixed mordant will be sure to wash out.

When the wool has been mordanted with a sulphate, *e.g.* alum or ferrous sulphate, it will always contain a little sulphuric acid; whereas when stannous chloride has been used the fibre takes up only a very little hydrochloric acid, if any at all, partly because the amount of this mordant used is small, and also because wool has probably a smaller capacity for absorbing hydrochloric acid than it has for sulphuric acid. Should the acid so absorbed be found to have an unfavourable effect on the dye, the defect may be remedied by adding a little ammonia, to neutralise the acid, towards the end of the dyeing process. This is frequently done in dyeing with logwood, and the same effect may be produced by means of calcium acetate (obtained by correcting the water with acetic acid), the favourable influence of which salt in logwood dyeing is thus explained.

In the foregoing method of mordanting, it is always customary to add a small quantity of some acid substance to the bath, such as potassium bitartrate, oxalic acid, or sulphuric acid, the first named being most frequently used, notwithstanding its high price. The part played by these adjuncts has not yet been elucidated; but it is assumed that in mordanting with sulphates, chlorides, etc., they retard the dissociation of the salts in question and protract the absorption of the hydroxides by the fibre. In ordinary mordanting with potassium bichromate these acid substances play a different part, as will be set forth in the description of the process later on.

When dyeing with hard water and using bitartrate, it will be necessary to correct the water beforehand by an addition of 5–10 per cent. of 8° B. acetic acid, since otherwise the bitartrate would be neutralised by the lime in the water, and would cease to act.

Mordanting Silk.

Silk has a high capacity for absorbing the most divergent substances of acid and basic character, though this property is manifested in a different manner to that of wool, being greater in the cold and at medium temperatures than at boiling heat; consequently, if an attempt be made to mordant silk in the same manner as wool, only a very small quantity of the hydroxide will be taken up. The most suitable mordants for silk are cold concentrated solutions of basic salts, readily dissociated by dilution with water. On prolonged immersion in such solutions the silk takes up a portion of the hydroxide and a part of the acid present—just as in the case of wool. On then washing the material in water, the unfixed excess of the mordant is removed, on the one hand, whilst, on the other hand, a part of the same is dissociated by the dilution, and a further amount of the hydroxide is fixed on the fibre. To complete the fixation the silk is finally entered in an alkaline bath, which removes the last traces of acid present, before washing. The operation of washing between the mordanting and the fixing processes is performed with a large volume of (preferably running) water, a special washing apparatus being used, consisting of a series of hollow, perforated porcelain cylinders. These are set parallel, side by side, and are caused to revolve after the silk hanks have been hung upon them. By means of water discharged through the perforations and through jets placed between the hanks, the material receives a thorough washing.

The best mordants for silk are basic alum, aluminium acetate, basic ferrous sulphate (" Rouil mordant "), basic chromium chloride, chrome mordant GA III, and stannous chloride.

Mordanting Cotton.

Cotton differs from wool and silk in having practically no absorptive capacity for metallic hydroxides, and must therefore be mordanted in a different manner. There are two ways of doing this. In one the metallic hydroxide is deposited in and upon the fibre by first impregnating the latter with acetic acid, the bulk of which is then volatilised by drying and the remainder eliminated by treatment in an alkaline bath. In the other method the hydroxides are precipitated on the fibre as insoluble tannates or fatty-acid salts by first steeping the cotton with tannic acid or fatty acid, and then treating it with the metallic salt used as the mordant.

The former method is used exclusively in dyeing piece goods, being difficult to perform with regularity in the case of yarns. Moreover, it is restricted to mordanting with alumina and iron. The *modus operandi* is as follows:—The cottons are first impregnated in a thoroughly uniform manner, with a dilute solution of aluminium acetate or iron pyrolignite in a padding-machine, the operation being termed " padding."

In the padding-machine sketched in Fig. 23 the goods are unwound from the roller *a* and passed over the stretcher *b* to the trough *c*, which contains the mordant and three guide rollers *d*; thence the piece passes between the wringer rollers *e*, *f*, and is finally wound on the roller *g*. All the rollers are of wood, and their trunnions rest on sloping arms *h*, so that the roller *g*, which is driven by the upper wringer roller, can move slowly upwards in proportion as its diameter increases in consequence of the cloth being wound upon it. The upper wringer is weighted by the weight *m*, which acts through the levers *i*, *l*, and the rod *k*, the length of the latter being adjustable by turning the extension screw *n*.

With light goods a single passage through the padding-machine is sufficient, but heavy goods require to be put through twice. This done, the piece, instead of being wound on the roller *g*, as shown in the figure, is led (over as few guide rollers as possible) up and down through a gently heated chamber, known as the "hot flue," where it is dried sufficiently to make it fit for transport. In this manner the cotton retains the mordant acetate in an almost entirely unaltered condition. The amount depends on the concentration and on the pressure exerted by the wringers, this being usually adjusted so that the goods retain about their own weight of mordant solution. The next stage is to hang the goods in a warm chamber, extending through several storeys in the building and heated by steam pipes laid on the floor, covered by a layer of spars. A second set of heaters is preferably arranged

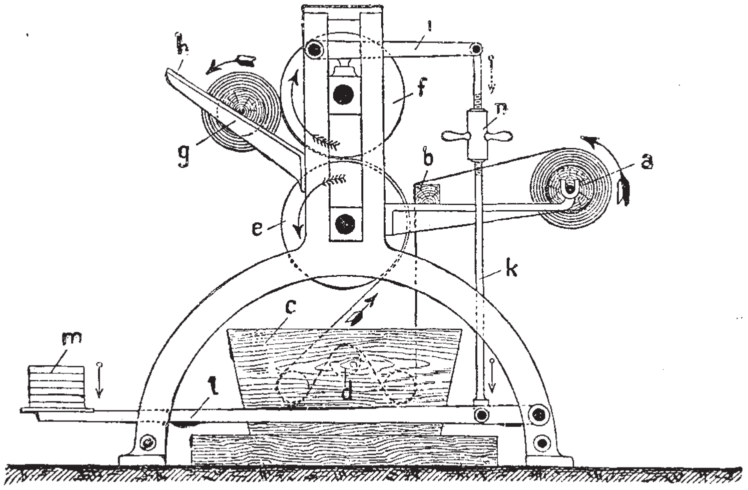

FIG. 23.

above the ceiling, to prevent the goods being spotted by condensed moisture. In addition to a high temperature, a certain degree of moisture in the atmosphere is necessary to the due performance of this process, for which purpose water vapour is introduced into the chamber by allowing drops of water to trickle on to the heating-pipes from perforated pipes mounted just over the latter. The degree of moisture is registered by a suitable hygrometer. Ventilation is provided by means of air-pipes reaching from the floor up to above the level of the roof. The printed goods are hung in this chamber for about forty-eight hours, at a temperature of about 30° C., the wet bulb of the thermometer indicating some 3–4° lower.

This operation is often styled the "oxidation process," probably because it is frequently employed for developing aniline black, in which case oxidation actually occurs. When the goods have been mordanted with acetate, the acetic acid is volatilised in the hot chamber, leaving the metallic hydroxide deposited on the fibre in the finely divided state necessary for the subsequent dyeing. When iron is used, a gradual oxidation to ferric hydroxide also occurs. It is essential that this process should be carried on in a very gradual manner, since, if the hydroxide be fixed rapidly —for example, by steaming for a short time—the colours will come out less full and handsome in dyeing.

To thoroughly fix the hydroxide, the residual traces of acid must be removed by a mild alkali, for which purpose the goods are next "dunged" by passing them over guide rollers through several vats—at least two—containing a decoction of cow dung and levigated chalk (see Fig. 24). This decoction is prepared by boiling 4 parts by weight of cow dung and 0·3 part of levigated chalk in 7 parts of water for about two hours. The first vat is charged with 8 cwt., and the second with 6 cwt. of the preparation, the temperature being maintained at 60° and 50° C. respectively. When about 600 yards of material have been passed through the vats, the baths are replenished with about 30 lb. of the preparation. The goods remain in the bath for about two minutes.

The levigated chalk and the faintly alkaline substances present in the cow dung neutralise the residual traces of acid in the material.

Many attempts have been made to replace cow dung by faintly alkaline salts, such as ammonium carbonate, sodium phosphate, arsenite, silicate, etc., but though these all act in the desired direction the best colours are still obtained by the use of cow dung. This may probably be attributable to the mucinous condition imparted to the water by the substances dissolved out of the dung, in consequence of which no scouring action is exerted on the goods during their passage through the bath. The best substitute for cow dung out of those named above is ammonium carbonate, employed in the state of a 2 per cent. solution, and at ordinary temperature.

The mordanting process is completed by swilling off the impurities collecting on the fibre in the dung bath, and by a thorough washing.

Similar in principle, but less objectionable in performance, is the mordanting of cottons with chromium bisulphite or chromium acetate, the goods being padded with the dissolved mordant, and fixed with boiling hot soda solution after drying.

Mordanting with the assistance of tannic acid or fatty acids will be described later on in dealing with these fixing agents.

The Mordants used in practice are—salts of aluminium, iron, chromium, tin, or copper. The two last named are the least important, the principal mordants now used being those of the chromium group.

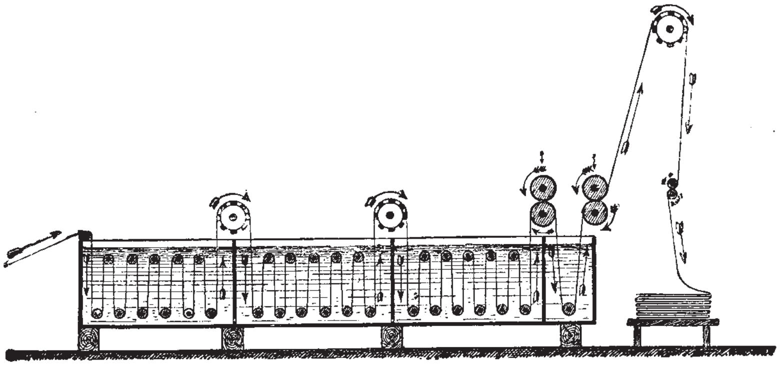

FIG. 24.

Alumina Mordants.—These are employed in the production of the following colours:—Alizarine red and alizarine orange, on all three classes of fibre; alizarine rose-red on cotton; amethyst, with cochineal, on wool; yellow shades with natural dye-stuffs; logwood blue on wool; and certain mixed shades, with alizarine and other dye-stuffs, on cottons.

In most cases the alumina mordants should be free from iron, the iron lakes being darker and duller in colour than the alumina lakes, so that, if present, even a small amount of iron would suffice to dull the colours produced by the aid of alumina mordants. For instance, alizarine gives a brilliant red with alumina mordant, but a dull violet lake with iron; consequently a handsome alizarine red can only be developed when iron is absent. According to the researches of Lunge and Keler, the aluminium sulphate used for dyeing alizarine red should not contain more than 0·001 per cent. of Fe. For the preparation of a 6° B. aluminium acetate for alizarine steam red, the aluminium sulphate may contain up to 0·005 per cent. of Fe without any ill effect on the colour.

The most important salt of alumina is alum ($Al_2(SO_4)_3K_2SO_4 24H_2O$), which is used both *per se* and in the preparation of other alumina mordants. Its active constituent is aluminium sulphate, the potassium sulphate playing no important part. Hence aluminium sulphate can also be used as a mordant, and, indeed, is preferable, inasmuch as it can now be obtained at a relatively lower rate, in comparison with the percentage content of alumina present, than alum. The latter continues to be used, however, in many places, its crystalline form being considered to afford a better guarantee of purity. Nevertheless, the commercial sulphate in lumps is also, for the most part, free from iron, but, its composition being irregular, needs checking by analysis.

Alum and aluminium sulphate are the only alumina mordants used for wool. The quantity of alum taken varies from 6 to 12 per cent., according to the nature and intensity of the dyeing, and it is employed in conjunction with 2–5 per cent. of potassium bitartrate or oxalic acid and a 30–40-fold quantity of water; the above percentages being calculated to the weight of wool under treatment.

Alum, as such, is unsuitable for mordanting silk and cotton, its sulphuric acid preventing the fixation of the hydroxide, unless previously neutralised, to some extent, by an alkali. A partly neutralised alum solution of this kind is known in practice under the name "basic alum," the assumption being that it contains a basic salt of alumina. Thus, for example, if one molecule of sodium bicarbonate be taken to neutralise the sulphuric acid in one molecule of alum, the reaction ensuing may be expressed by the following equation:—

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2.$$

Here, as in other cases where a basic salt is formed in an analogous manner, the formula deduced for the resulting salt from the equation is hypothetical only, and expresses the degree of neutralisation produced by the alkali.

With regard to the production and behaviour of these basic salts in general, and not merely those of alumina, the following observations may be made:—In their preparation, the dissolved alkali—generally soda—is added by degrees to the solution of the salt to be rendered basic, and kept stirred, any resulting precipitate being redissolved by warming. This, however, is not always possible. The more strongly basic the mordant, the more readily does it undergo dissociation into the corresponding hydroxide or allied insoluble salt. This dissociation is accelerated by heat and dilution. Both the different mordants and the various salts of one and the same metal behave in a very divergent manner under this treatment; moreover, the capacity for dissociation of basic salts is appreciably influenced by the presence of extraneous salts. For instance, the basic salts of alumina dissociate more readily when they contain potassium sulphate, so that the basic alumina mordants prepared from alum dissociate more readily than those obtained from aluminium sulphate.

The alumina mordant for silk is prepared (according to the prescription of the Badische Anilin- und Sodafabrik) with a solution containing 60 grms. of alum and 6 grms. of soda crystals per litre.[1] After the addition of the alkali to the alum solution the liquid is warmed until the resulting precipitate has redissolved, whereupon the silk is entered in the bath, worked about for ten to fifteen minutes, and left in soak for at least twelve hours. It is then well wrung or drained in the hydro-extractor and entered in a bath of ½° B. sodium silicate, worked about for a quarter of an hour, and carefully washed. The silicate treatment causes the deposition of aluminium hydroxide, and not aluminium silicate, on the fibre.

For mordanting cotton with alum, concentrated solutions are used, containing 100–200 grms. of aluminium sulphate per litre (10 to 20 per cent.), and are neutralised as far as possible with soda. Further particulars on this point will be given in treating of the fixing agents (fatty acids).

Aluminium acetate is prepared by dissolving aluminium hydroxide in acetic acid or by decomposing alum or aluminium sulphate with lead acetate. When three molecules of lead acetate are taken to one molecule of aluminium sulphate, normal aluminium acetate is produced—

$$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = Al_2(C_2H_3O_2)_6 + 3PbSO_4,$$

but on lowering the proportion of lead acetate sulphacetates are formed—

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 = Al_2SO_4(C_2H_3O_2)_4 + 2PbSO_4.$$

For use as a mordant, it is unnecessary that the whole of the sulphuric acid present in aluminium sulphate should be thrown

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[1] These proportions correspond to one molecule of sodium carbonate per three molecules of alum, and the resulting alumina salt will have the formula $Al_6(SO_4)_8(OH)_2$. In making calculations of this kind, the water of crystallisation in the different substances must not be forgotten.

down; in fact, it is preferable in practice to select the proportions in the preparation of aluminium acetate so that a sulphacetate is produced instead of the normal acetate. Generally not more than a half to three-quarters of the total sulphuric acid is removed.

For use in calico-printing these mordant solutions are made as highly concentrated as possible, one method adopted being to dissolve the one salt and add the other in the condition of powder. For example, a 15° B. mordant can be obtained by dissolving 1 part by weight of aluminium sulphate and 1 part of lead acetate in 2 parts of water, this solution being diluted according to requirements, and occasionally rendered basic by an addition of chalk.

The various acetates may be diluted with water without undergoing dissociation; a few of them throw down a deposit when heated, but this is redissolved on cooling.

The aluminium acetate mordants are chiefly used in calico-printing, and also in piece dyeing cottons. For Turkey-red dyeing, solutions of 2–3° B. strength are used.

Silk can be mordanted with 6° B. aluminium acetate just as well as with basic alum.

In the case of wool these salts are not used as mordants, but are employed as waterproofing substances in the dressing process.

For dull colours the pure salt is replaced by the cheaper aluminium pyrolignite.

Aluminium sulphocyanide is prepared, by double decomposition, from alum or aluminium sulphate and barium or calcium sulphocyanide—

$$Al_2(SO_4)_3 + 3Ba(CNS)_2 = 3BaSO_4 + Al_2(CNS)_6.$$

It is used to replace aluminium acetate for alizarine steam red in calico-printing, since it does not corrode the steel doctors of the printing machine and does not introduce iron into the printing colours. As, however, it readily corrodes cotton fibre when hot, the printed goods must be hung some time previous to steaming. The salt has no other uses.

Sodium aluminate ($NaO . AlO$) is prepared by dissolving aluminium hydroxide in caustic soda and neutralising the excess of the latter. On account of its strongly alkaline reaction, this mordant can only be used for cotton, for which purpose it has several advantages over the other aluminium mordants. For instance, an alizarine red developed by its aid is less susceptible to the influence of iron and heat, and is easier to discharge. In mordanting cotton, the pieces are impregnated with a solution of sodium aluminate, dried, and passed through a warm solution of ammonium chloride (sal ammoniac), whereby aluminium hydroxide is precipitated on the fibre. It is used for Turkey-red in the Schlieper and Baum method—though then fixed in a different manner—and also as an adjunct to naphthol preparations for nitraniline red, as well as being employed as a reserve under aniline black.

Aluminium fluoride forms a good mordant for wool, the colours being brighter than with alum; it is not used, however, in practice.

Of the other salts of alumina only the nitrate, chloride, and chlorate need be mentioned. These are used in calico-printing, the nitrate sometimes for alizarine steam red, the other two for red discharge on vat blue with alizarine. Aluminium chloride is also used in carbonising (*q.v.*).

Iron Mordants.—These play a most important part in black dyeing all three fibres with logwood; they are also used for dyeing wool brown with dye-woods, and on cotton for catechu and several alizarine dyes, for alizarine violet in calico-printing, for green with nitroso dyes, for Berlin-blue and chamois on cotton, and for darkening sundry tannin dyeings. The salts used as mordants are ferrous sulphate (green vitriol), iron pyrolignite, and so-called iron nitrate.

Ferrous sulphate and "Salzburg vitriol" (a mixture of ferrous sulphate and copper sulphate) are the only iron compounds used for mordanting wool. When the dyeing is for logwood black, a preliminary mordanting is given; in other cases the darkening method is practised. (*See* Dyeing.)

On cotton, ferrous sulphate is fixed on the fibre by means of tannic acid (*q.v.*); it is no longer in use for silk, except sometimes for black.

Finally, this salt is also used as a reducing agent in the so-called vitriol vat.

Iron pyrolignite is prepared by dissolving scrap iron in crude pyroligneous acid, and forms the most important and almost the sole iron mordant for calico-printing. In cotton-dyeing it is used according to the two methods already described, the solution employed for dark colours being only a few degrees B. in strength.

The chief constituent of iron pyrolignite is ferrous acetate, which, however, in the pure state is not a good mordant for cotton, being too readily oxidisable, and consequently poorly fixed on the fibre. The pyrolignite, on the other hand, forms a good mordant owing to the presence of other matters which retard the oxidation of the acetate. With the same object, and also to retard the fixation of the hydroxide, it is customary to add a solution of arsenic in acetic acid. Sometimes, however, *e.g.* for pale chamois (and also for alizarine violet), pure ferrous acetate, prepared from ferrous sulphate and lead acetate, is employed; this product frequently contains an excess of lead acetate, which then comes down as lead hydroxide in with the iron chamois and lightens the shade.

When iron pyrolignite is used for mordanting piece cottons along with aluminium acetate, the latter should be as free as possible from sulphuric acid, since otherwise ferrous sulphate will be formed, and this is difficult to fix. In silk-dyeing, the pyrolignite is used for black, and is fixed with tannic acid (*q.v.*). For wool, it is used only in the case of pelts, etc., that are mordanted cold.

Iron nitrate is the name given to a class of mordants produced by the action of nitric and sulphuric acids in variable quantities on ferrous sulphate, and consisting of a mixture of neutral and basic ferric sulphates and ferric nitro-sulphates.

The following proportions of the said reagents are used in the preparation of normal ferric sulphate:—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

By using less sulphuric acid, *e.g.* only half the above quantity, a basic ferric sulphate is obtained—

$$12FeSO_4 + 3H_2SO_4 + 4HNO_3 = 3Fe_4(SO_4)_5(OH)_2 + 4NO + 4H_2O.$$

By employing more nitric acid, nitro-sulphates are produced.

In reality these mordants do not contain any nitrates, and the term by which they are known is therefore inaccurate. They are put on the market in the form of reddish brown concentrated solutions, frequently containing free nitric acid.

The fixation of these mordants on the cotton fibre is effected by the aid of tannic acid, as in the case of iron pyrolignite. Their principal application is in the black dyeing of silk, for which purpose a mordant is prepared, the composition of which nearly corresponds to the formula in the above equation, viz. $Fe_4(SO_4)_5(OH)_2$, and which is known as "Rouil mordant." The method of use differs according as the silk is in the raw, souple, or scoured state. The last named is mordanted in the following manner:—

The silk is immersed in a 30° B. solution of the mordant for about an hour, after which it is taken out, unwound, and carefully washed, preferably in hard running water.

These operations are usually repeated several times over, the final fixation of the mordant being effected in a boiling hot soap bath. The mordanted silk must not be allowed to dry, or it will be corroded by the mordant. Raw and souple silk are mordanted in a weaker solution, and, for the sake of cheapness, the fixing is generally performed with soda instead of soap.

Chrome Mordants.—At the present time the chrome mordants are the most important in use, many dyeings formerly mordanted with alumina or iron salts being now treated with chrome salts instead; and, with the exception of a few of the alizarine dyes, all artificial mordant dye-stuffs are fixed with chrome mordants exclusively. Their chief use is in the fast dyeing of wool.

These mordants differ greatly in behaviour from the iron and alumina mordants, being, on the one hand, more difficult of dissociation, and therefore harder to fix on the fibre, whilst, on the other hand, the combination of the fixed chromium hydroxide—*i.e.* the formation of the colour lake—is effected more readily. As regards the first-named property, this comes in evidence already during the treatment of the solution with alkaline substances, the quantitative precipitation of the hydroxide generally requiring the temperature of boiling-heat for its accomplishment, a property that is termed "passivity towards precipitants." In the case of the iron and alumina mordants, the acetates give up the hydroxide more readily than the sulphates, the converse being, however, the case here. The chromium acetates are so difficult to decompose that they cannot be used like the acetates of alumina and iron.

A further peculiarity of the chromium salts is that they exist in two modifications, one violet and the other green, which differ in their behaviour towards precipitants and also in mordanting. It is assumed that the violet solutions are neutral salts, whilst the green solutions contain a mixture of acid and basic salts. The transference of the one modification into the other is an easy matter.

The aforesaid passivity towards precipitants was for a long time a hindrance to the employment of the chromium salts as mordants for cotton.

The chrome mordants consist of the following salts:—Chromium acetate, bisulphite, fluoride, basic chloride, alkaline chrome solutions, potassium and sodium bichromate, and chromic chromate. Unlike the corresponding salts of iron and alumina, chromium sulphate and chrome alum are unsuitable for mordanting wool, the dyeing being irregular unless plenty of potassium bitartrate is used as well. Chrome alum, a cheap by-product of alizarine manufacture, forms a raw material for the production of other chromium salts.

Chromium acetate is produced, by double decomposition, from chrome alum and lead acetate. As was the case with aluminium acetate, the product is not the normal acetate but a sulphacetate, and only about one-half to two-thirds of the sulphuric acid present in the chromium sulphate is precipitated. These compounds are almost exclusively used as chrome mordants for steam dyes in calico-printing; for mordanting cotton their use is restricted to piece goods.

The above-mentioned properties of the chromium salts are exhibited in a high degree by the various chromium acetates. The green solutions undergo gradual conversion into the violet form, the latter being more difficult to decompose. The behaviour of these salts, therefore, alters during storage; they have also the property of dissolving lead sulphate, this power increasing with their basicity.

Similar behaviour is exhibited by the chromium sulphocyanides, which, however, are rarely used (in calico-printing) as mordants.

Chromium bisulphite is prepared by treating a solution of chrome alum with an excess of sodium bisulphite or calcium bisulphite, and is used in mordanting cotton piece goods, for which purpose it is the most suitable of any of the chrome mordants.

Chromium fluoride, like the bisulphite, has only recently been introduced into practice as a mordant, and is now highly esteemed for treating wool, being especially valuable in cases where the oxidising action of potassium bichromate renders this latter unsuitable. An additional advantage of the fluoride is that it mordants the wool fibres in a very ready and uniform manner, without affecting their spinning properties or the feel of the resulting goods. It is used both for mordanting before dyeing and for after chroming (*see* Mordant Dye-Stuffs), the mordanting bath in the former case consisting of 4 per cent. of chromium fluoride and 1–2 per cent. of oxalic acid (counted on the weight of the goods), and the operation being performed in the same manner as for wool in general.

Chromium fluoride corrodes both glass and metals, and must therefore be stored in wooden vessels. When employed in copper dye vats, its action on that metal may be prevented by hanging strips of sheet zinc in the vessel.

A basic chromium chloride may be prepared by dissolving chromium hydroxide in chromium chloride, and is used for mordanting silk and cotton yarns. In mordanting silk (according to the recipe of the Badische Anilin- und Sodafabrik) the goods are immersed for six hours in a 20° B. solution of chromium chloride, then washed in plenty of water, treated in a cold bath of 1° B. sodium silicate for a quarter of an hour, unrolled, and carefully washed.

The mordanting of cotton yarn with this reagent is effected in two ways—in one, the yarn is impregnated with the mordant solution, dried, and passed through a boiling hot solution of soda; whilst in the other, the hydroxide is fixed by the aid of tannic acid or oleic acid. (*See* Fixing Agents.)

Alkaline chrome solutions are obtained by dissolving chromium hydroxide in caustic soda, or by treating a dissolved chromium salt with sufficient caustic soda to redissolve the precipitate first formed. On account of their strongly alkaline reaction, their use is restricted to cotton. This fibre is mordanted by impregnating it with a solution of this kind and leaving it to stand for twenty-four hours, finally washing with water to get rid of the excess of the solution.

Potassium bichromate, often called "chromate of potash," is the most important of all the chromium salts, and plays a great part in the dyeing and printing of fabrics, its applications being many and varied. As a mordant its employment is restricted to wool, for which it forms the principal reagent of this class.

The chroming of wool has been the subject of considerable study, the results obtained being as follows:—If wool be mordanted by bichromate alone, the material absorbs chromic acid, leaving a normal chromate behind in the bath. Since the composition $K_2CrO_4+CrO_3$ must be ascribed to the bichromate in aqueous solution, the wool apparently takes up only the free chromic acid present, and therefore it is usual to increase the activity of the bath by an addition of sulphuric acid, which liberates chromic acid from the normal chromate, this extra acid being then absorbed by the wool: $K_2CrO_4+H_2SO_4=CrO_3+K_2SO_4+H_2O$.

Thus rather less than 1 part by weight of sulphuric acid is required (theoretically) for 3 parts of bichromate; and this proportion is employed in practice, inasmuch as the solution used contains 3 per cent. of bichromate and $\frac{1}{2}$–1 per cent. of sulphuric acid (calculated on the weight of wool) with a 30–40-fold quantity of water. For very dark shades—especially when dyeing with polyoxyanthraquinone dyes (alizarine cyanines, etc.)—$4\frac{1}{2}$ per cent. of bichromate and $1\frac{1}{2}$ per cent. of sulphuric acid are used. The bath is never exhausted, a considerable quantity of chrome being left behind.

The precise form in which the chromic acid is contained in the wool is unknown, but, from the yellow colour of the mordanted fibre, it is assumed that a portion of the acid is in the free state. On prolonged storage, especially exposed to light, an appreciable reduction to chromic oxide occurs, and this circumstance may lead to subsequent irregularity in dyeing.

It is assumed that the mordanting action of the chromic acid is confined to the portion reduced to the state of chromic oxide by the wool and the dye-stuff.

The method described is but seldom advantageous, more handsome colours being obtained when the sulphuric acid is replaced by potassium bitartrate or oxalic acid. In such event, as may be concluded from the green colour of the mordanted wool, a much more extensive reduction of the chromic acid to chromium hydroxide occurs; and that this is actually the principal effect of these adjuncts is evident from the fact that these two reagents may be successfully replaced by other organic substances. Finally, mention may be made of the following fact:—When wool mordanted with bichromate and sulphuric acid is treated with a reducing agent, such as bisulphite, it turns green, and then gives the same results in dyeing as though mordanted with bichromate and bitartrate. For this purpose the wool may be treated with 5 per cent. of commercial bisulphite solution for ten to fifteen minutes in a lukewarm bath.

The circumstance that wool mordanted with bichromate and sulphuric acid generally furnishes dull colours may be explained by the assumption that the chromic acid oxidises a portion of the dyestuff to discoloured products.

The adjuncts, bitartrate and oxalic acid, do not behave alike, the former usually giving purer colours than the latter, and being therefore more often used, notwithstanding its higher price. A purer, semi-crystal form of the bitartrate is employed for specially brilliant shades. The mordant for dark tones consists of 4 per cent. of potassium bichromate and 3 per cent. of bitartrate, whilst for lighter shades 1 per cent. of each is taken.

In some cases the other adjuncts to the chrome bath are equal, and even superior, to bitartrate; thus, in mordanting hat bodies for light shades, oxalic acid is preferable on account of its cleansing properties; for dark shades with alizarine red and alizarine orange, sulphuric acid is the best adjunct to the bath, as giving very fast colours to milling.

Latterly, the use of a concentrated solution of lactic acid has been warmly recommended in many quarters as a substitute for bitartrate, and in fact it is both well adapted for this purpose and cheap. According to C. H. Boehringer's recipe, the mordanting bath in this case consists of $1\frac{1}{2}$ per cent. of bichromate, 3 per cent. of lactic acid, and 1 per cent. of sulphuric acid.

A consideration of some practical importance is the fact that light shades are rendered faster towards light when mordanted with chromium fluoride than with bichromate and one of the above adjuncts. The only explanation of this is by the assumption that wool mordanted with bichromate always retains part of the chrome as chromic acid, which then acts destructively on the dye in presence of light.

Bichromate is an important agent in cotton-dyeing and calico-printing; it is used as an oxidising agent for aniline black, for catechu dyeing, to improve the fixing of certain tannin dyeings, as a discharge for vat blue, and finally for the production of chrome yellow and orange on the fibre.

Sodium bichromate is very similar to the potassium salt, from which it differs only in its hygroscopicity, ready solubility, and cheapness; it may therefore advantageously replace potassium bichromate. According to E. Knecht, the only instance in which the behaviour of the two is different is in the mordanting of wool. The commercial grade of this salt is of variable composition, and should therefore always be checked by analysis.

Chromic chromates are put on the market in three marks—GA I, GA II, GA III—by the Höchst Farbwerke, the two first grades being suitable for mordanting cotton by the following method:—Before use, the mark GA I is diluted with 2–4 parts of water, the goods being then immersed for twelve to twenty-four minutes, and carefully washed with water. Before rinsing, it is advisable to treat them with a weak (½ per cent.) solution of soda for twenty to thirty minutes at 60° C. Piece goods are impregnated with the solution by padding, then wound on a roller and left covered up, the remainder of the treatment being as already described.

The GA II mordant can be fixed on the fibre by a gentle steaming or hanging in the oxidising chamber, and is better adapted for piece goods. The mordant is diluted with four times its own volume of water, and receives an addition of 8 to 10 per. cent its volume of glycerine; in this solution the goods are padded, then steamed for ten to twenty minutes without pressure, and finally treated as in the preceding case. Both these mordants are sensitive to light, a circumstance that should be borne in mind when they are being used.

Finally, the mark GA III is recommended for wool-printing and for mordanting silk, the latter being steeped for twelve to twenty-four hours in the mordant solution—previously diluted with about four volumes of water—and washed after lifting.

Tin Mordants.—As independent mordants the tin compounds are of inferior importance; they are used for producing bright yellows with natural dye-stuffs, for cochineal scarlet on wool, to improve the brightness of alizarine red on cotton, and for a fast acid red with santal-wood on cotton (in mixed wool and cotton goods). The chief of these salts are the chlorides—stannous chloride or "salts of tin," and stannic chloride—and sodium stannate.

Stannous chloride is the most important mordant for wool. The bath is prepared with 1½ to 4 per cent. of stannous chloride and 2 to 4 of oxalic acid or bitartrate, and the operation is generally conducted by the single bath method. The use of tin mordants, however, lowers the capacity of the dyes for resisting the action of the milling process.

In the case of silk, stannous chloride is used, not for mordanting, but for loading the fibre in black dyeing with cutch (catechu); whilst for cotton it is employed to brighten the colour in Turkey-red dyeing.

By reason of its reducing action, stannous chloride forms an important discharge in calico-printing. It is also used in the production of the so-called "carmines," *i.e.* colour lakes prepared by precipitating dye-wood extracts with stannous chloride

A certain amount of care is required in dissolving this salt in water, owing to its tendency to separate out, in part, in the form of an insoluble basic salt ($SnOHCl$). The best way is to dissolve in a minimum of water and hydrochloric acid, in an atmosphere of carbon dioxide.

Stannic chloride (tetrachloride) is the chief tin mordant for cotton and silk. On cotton it is fixed by the aid of tannic acid (*q.v.*). The method of mordanting silk with this salt—though seldom used—is as follows:—The silk is steeped for one hour in a clear 32° B. solution of stannic chloride, after which it is well washed with water and treated in a hot bath of soap and soda—or of the latter alone, according to the quality of the silk,—followed by another washing. Stannic chloride is very largely used for loading white or light-coloured silks. The method formerly adopted was that just described for mordanting with tin, but this has now been generally superseded by the following, which enables a heavier loading to be obtained. The silk, after passing the tin bath and the subsequent washing, is immersed in two baths at 50° C.—one hour in each—the first consisting of an 8° B. solution of sodium phosphate, the second of a 6° B. solution of sodium silicate. By this means the weight of the silk is increased by 18 to 20 per cent., or still more if the operation be repeated. Any stains produced in the silicate bath may be removed by ammonia. The tin escaping in the washing water may be recovered by precipitation with lime.

Formerly the so-called "pink salt" ($SnCl_4 2NH_4Cl$) was largely used for the same purposes as stannic chloride. A crystallised chloride ($SnCl_4 5H_2O$) is also sold under the above title.

Sodium stannate is frequently styled "preparing salt," owing to its employment in preparing fabrics for printing. Its chief use is in printing woollens, its employment for cottons being now mainly confined to the so-called "Luccas."

Jute, also, is often prepared for printing by the aid of sodium stannate, the fabric being first padded with a weak solution of this salt (then dried, in the case of vegetable fibres), and then passed through dilute sulphuric acid, which precipitates stannic acid on the fibre; the process concludes with a thorough washing.

Sodium stannate is often used to brighten the colours in Turkey-red dyeing.

Various tin mordants, formerly playing an important part in dyeing,—under the name of "tin solution,"—can be obtained by dissolving tin in different proportions of nitric and hydrochloric acid. At present only one of these is used to any extent (for producing cochineal scarlet on wool), viz. the so-called "scarlet acid." This is prepared in various ways, the following recipe, however, giving a mordant that produces an excellent scarlet:—16 parts by weight of tin are dissolved in 50 parts of nitric acid, 15 parts of hydrochloric acid, and 78 parts of water, the metal being added by degrees. As considerable heat is evolved by the reaction, the mixture will require to be cooled when prepared in the summer.

Of the other compounds of tin, the following find a limited application in calico-printing as adjuncts for steam alizarine red, in order to enliven the colour and protect it against the dulling effect of iron:—Tin hydroxide, in the form of "tin paste" (prepared from stannic chloride and soda); tin sulphocyanide; tin acetate (prepared from stannous chloride and lead acetate, or by dissolving stannous hydroxide in acetic acid); and tin oxalate (by dissolving stannic hydroxide in oxalic acid).

Copper Mordants.—These mordants play a small but important part in dyeing, their colour lakes being extremely fast, if not particularly handsome. At present copper mordants are rarely used alone, but are mostly associated with iron or chrome mordants in black-dyeing wool and cotton, in dyeing cotton with cutch, and for a few single-bath brown-dyeings with natural dye-stuffs on wool. In some of these cases, *e.g.* cutch, they act not merely as a mordant, but also as an oxidising agent.

Copper sulphate, or blue vitriol, is the only copper salt employed for the above purposes. In dyeing with aniline black, and as a reserve under vat blue, it acts solely as an oxidising agent; finally, it also serves for "coppering" with many substantive dyes, in order to increase their fastness to light; its action in this connection has not been elucidated.

Of the other copper compounds, the sulphide is used as a carrier of oxygen in dyeing with aniline black.

Amongst other metals, mention may be made of zinc, nickel, lead, manganese, lime, and magnesia. Zinc gives good colour lakes with a number of dye-stuffs, but the only form in which it is used in practice is as zinc sulphite for alizarine steam blue in calico-printing, in which case it furnishes a handsomer though less stable colour than is obtainable with chrome mordants.

The salts of nickel have several times been proposed as mordants for alizarine, but their high price has hitherto hindered their use.

Lead was in use for some time in fixing eosine dyes on cotton, but does not give very good lakes, and at the present time only the acetate is of practical importance, this salt being employed in the preparation of other acetates, for chrome yellow and orange, and as an adjunct to reserves under vat blue.

The supplementary mordants already referred to comprise salts of lime, magnesia, manganese, and zinc. In some dyeings—alizarine red, for instance—lime in particular plays an important part, its presence being essential to the mutual combination of the alizarine and the alumina. In other cases, *e.g.* many steam dyes in calico-printing, the supplementary mordants serve to increase the fastness of the colours produced by the aid of other mordants. They are used in the form of acetates.

Manganese salts are used solely in the production of a brown colour, manganese bistre. Finally, in the form of potassium permanganate, this metal finds employment as a bleaching agent.

THE FIXING AGENTS (ACID MORDANTS).

I. The Tannic Acids. II. The Oleic Acids.

A whole series of bodies, such as tannic acids, many oleic acids, albumin, precipitated silica, etc., have the property of fixing a certain class of dye-stuffs on cotton, for which they otherwise have but a slight affinity. Of the foregoing substances only the first three are of any practical importance, and one of them, albumin, will be described later, its use being restricted to calico-printing.

The tannic acids and some oleic acids play a very important rôle in the dyeing and printing of cotton, where they are used for fixing basic dyes and mordants. Their mode of action is only partly understood, though the formation of an insoluble tannic or fatty acid compound of the metal must be assumed when a metallic oxide is fixed by the aid of a tannic acid or a fatty acid. However, in the case of fixing basic dyes, no chemical combination between the colour base and the tannic or oleic acid is probable. At all events, the part they play is not so important as that of the mordants in the case of the adjective dyes, and for this reason they have received the distinctive title of "fixing agents," though some colour chemists, in the assumption that a combination occurs between the colour base and the tannic or oleic acid, class them as "acid mordants."

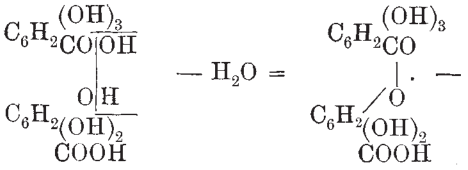
1. The Tannic Acids.

The vegetable kingdom furnishes a number of substances possessing very similar properties. They have an acid character, and act as precipitants of egg albumin, gelatin, alkaloids, etc. A few of them are used for tanning leather, on which account they have received the group name of "tannins" or "tannic acids."

The chief tanning materials are oak bark, gall nuts, cutch, sumach, chestnuts, myrabolans, divi-divi, etc.

Gall nuts are diseased excrescences produced on various plants, notably the oak tree, by insect punctures. They furnish the best known and, for the dyer's purpose, the most important of the tannic acids, viz. tannin, which is obtained by extraction with water, alcohol, and ether. The tannin is chiefly in the aqueous extract, and is recovered by evaporation. On evaporating to dryness a solution of tannin, to which alcohol and ether have been added, in slowly thickening liquid froths up under the influence of the escaping vapour and finally leaves a very loose mass, which comes into commerce as powdered tannin, and is held in high esteem on account of its ready solubility in water. "Tannin in needles" is the commercial crystalline form, and is prepared by evaporating to syrupy consistence a solution of tannin, drawing it out into threads, drying these on heated metal drums, and finally comminuting the product.

Gallotannic acid contains as its most active ingredient a digallic acid, resulting from the condensation of two molecules of gallic acid, the condensation being assumed to proceed on the following lines:—



$$\begin{array}{l} C_6H_2\begin{array}{l}(OH)_3\\ CO|\overline{OH}\end{array} \\ \qquad\quad O|H \\ C_6H_2\begin{array}{l}(OH)_2\\ COOH\end{array} \end{array} - H_2O = \begin{array}{l} C_6H_2\begin{array}{l}(OH)_3\\ CO\end{array} \\ \qquad\quad |\,. \\ \qquad\ /O \\ C_6H_2\begin{array}{l}(OH)_2\\ COOH\end{array} \end{array} \; —$$

Cutch, or catechu, is employed as a dye-stuff and tanning material.

Sumach is composed of the leaves and twigs of a shrub of the Rhus family, the best quality being furnished by *Rhus coriaria* (Sicily, Spain, the Balkans, etc.). Latterly it has also been sold in the form of a 30° B. extract. It contains gallotanic acid.

Chestnut extract is obtained from the wood of the horse-chestnut.

Myrabolans are the fruit of various trees (*Myrabolanus chebula*, etc.) occurring in China and the East Indies.

Divi-divi is the name given to the fruit of *Cœsalpinia coriaria*, Willd., found in the West Indies and South America.

Of all these substances the most important for the dyer are tannin, sumach, and cutch; of the rest, chestnut extract is principally used in black-dyeing silk.

All tanning materials exhibit a tendency to turn, on oxidation, into yellow or brown dye-stuffs, which have an affinity for cellulose. They are all therefore more or less strongly coloured, except tannin, which can be prepared quite colourless, and is therefore the only one that is suitable to use for light and bright shades. Of late, however, a decolorised sumach extract has been put on the market, and is adapted to replace tannin in most cases.

When exposed to the air, dilute solutions of tanning materials oxidise and deposit a brown precipitate, and therefore should not be kept stored.

In working with tannic acids, care should be taken to keep them out of contact with iron, since they form a dark-coloured compound with that metal.

Application of Tannic Acids to Cotton.

The employment of these substances in cotton-dyeing is principally based on their absorption by this fibre. On cotton being immersed in an aqueous solution of tannin, a portion of the tannic acid is gradually and uniformly taken up by the fibre. After some time the absorption ceases, a state of equilibrium then existing in respect of the distribution of the tannic acid between the water and the fibre. In any case, the amount absorbed is only very small, the absorption being least at boiling-heat, and most at a not very precisely determined medium temperature of about 40° C.

Other factors influencing the absorption are—the quantity of water, tannic acid, and cotton present, the influence being exerted in a very regular manner, which is quite analogous to the absorption of dye-stuffs by textile fibres, and in accordance with the law of distribution, which will be more fully discussed in dealing with the theory of dyeing. The higher the proportion of tannic acid and the lower that of water taken, in comparison with the amount of cotton present, the larger the quantity of tannic acid absorbed. The necessary consequence of this behaviour is, that the fixing baths must contain as little water as is compatible with the dissolving of the tannin or sumach.

If the cotton be washed with a large volume of water after passing through the tannin bath, nearly all the absorbed tannic acid will be driven out again, and consequently no more than a gentle rinsing is permissible.

Cotton treated with tannin is then capable of fixing basic dye-stuffs, inasmuch as it takes up the colour base and leaves the acid behind in the bath. Both these dyeings and the precipitates ensuing, on treating the corresponding dye-stuff solutions with tannin, are soluble in water as well as in an excess of tannic acid; consequently, the tannic acid salts of the colour bases cannot be fixed on the fibre. However, if the cotton be treated in a solution of a metallic salt after passing the tannin bath, there is formed an insoluble metallic tannate, firmly adherent to the fibre, and far more capable than free tannic acid of absorbing basic dyes from solution, and fixing them so as to stand washing. Whether under these conditions there occurs any chemical combination with the tannic acid attached to the metallic oxide is unknown, and is, moreover, improbable, since the absorption of the colour bases goes on with great readiness, even at the ordinary temperature.

This important method of fixing basic dyes on cotton was discovered by John Dale and Thomas Brooke in the "sixties." It is generally effected by the aid of tartar emetic as the metallic salt, the operation being performed in the following manner:—The cotton yarn is first well damped with hot water, and then left overnight in a hot solution of tannin or sumach, the amount of tannin varying—according to the depth of colour in view and the nature of the dye-stuff to be used—within somewhat wide limits: about 1–10 per cent. of the weight of the yarn, the usual amount being 2–4 per cent. For darker shades sumach is used; and it may be taken for granted that 3–4 parts, by weight, of sumach extract are equal to 1 part of tannin. Sufficient water should be used to just cover the yarn, and a hot bath has the advantage of expelling all the air out of the material, and thus facilitating impregnation. Moreover, in this case the gradual cooling of the bath during its sojourn overnight will enable it to retain for a longer period the medium temperature already mentioned as the most favourable for the absorption of tannic acid by cotton.

After the cotton is taken out of the bath, it is well drained, and is then worked about in a bath containing, on the average, 1–2 per cent. of tartar emetic, *i.e.* about half the weight of the tannin used, and is finally washed with care. According to results obtained by Falke, only $\frac{1}{2}$ per cent. of tartar emetic is required to fix 2 per cent. of tannin, and only 1 per cent. to fix 6 per cent. of tannin, thus showing that a large excess of tartar emetic is used in practice. This is, however, no particular drawback, as it ensures the thorough fixation of the tannin; and as the tartar emetic bath is used over and over again, there is no waste of antimony.

After a slight tannin treatment, the cotton is only left in the tartar emetic bath for about ten minutes, the time being increased from a quarter to half an hour when a stronger tannin bath has been used. The rapidity of the fixing process is in direct ratio to the concentration of the tartar emetic solution.

Cotton piece goods should not be left to stand in the tannin solution, but are wound through a 5–20 per mil. solution of tannin by means of a jigger (*q.v.*) for some time, and then treated in the same way in a strong solution of tartar emetic; or the pieces are drawn through a warm concentrated solution of tannin, then wound up on a roller, left to stand for one to two hours, and fixed in the same manner as before.

Although the process of fixing with tannin and tartar emetic has been known and practised in various ways for a long time, some uncertainty still prevails as to the best temperature for the tannin bath, and the time required for arriving at the state of equilibrium in the distribution of the tannic acid between the fibre and the water. The tartar bath is used cold, lukewarm, and hot, and equal uncertainty prevails as to the best temperature for the formation of the antimony tannate, and the amount of tannin to be brought on the fibre, in any given instance. Weber, it is true, elaborated a method for estimating the amount of tannin required to ensure the complete precipitation of the different basic dyes from solution; but the method itself is difficult of performance, and, besides, necessitates the previous determination, in each case, of the amount of tannic acid taken up by the cotton.

Since the badly fixed dyeings with basic dyes on cotton are of very low stability, it is always well to use more tannin and antimony than are absolutely needed, the baths being used again. In the case of the tannin bath, the liquor may be recuperated by adding a very small fraction of the original charge, the quantity absorbed being so small. The tartar emetic bath should always contain a readily detectable amount of antimony, and be free from acidity and dirt. The water used for dissolving the tartar emetic should be pure. Acidity in this bath is the result of an accumulation of potassium acid tartrate, owing to the absorption of the antimony by the cotton. It may be neutralised by an addition of chalk, which is preferable, for this and similar purposes, to any other alkaline substance, inasmuch as it dissolves only just in the same proportion as the acid salt is formed. Old tartar emetic baths contaminated with dissolved dye-stuffs must be clarified by settling or filtration before use again.

The tannin and antimony fixing process has not suffered much alteration since its first introduction. Other organic acids, *e.g.* benzoic acid and phthalic acid, are able to fix basic dyes on cotton; but the colours obtained are deficient in fastness, though handsome, so that none of these substances has found any practical application. For some time zinc sulphate was used to replace tartar emetic in fixing tannin; but the colours were less fast, and, indeed, no other metal is as good as antimony for this purpose. Other antimony compounds equally as suitable as tartar emetic are—antimony hydroxide, potassium-antimony oxalate, and antimony fluoride, in the form of double salts, etc., which have been frequently recommended as "tartar emetic substitutes," and employed as such.

Antimonyl potassium oxalate ($SbK_3(C_2H_4)_3 . 4H_2O$) may be used to replace tartar emetic, weight for weight, notwithstanding its far smaller percentage of antimony; and, being readily soluble, is also suitable for reserves under basic dyes.

The introducers of the last-named salt (Koepp & Co., of Oestrich-on-Rhine) have also put on the market a double fluoride of antimony and sodium ($SbF_3 . NaF$) as a substitute for tartar emetic; 658 parts by weight of the new salt being equivalent to 1000 parts of the old.

The "antimony salt" of E. de Haen (List, near Hanover) corresponds to the formula $SbF_3 . (NH_4)_2SO_4$, and 9 parts are equivalent to 10 parts of tartar emetic.

The double fluorides of antimony are strongly acid, and must therefore be neutralised before use.

The property of tannic acid for forming, with the metallic mordants, insoluble salts that adhere to the fibre of cotton renders it very valuable as a fixing agent for mordants, the method of application being to first treat the cotton in a bath of tannin or sumach and then in a cold solution of the mordant used. Iron, tin, and alumina are fixed on the fibre in this manner, the method being chiefly valuable for yarn-dyeing.

For fixing iron, the following procedure is adopted:—The cotton, after being treated with sumach, is passed through lime-water and then immersed in the iron mordant solution for a quarter of an hour to an hour, according to the amount of sumach used, the process concluding with a washing, preferably in hard water or water containing chalk, to neutralise the acid. The lime bath treatment produces calcium tannate, the neutralisation of the acid thus facilitating the formation of iron tannate in the subsequent iron mordant bath. The method is modified in various ways, the lime-water treatment sometimes following the iron bath, whilst in other cases chalk is added to the iron bath itself. The iron mordants used for this purpose are—ferrous sulphate, pyrolignite, and nitrate, a few degrees Baumé in strength. As iron tannate is of a greyish colour, the cotton treated in this way will also be grey or black, which is the reason why the use of iron in this connection is restricted to the production of dark shades. Blues fixed with tannic acid and antimony are often passed through an iron solution when required to be darkened. Iron tannate is also employed as an independent dye, an iron-grey of this kind being produced in yarns, notwithstanding that it hardens the fibre. The only use for iron, fixed with tannic acid, as a mordant is in black-dyeing.

For mordanting with tin, the cotton after passing through the tannin bath is treated for about half an hour in a cold solution of stannic chloride (2–5° B. strength) and then washed with water containing lime.

As a fixing agent for alumina the sole use made of tannic acid is in Turkey-red dyeing (*q.v.*), where it is employed to make the colour lake faster.

Application of Tannic Acid to Silk.

In silk-dyeing, tannic acid is used for loading the fibre, fixing the iron, and solidifying the colour.

Except in the case of light shades, the loading of silk by tannic acid is effected solely by the aid of sumach extract or chestnut extract. Some prefer to load after dyeing, but generally the loading and dyeing are combined in the same bath. The most favourable temperature for the absorption of tannic acid by silk is about 70° C.

For ordinary black-dyeing on silk (*q.v.*) the tannic acid is supplied by catechu, which serves both as a loading material and as a fixing agent for the iron. Souple silk is often loaded, and simultaneously mordanted with iron, by alternate treatment with a solution of tannin (principally chestnut extract) and a bath of iron pyrolignite. After the iron bath the silk is exposed to the air for a short time (about half an hour) in order to oxidise the ferrous tannate. The treatment with tannin and iron is often several times repeated, the strength of the later tannin baths being increased, and the operation being concluded with a washing in hard water. After repeated use the iron baths become acid through the liberation of pyroligneous acid, which is then neutralised by an addition of iron filings enclosed in a bag.

The solidifying process is employed to improve the fastness of the dye, and is performed by immersing the dyed silk in a lukewarm 8 per cent. tannin bath until the latter has become cold, whereupon the silk is washed, passed through a 4 per cent. bath of tartar emetic, again washed, and finally revivified. (*See* Dyeing.)

In the case of wool the tannic acids are very little used, and then only in the form of sumach for a few single-bath dyeings with natural dyes. (*See* Mordant Dyes.)

2. The Oleic Acids.

These substances are almost exclusively used for cotton. The earliest application of fatty bodies in dyeing occurred in the Turkey-red industry, which, even at the present time, consumes large quantities, chiefly of the sulphonated "tournant" oil class, to perfect the fastness of the colour by fixing the alumina of the colour lake, etc. (*See* Turkey-Red.)

The so-called Turkey-red oil was first introduced about the middle of the nineteenth century. It is prepared by treating olive oil or castor oil (ricinus oil) with concentrated sulphuric acid, the proportions employed varying from $1\frac{1}{2}$ to 4 parts of acid per 10 parts of oil, more acid being used in winter than in summer. The method of procedure is, however, the same all the year round, the acid being poured slowly into the oil, with constant stirring, and the whole then left to stand until a sample of the product is found to dissolve completely in water, whereupon the whole is poured into water and washed with a solution of common salt to remove the excess of sulphuric acid. The residual acid is neutralised with soda or ammonia.

While the acid and oil are being mixed, the temperature must be prevented from rising above 40° C., since otherwise the acid will exert an oxidising action, a condition revealed by the copious evolution of sulphur dioxide, in which case the product will be dark in colour and furnish poor results in dyeing.

Good Turkey-red oil should dissolve to an almost perfectly clear solution in water; any slight turbidity formed can be removed by the aid of ammonia.

As the name indicates, Turkey-red oil is mainly used in Turkey-red dyeing, where it serves to increase the brightness and fastness of the colour. Its composition formed the subject of numerous investigations by Liechti and Suida, Müller-Jacobs, P. Juillard, and many others, who devoted a great deal of attention to a thankless task in the hope of elucidating the process of Turkey-red dyeing. It is found that by the action of sulphuric acid on castor oil, under the conditions prevailing in the production of Turkey-red oil, a large proportion of the oil is left unaltered, whilst another portion furnishes a sulphoricinoleic ester and ricinoleic acid; in addition, sulphonated glycerine ether and polymerised compounds (polyricinoleic acids) may also be formed, according to the conditions (temperature!) of the operation. These products, however, have little practical effect in Turkey-red dyeing.

This was first demonstrated by P. Lochtin, who obtained with an acid ammonium ricinoleate just as good a red as with Turkey-red oil. Similar "acid soaps," obtained by treating a dissolved soap with a quantity of acid just insufficient to produce separation of the fatty acids, are now largely used to replace Turkey-red oil; and it would seem that the practical value of the use of sulphuric acid in preparing Turkey-red oil from castor oil is confined to rendering the latter soluble.

Turkey-red oil forms a good fixing agent for mordants, but its practical application in this direction is confined to the fixing of alumina by various methods. For Turkey-red, for example, the fibre is first impregnated with a strong solution of Turkey-red oil (by the same appliances as were used in the old red-dyeing process), and then dried, the cotton being afterwards immersed for some time in a solution of basic alum or aluminium acetate, and finally washed with water containing chalk (to neutralise the acid), followed with pure water. Piece goods are left rolled up for some time after passing the alum bath, to facilitate the fixing of the aluminium fatty acid salt.

The fixing process is also effected in other ways, a solution of soap being frequently used in place of the Turkey-red oil; for instance, the cotton is steeped for several hours in a solution of basic alum, then lifted, drained, and treated with a hot soap solution, followed by washing, the whole procedure being repeated if necessary.

Turkey-red oil can also be used for fixing basic dyes on cotton, but the resulting colours are less stable, though more handsome, than those obtained by the tannin-antimony process. The goods may be impregnated with Turkey-red oil, and then dyed after drying; or, better still, the oil is fixed as above, with alumina. Practically, however, this method is only of value in the case of rhodamine, which dye-stuff gives only a dull lilac when fixed with tannin and antimony, but a beautiful rose-red when fixed with Turkey-red oil. In this special case the following method is adopted:—The cotton is first treated for ten minutes in a 10 per cent. solution of Turkey-red oil, and, after draining and drying at a moderate heat, is worked about several times in a 6° B. solution of aluminium acetate (or aluminium sulphocyanide), followed by draining and drying. After rinsing, the mordanting operations are repeated in the same baths, and the goods slightly rinsed again, the dyeing being finished before they are allowed to dry.

Another very frequent use of Turkey-red oil is in the preparation of cotton piece goods for calico-printing (*q.v.*).

Application of Oleic Acids to Silk.

These substances are used for two purposes in silk-dyeing, viz. for brightening the colours and for softening the fibre.

In the first case use is made of an emulsion of olive oil or "tournant oil," more or less strongly acidified. (*See* Acid Dye-Stuffs.)

For softening purposes, especially in the case of "souple" silk, the so-called "*deux huiles*" (two oils) are used, consisting of a mixture of equal parts of sulphuric acid and olive oil. The acid is poured slowly into the oil, which is kept rapidly stirred, the mixture being diluted with warm water, when bubbles begin to form; and the silk is drawn through this bath for a short time, whereby it is immediately softened. The usual proportions are 2 per cent. of oil (calculated on the weight of the silk) and an equal quantity of acid. (*See also* Application of Acid Dye-Stuffs to Silk.)

CHAPTER IV

DYEING

For the sake of convenience, the diversified subject matter of this chapter has been divided as follows:—

I. Theory of colour; combination of colours; dyeing to pattern.
II. Theory of dyeing.
III. Classification of the dye-stuffs; methods of dyeing.
IV. Dyeing textile fibres on the large scale.
V. Trial dyeings; colorimetric determinations; reactions of dye-stuffs on the fibre; tests for fastness.

I. Theory of Colour; Combination of Colours; Dyeing to Pattern.

It is usual to regard the *colour* of any substance as a special property of that substance, inherent to and dependent on its nature solely; but what we are accustomed to call the true colour of any object depends not upon itself alone, but on the eye of the observer and on the light rays by which the object is illuminated. Colours have no real existence, but are mere subjective impressions that we receive from the light falling upon the object in question. It is more than probable that no two persons receive exactly the same impression from the observation of any colour, even though they employ the same word to express it.

This divergence in the vision of colours may extend to colour-blindness, or the incapacity for distinguishing between widely different colours—generally red and green. A still more important part in this connection is played by light, since the colour of any object is nothing more or less than that portion of the impinging light that is reflected by the object. The light we have solely to consider is that of the sun, which is composed of light rays of all colours. If this light be allowed to fall on a glass prism it will be analysed into its constituents, the various light rays undergoing different degrees of refraction, and in this manner we obtain a coloured strip containing all the colours present in sunlight, each one separated from the others. These are known as "the colours of the spectrum," and if the same light rays be reunited we again obtain white light.

Again, certain colours of the spectrum will furnish white light if united in pairs; and such colours are termed "complementary colours," their arrangement being as follows:—

Red and bluish green.
Orange and greenish blue.
Yellow and blue.
Greenish yellow and violet.
Green and red violet.

White is therefore not a colour capable of physical definition, but is merely a mixture of sensations, a physiological phenomenon, caused by the incapacity of the human eye for analysing a mixture of various light rays as the ear distinguishes the several notes in a musical chord. This incapacity for distinguishing between simple and compound colours is not confined to white, but extends to all other colours as well, the eye receiving merely a total impression; in fact, so little is the organ in question capable of differentiating between colours simultaneously impressed on the retina, that the effect of a uniform colour can be produced by a skilful blending of several different colours, as is actually done in Parisian Gobelins fabrics.

Consequently when we speak of the true colour of an object, this term merely implies that the object has the property of absorbing all the rays in sunlight except those corresponding to the said true colour. For this reason it will appear of a different colour if illuminated by another kind of light. Thus, for example, a red object illuminated by a white light compounded of blue and yellow rays will absorb both these colours, and appear to be no longer red, but black.

The colours of all terrestrial objects, as also of all natural and artificial dye-stuffs, are neither so homogeneous nor so intense as the colours of the spectrum. For instance, there is no single red that—like the red of the solar spectrum—consists solely of this colour without any admixture of yellow or blue. Again, since such colours lack the intensity of those of the spectrum, their mixtures do not furnish a white—like the complementary colours of the spectrum—but a more or less dark grey.

Grey is therefore a white of low intensity; whilst, considered from a physical standpoint, black is not a colour at all, its intensity being *nil*. Therefore when we view a white surface the sensation of light is so intense that the formation of a clear conception thereof becomes difficult, such an effect being unattainable by our natural and artificial dye-stuffs. A further consequence of this is that the dye-stuffs or any other coloured materials destroy more of the impinging light than pure white bodies. Hand in hand with this absorption of light proceeds the absorption of heat by the colour, a circumstance that may account for the known faculty possessed by the blind of distinguishing between colours by touch.

The comparative intensity of colours can be determined and expressed in numerical values by the aid of a very simple piece of apparatus. For this purpose a circular white disc is divided into four sectors, two of them being then painted a deep black, as shown in Fig. 25. On setting this disc in rapid rotation, the mixed impressions of black and white produces the sensation of grey, the intensity of which is evidently determined by the angle of the two white sectors. If we set down the intensity of white as 1 and that of black as zero, the grey resulting from the rotation of the disc in Fig. 25 will have the intensity $\frac{60}{360} = \frac{1}{6}$. To measure the intensity of any colour, the two opposite sectors of a white disc are painted over with that colour, and the remainder of the disc painted with a complementary colour, the angles of the painted sectors being then varied until a grey is obtained on rotating the disc. By determining the intensity of this grey in the manner described above, we have a measure of the intensity of the two colours on the painted disc, when it is recalled that these intensities are inversely proportional to the dimensions of the angles of the respective sectors. Hence if the two complementary colours are of equal intensity, exactly one-half of the disc must be painted over with each in order to produce a grey on the disc being set in rotation. On comparing the various available colours by this means, their intensity will be found to vary considerably, there being, for example, no single blue, green, or violet equal in intensity to the yellow of lead chromate.

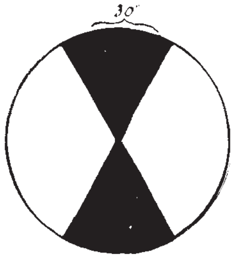


FIG. 25.

In everyday life, as also in the dyeing and printing industries, an entirely erroneous conception exists as to the meaning of the "intensity" of a colour, this being generally confounded with depth of colour—a totally different property. Thus, for example, if a blue be mixed with black, it becomes deeper in colour, but not more intense, the intensity of black being *nil*. In this way dark dyeings may be produced with a very little dye-stuff; and as the beauty of the colour is improved by the admixture of an *absolute* black, a black of this kind would be very valuable, provided it also possessed the other qualities demanded of a good practical dye-stuff. With such a black it would be possible to produce a series of dark shades much handsomer and more cheaply than is obtainable by existing methods. On mixing colours with blacks of the kinds now available, the following modifications are produced:—

Yellow with black gives brown.
Green ,, ,, olive.
Red ,, ,, red brown.
Blue ,, ,, grey blue.

If the intensity of the colours be reduced by applying them in thinner layers, they suffer a peculiar change of tone, becoming poorer in red. Thus, orange becomes yellow, blue turns more greenish blue, etc. Therefore, if it be desired to lighten a colour without altering its tone, it must receive an admixture of red.

The knowledge of which colours are complementary to each other is of considerable practical value. In dyeing textile fibres the colours are mostly produced by combining two, three, or even more dye-stuffs,—mode colours, for instance, being generally obtained by combining yellow, red, and blue, the dye-stuffs used having to fulfil two principal requirements—suitability for combination and good equalising properties. Most of the dye-stuffs of any one group will combine well together; but dyes that require a strongly acid bath will combine badly with such as have to be dyed in a neutral or weak acid bath. Equalising implies the uniform distribution of the dye throughout the fabric, etc., without difficulty.

In addition, however, certain other factors have to be considered, such as fastness to light, the shade, brilliancy, and price of the dye-stuff; so that it is sometimes a matter of difficulty to fix upon the most suitable dyes for a given colour.

Occasionally in combination dyeing a hitherto unexplained phenomenon is noticed, some unstable dye-stuffs giving fast colours when combined with other dyes, *e.g.* the case with methyl-violet along with alizarine on cotton.

If a fabric be dyed with a blue, a yellow, and a red dye-stuff in certain proportions—entirely dependent on the properties of the dye-stuffs themselves, such as tone, productivity, and affinity towards the fibre—a grey will be produced. Hence these three colours should be complementary. However, yellow and blue have already been given as complementary, and should therefore suffice to give a grey when combined; the addition of red should consequently furnish a brownish red. To find an explanation of this apparent paradox it should be remembered that the colours at our disposal are not homogeneous, green being present both in blue and yellow.

On the two being mixed together, one complements the other and grey is formed, but now the green present in both makes itself apparent, and we have, instead of grey, a greenish colour.[1] Now, in presence of the red, this latter combines to form a grey the red and green being complementary colours. If in such a combination the yellow preponderates, a yellowish grey, drab, or brown will be produced, a predominance of blue giving a greyish blue, and so on. The colours resulting from combinations of only two of these colours can be easily deduced: blue and yellow furnish green; blue and red, a bluish red or violet; yellow and red, orange.

Knowledge of such combinations mostly finds its application in dyeing to pattern, which consists in producing a colour that shall exactly match a given pattern.

In many dyeings only a single dye-stuff is employed, but if the dyeing is to be strictly to pattern, the aid of other dye-stuffs has often to be sought in order to obtain the desired tint. Thus if in dyeing a blue, for example, the colour has come out rather greener than the pattern to be matched, it must be shaded off by adding a small quantity of red or violet. A bluish black can be shaded or converted into coal black by the aid of a yellow dye.

One circumstance in particular occasionally renders dyeing to pattern a really difficult task, namely, that a simple comparison with the pattern immediately after dyeing is not sufficient, it being necessary to take into consideration the changes the colour is likely to suffer in the subsequent operations of washing, drying, finishing, etc. This necessitates an accurate acquaintance with the behaviour of the particular dye-stuff in question—a knowledge only to be acquired by practice. Thus if it be known, for instance, that a given yellow dye has the property of becoming greener in the subsequent operations, then, in order to arrive at an exact match to the pattern, it will be necessary to at first dye somewhat redder than the required shade.

Occasionally, too, it is necessary to dye a colour over with a small quantity of another dye-stuff, particularly when it is desired to increase the brightness of the colour. In such event a bright dye of the same shade and with good equalising properties is used.

The comparison of a dyeing with the original pattern is known as "matching"; and in this operation the following considerations must be borne in mind:—

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[1] On mixing yellow and blue—not substantially, but in the state of the sensations produced by both colours on the retina—a grey is obtained, as may be demonstrated by the rotating disc aforesaid.

1. Colours have a different (generally darker) appearance on the wet material than on the dry fibre; consequently, in matching, a small piece of the dyed material must be taken and dried; though, with practice, wet matching is possible.

2. The general and particular appearance of the two specimens must be compared, so as to enable an *immediate* judgment to be formed as to their similarity or difference. The longer the eye looks at colours the less sensitive does it become to slight differences between them.

3. The samples should never be viewed by artificial light, but always by diffused daylight. Even in this case, however, one and the same colour will sometimes have a different appearance, this being more particularly observable in the case of certain aniline drabs on wool, which appear greener at one time and more reddish at another, according to the lighting of the place where the inspection is made.

Finally, it should be mentioned that in harmonising colours (in cloth-printing) the best results will be obtained when the colours in juxtaposition are mutually complementary; also, that the brighter colours ought to be allotted a correspondingly smaller space than the others, in order to prevent the total effect being spoiled by the predominance of one or two of the colours.

2. Theory of Dyeing.[1]

The two principal factors influencing the method of performing any operation of dyeing, and the behaviour of the colour when finished, are the dye-stuff and the fibre. Dye-stuffs behave variously in dyeing, the difference being dependent on their chemical composition and on the nature of the fibre to which they are applied.

An examination of the classified dye-stuffs shows that the mutual relation of the members of each class depends more on a single property held by them in common than on their constitution. Thus all the numerous acid dyes, be their constitution never so divergent, behave in a perfectly analogous manner when applied to the different textile fibres, and exhibit no fundamental differences. This they evidently owe to their acid character, due to the presence of sulpho-, nitro-, and hydroxyl groups, the last named playing the principal part in this connection.

The basic dye-stuffs, whether azo compounds like chrysoidine or belonging to the triphenylmethane derivatives like fuchsine, all

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[1] The following sources have been drawn upon in compiling this section:—Georgievics:—*Mitth. Techn. Gew. Mus. Wien*, 1894, p. 165; *ibid.* pp. 205–220, 349–361; *Monats. f. Chem.* v. 15, p. 705–717; 16, pp. 345–350. Lehne's *Färber Ztg.* 1895-96, pp. 17–18. *Chemiker Ztg.* 1895, p. 426.

exhibit the same pigmentary character, thanks to the one or more amido groups present in each.

The substantive dyes, without exception, contain both acid and basic groups at the same time. Their capacity of dyeing cotton direct must be sought in the basic part of their molecule.

In the case of the mordant, or adjective, dyes, the relation between their constitution and their capacity for dyeing mordants has not yet been thoroughly investigated. This much is certain, that here also the hydroxyl groups play the principal part, this property being due to a special quality, and not to their acid character alone, since otherwise the far more strongly acid sulpho groups would exhibit a similar influence, which is not the case, the capacity of a dye for fixing with mordants being diminished by the presence of sulpho groups.

The insoluble dyes, like the developing and albumin dyes, can only be compared with the other groups when in their developed and finished state.

However different the various dye-stuffs and fibres may be, all dyeings have so much in common, in respect of their method of production and their behaviour, that they must be regarded as belonging to the same type of phenomenon, their difference being merely one of degree and not of principle.

As regards the method of production, the following observations apply:—

The dye is taken up gradually by the fibre—and best in the warm—the operation being complete in a short time, usually within the hour. At the expiration of this period no more of the dye is absorbed, even though the fibre be left in the bath for days. The slower the rate of absorption the greater its power of withstanding the influence of washing when once fixed on the fibre, though this only applies within certain limits. A portion of the dye always remains behind in the bath, this proportion being the greater the larger the amount of water and dye present in relation to the quantity of fibre and the degree of instability—as regards the influence of washing—of the dye itself. The larger the quantity of dye taken up by a fibre, the less is it capable of absorbing a further amount of the same; consequently. the first portions of dye are absorbed more rapidly and with greater energy, and therefore adhere more firmly to the fibre. The latter has a tendency to absorb relatively more dye from dilute than from concentrated solutions; and a light shade of dye is always relatively faster to washing than a darker shade produced by the same dye-stuff. If it be attempted to re-extract absorbed dye from the fibre by means of water, the following characteristic phenomenon is observed, namely, that, with extremely rare exceptions, this removal is incomplete, even when enormous quantities of water are used, thus showing that the dyeing process is by no means an entirely reversible one in the majority of instances.

When several colours are applied to the same fibre, the amount of each finally absorbed is independent of the order in which they come into action. It is therefore immaterial, so far as the final result is concerned, whether the several dye-stuffs be applied together or in succession; though it is essential that the same bath be used, that the dyes taken do not precipitate one another from solution, and also that the fibre be immersed in the bath until equilibrium is established as regards the distribution of the dye between the fibre and the dye-bath. This, however, as a general thing, only applies to hot dyeings; in dyeing at the ordinary temperature, a superposition, or overlaying of one dye above another, may sometimes occur.

This behaviour of dye-stuffs in dyeing must be based on some definite law, which may be ascertained by the quantitative examination of the distribution of a dye between the fibre and the bath. By determining how much dye has been taken up by the fibre, and how much is left in the bath, and calculating from these data what quantities of dye are contained in equal weights of the fibre and the bath liquor, we obtain two values, which may be expressed by Cf. (fibre), and Cb. (bath). The quotient Cf. ÷ Cb. is termed the coefficient of distribution, and its dimensions depend on the nature of the dye-stuff and fibre, the temperature of the dyeing process, and the concentration of the bath liquor in relation to the amount of fibre treated. The rule is that the coefficient of distribution slowly sinks as the concentration of the bath increases.

If this diminution of the coefficient of distribution be actually quite uniform, then, for mathematical reasons, the expression $\frac{\sqrt[x]{Cb}}{Cf}$ must possess a constant value independent of the concentration. This is, in fact, actually the case in two instances, viz. the dyeing of silk with indigo-carmine at boiling-heat, and in dyeing mercerised cotton with methylene blue in the cold.

When it is considered how varied are the circumstances and factors coming into play in these two dyeings, and that a gradual reduction of the coefficient of distribution is also noticed in numerous other instances of dyeing, there will be no hesitation in according the above expression the dignity of a law, which, however, for reasons that cannot be argued out in detail here, only applies in its full extent to light and medium colours.

The aforesaid peculiarities of the dyeing process find their precise mathematical expression in the formula

$$\frac{\sqrt[x]{\mathrm{Cb}}}{\mathrm{Cf}} = \text{a constant,}$$

the "law of distribution," and can also be deduced therefrom. Furthermore, the value of the root-sign x affords a measure of the affinity of the dye for the fibre, and naturally varies for different dyeings, being greater in proportion as the affinity of the dye-stuff for the fibre increases.

From this law of distribution follows the practically important fact that the absorption of the dye—especially those that are not taken up readily—is primarily dependent on the volume of the bath liquor. It would therefore be more correct to apportion the weight of dye taken to the volume of the bath liquor, and not, as is the usual practice, to the weight of goods to be dyed.

Another circumstance, and one that has not yet been mentioned, influences the dyeing of the textile fibres, namely, their fibrous structure. If a textile fibre be dyed in its fibrous condition, and in the state of powder, it will be found that the powder takes up more dye in the cold than the fibrous form, this resulting from the greater amount of surface exposed. In the warm, the conditions are reversed, the fibrous structure in this case offering the greater resistance to the extractive action of the bath water. As a matter of fact, it is invariably found that materials dyed in the state of fibre exhibit greater fastness to washing than such as have been dyed in the state of powder.

How great is the importance of structure in dyeing is most clearly seen in the case of bodies with only very slight affinity for dyes, by dyeing them with substantive dyes, in both forms, structural and amorphous. A good example of this is afforded by asbestos, which, in the powdered state, absorbs little or no dye, but takes up a fair amount in the fibrous condition.

Structure introduces a new factor into the dyeing of textile fabrics, namely, capillarity, the influence of which, as may be gathered from the foregoing, is favourable. Nevertheless, it does not effect any modification of principle in the nature of the distribution of the dye between fibre and dye-bath, and consequently the law of distribution $\frac{\sqrt[x]{\mathrm{C\ bath}}}{\mathrm{C\ fibre}} = K$ is independent of the structure, the influence of the latter only coming into play in the value of K. Finally, the favourable influence of structure on dyeing is also made manifest in the phenomenon of equalising (*q.v.*). Some dyes equalise very well, so that any patchiness becomes thoroughly obliterated as dyeing progresses, a transference of dye occurring from one part of the fibre to another—apparently favoured by the structure—until the distribution is uniform. The cause of this phenomenon is, however, deeper, and can be deduced from the law of distribution in the following manner:—Let us assume that a sample of stuff to be dyed has first been bound round in one particular place, and is then immersed in a solution of a good equalising dye until equilibrium ensues. On then untying the stuff, and immersing the undyed portion again in the dye-bath, what happens? That portion which was protected from the action of the dye enters into mutual reaction with the dye-bath, and continues to absorb dye until equilibrium is accomplished in accordance with the law of distribution. The bath, however, is thereby weakened, and thus the equilibrium between the bath and the rest of the stuff is disturbed, the result being that a portion of the dye is removed from all parts of the latter that were dyed previously. This performance is repeated until proper distribution is accomplished between the dye-bath and the entire stuff.

From this explanation of the phenomenon of equalising, it follows that the equalising property of a dye is in inverse ratio to its power of withstanding washing; the more completely reversible the dyeing, the more readily will any initial irregularity be equalised.

It is next essential to give attention to the properties of the finished dye; and all that can be said on this point can be told in few words, viz. that the dye behaves in nearly all its reactions just as though no fibre were present. Martius yellow and similar dyes separate from the fibre, by sublimation, when heated; fluoresceine is converted into eosine by the action of bromine; dyes containing a free amido group can be diazotised on the fibre, and converted into more complex azo dyes by coupling with phenols and amines; very dark dyeings with fuchsine, methyl violet, and similar dyes, will bronze just in the same manner as the dye-stuffs themselves, etc.

Only, in fact, in two respects, viz. fastness to light and washing, does the presence of the fibre make itself felt. The washing fastness of a dyeing, or its behaviour towards solvents, depends not only on the solubility of the dye in question, but also on its affinity for the fibre and upon the way in which it is fixed thereon; and the solvent, in addition to the task of dissolving out the dye, has also to overcome its affinity for the fibre, a task which is naturally lighter in proportion as the fixing is defective.

The fastness of any dye towards light is chiefly dependent on the constitution of the dye itself. Here, however, we are in presence of a phenomenon that, until quite recently, was entirely enigmatical, namely that the fastness of one and the same dye towards light differs on different fibres, the reason for this being that a dye may be absorbed in varying molecular dimensions by different fibres.

This may be traced from the law of distribution, but, in order to do this, some brief consideration must be devoted to another process—that of solution. Under the term solution we understand an intimate molecular admixture of two or more substances. If we allow two non-miscible solvents, such as water and ether, to act simultaneously on a substance that is soluble in both, we find that —just as in the case of dyeing, where a part of the dye is absorbed by the fibre, whilst part remains in the bath—a regular distribution of the substance occurs between the two solvents, and in such a manner that the ratio of concentration, the coefficient of distribution, is a constant value. This is known as Henry's law.

Instances are, however, known where the coefficient of distribution is not constant, but varies with the concentration. Van t'Hoff, Nernst, and Küster have proved that in these abnormal cases the molecular constitution of the dissolved substance is different in the two solvents, but that here also a constant expression for the distribution of the dissolved matter can be obtained.

If the concentration of the substance in the one solvent be expressed by C_1, and that of the other by C_2, and we assume that the substance in question is dissolved as single molecules in the first solvent, and as double molecules in the second solvent, the expression $\frac{\sqrt[x]{C_2}}{C_1}$ will furnish a constant value.

Now this formula is evidently identical with that we already know as expressing the regular distribution of a dye between the fibre and the dye-bath, and we can therefore deduce from its form $\frac{\sqrt[x]{C \text{ bath}}}{C \text{ fibre}} = K$ the conclusion that—just as in solutions, so also in dyeings—the dye-stuff must exist in different states of molecular constitution in the fibre and the bath; the fibre takes up simple molecules, leaving more complex molecules of dye-stuffs behind in the bath.

This is in perfect accord with the fact that dyeing is better effected in the warm than in the cold, the heat causing the complex molecules to break down into a simpler form, which is then taken up by the fibre. The difference in molecular dimensions between the absorbed and residual dye is expressed in the value of the root-sign x, which, as already stated, is dependent on both the dye-stuff and the nature of the fibre. The dye is therefore absorbed differently, as regards molecular dimensions, by different fibres, a circumstance which explains the varying fastness to light of one and the same dye on different fibres.

Dyeing and solution are therefore analogous phenomena, a fact that, after being theoretically assumed by O. N. Witt, was first experimentally demonstrated by the author. Certain divergences, however, exist between the two, so that we are not justified in regarding the dyeing of textile fibres as a kind of "solid solution," since, were the dye really dissolved in the fibre, and the latter consequently permeated in a perfectly homogeneous manner, the ratio of distribution would be independent of the mechanical properties of the fibre. This, however, is not the case, it having already been shown that a powdered fibre is able, in consequence of its greater surface, to absorb far more dye in the cold than when in the fibrous condition.

The behaviour of dyeings towards water also tells against the solid solution hypothesis. Most dyes are absorbed better in the warm; hence, if the dyeing process be regarded as a phenomenon of solution, it must be assumed that at higher temperatures the solvent power of the fibre for dyes is greater than that of water, and that, conversely, at low temperatures the dye-stuff is more readily soluble in water than in the fibre. If this were the case, it would also follow that the dyed material would part with a larger quantity of dye when washed in cold weather than with hot, whereas, as is well known, the contrary is the case.

Some chemists regard dyeing as a kind of chemical combination between the dye and the substance of the fibre. According to this "chemical theory of dyeing," the keratin of wool and the fibroïn of silk behave like the amido acids in exhibiting simultaneously an acid and a basic character, playing the part of an acid in presence of basic dyes, and acting like a base in presence of acid dyes. Knecht afforded some support to this view by his discovery of the fact that, in dyeing wool and silk with fuchsine and similar basic dyes, the colour base alone is absorbed, leaving behind in the bath the whole of the hydrochloric acid with which the base is combined. The explanation offered for this process was to assume that the wool and silk decomposed the fuchsine into hydrochloric acid and colour base, and formed with the latter a compound resembling a salt, since it was considered impossible for the colour to be due to the free rosaniline base, which is colourless.

This explanation of fuchsine dyeing became, however, untenable when it was proved that the decomposition of the fuchsine is effected already by the water of the dye-bath; also that the rosaniline base exists in a coloured form; and, finally, that the hydrochloric acid of the fuchsine remains behind, quantitatively, in the bath in the dyeing of inert substances like glass, clay, etc.

A further support to the chemical theory of dyeing was regarded by some as afforded by the fact that all dyes exhibit an acid or a basic character, or the two combined, a body of perfectly inert chemical character having no dyeing power. In this view, however, one consideration is forgotten, viz. that a whole series of physical processes are also influenced by the chemical character of the substance coming into play. Thus, to give only one example, the well-known fact that aqueous solutions of caustic alkalis will adhere firmly to glass, whilst aqueous solutions of acids adhere only to a slight extent, and mercury not at all, has never yet been explained by anyone as due to chemical interaction. In reality, not one single fact is known that would indicate the probability of the occurrence of chemical combination between the dye-stuff and the fibre in dyeing; whereas, on the other hand, there are a number of weighty reasons proving the contrary, viz.:—

1. In chemical compounds the combination occurs in definite molecular proportions; whilst the case is altogether different in dyeing, the quantity of dye absorbed being determined by the law of distribution, which definite and regular distribution could not be possible unless the dye-stuff were in exactly the same chemical condition in both the fibre and the bath. Hence, if the acid of a dye-stuff be found in a free state in the bath, it must also be present in the free state in the dyed fibre.

2. Chemical compounds possess different properties to those of their constituents; this is not the case in dyeing.

3. In the dyeing of wool and silk with acid dyes the absorption of the dye takes place in the presence of a strong acid, *e.g.* sulphuric acid. Now an increase in the amount of such strong acid would be the reverse of favourable to the production of a salt-like compound between the dye acid and the keratin or fibroïn present; whereas, as a matter of fact, an addition of sulphuric acid to the dye-bath leads to an increased absorption of dye.

4. A series of dyeings, of an indubitably mechanical origin—such as manganese bistre, and the dyeing of chemically inert bodies like asbestos, glass, etc.—clearly show that dyeing may be the result of adhesion alone.

5. It is also possible to dye one colour upon another.

For the above reasons it may therefore be concluded that dyeing is a phenomenon of absorption, the dye being retained on and in the fibre by adhesion.

III. Classification of Dye-Stuffs; Methods of Dyeing.[1]

Since in this chapter we are solely concerned with the application of the dye-stuffs in the processes of dyeing and printing, the sole principle of classification we can adopt is based on the method of dyeing necessary to bring them on the fibre. The different classes of dyes, therefore, may be set down as follows:—

1. Acid dye-stuffs.
2. Basic or tannin dyes.
3. Dye-salts or substantive cotton dyes.
4. Mordant dyes.
5. Vat dyes.
6. Developing dyes.
7. Albumin dyes.

1. Application of Acid Dye-Stuffs.

The acid dyes are mostly sodium salts of sulpho-acids, and this class comprises the different marks of tropeoline, ponceau, Bordeaux, scarlet, fast red, chromotrope, black azo dyes (such as naphthol black), acid violet, acid green, several aniline blues, patent blue, several fast blues or indulines, tartrazine, quinoline yellow, azo-carmine, indigo-carmine, etc., as well as such dyes as owe their acid character to the presence of nitro and hydroxyl groups—the nitro dyes and eosines.

Dyes of this class are more frequently used than any others for dyeing wool and silk, but are not well adapted for dyeing cottons.

Application to Wool.—The dyeing is effected in presence of acids or acid salts, viz. sulphuric acid, sodium bisulphate—mostly known as tartar preparation—Glauber salt (sodium sulphate), alum, acetic acid, ammonium acetate, or ammonium oxalate. The object of these acid adjuncts is to neutralise the calcium bicarbonate in the dye water, liberate the dye acid, and finally to diminish the solubility of this latter in water, thus facilitating its absorption by the fibre and helping the bath to " draw." The stronger the acid the better and more quickly is the dye absorbed by the wool.

An equally important rôle is played by Glauber salt, which acts as a regulator to ensure uniform absorption of the dye by checking the rate of absorption. The selection of the adjuncts to the bath depends, therefore, primarily on the equalising properties of the dyes used and their tendency to draw well or badly, as the case may be.

In addition, it has to be considered whether the dye in question

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[1] For details applicable to the separate dyes, the reader is referred to the instructions ssued by the various makers of dye-stuffs.

will stand a strongly acid bath or not; and another important factor influencing the selection of the adjunct is the quality of the goods to be dyed, closely woven goods being harder for the dye to penetrate uniformly than is the case with slack-twisted yarns. In the former case the operation must therefore be allowed to proceed slowly, and in a faintly acid bath.

Another factor regulating the absorption of dye is the temperature, the rate increasing as the latter ascends. Therefore, since high acidity of the bath and high temperatures accelerate the absorption of the dye, whilst Glauber salt has a restraining action, it is necessary, in the case of dyes that do not equalise well and goods that are hard to dye through, to commence operations at a low temperature and in a faintly acid bath containing Glauber salt. Should the dye-stuff draw badly, the acid is added in several portions during the operation, or delayed until the close; but with a dye that equalises readily it is possible to start with a very—sometimes boiling—hot, strongly acid bath, provided, of course, that the dye-stuff itself will stand a very strong acid bath. In some difficult cases the bath is allowed to become gradually acid during the operation, by adding ammonium acetate or oxalate, these salts being slowly decomposed, with liberation of ammonia, on heating.

The usual method of dyeing wool with acid dyes is as follows:—The bath is charged with 2–4 per cent. of sulphuric acid, 10 per cent. of Glauber salt, and the (filtered) solution of dye-stuff, the goods being entered at lukewarm or medium temperature and gradually raised to boiling, which is maintained for one hour to one and a quarter. This prolonged boiling is essential for securing the equalisation of the dye, though some dyes, such as indigo-carmine, dye well at somewhat lower temperatures. Only in the case of light shades is three-quarters of an hour's boiling sufficient; and here it is advisable, in the interest of better equalisation, to dye with less acid and more Glauber salt.

The foregoing method is applicable to the majority of dyes, and an addition of 2–2½ per cent. of sulphuric acid will generally be sufficient; naturally this is also influenced by the hardness of the water.

In the case of dyes that equalise well, *e.g.* quinoline yellow, naphthol yellow, patent blue, cyanol, fast acid violet 10 B., fast green (bluish), azo-carmine, chromotrope 2 R., etc., the goods are entered direct into the boiling bath. On the other hand, with a large number of dyes inferior in this respect, such as the ponceaus, scarlets, fast reds, Bordeaux, etc., the goods are entered at medium temperature, and an increased addition of Glauber salt—about 20 per cent.—is very desirable, though not absolutely necessary. In such cases it is usual, in practice, to use about 10 per cent. of Glauber salt and 10–15 per cent. of sodium bisulphate. With regard to the latter, which is also used alone, it is frequently contaminated with saltpetre, which may do harm in dyeing, owing to the liberation of nitric acid. Ten parts of the bisulphate may be replaced by 4 of sulphuric acid and 10 parts of Glauber salt.

The black acid dyes are mostly used in association with bisulphate, though a better plan is to commence dyeing with Glauber salt and acetic acid, a small percentage of H_2SO_4 being afterwards added to help to draw the dye.

In the most difficult cases of all, where the dyes equalise badly and the stuff is hard to dye through, the material is first boiled for some time in more or less strongly acidified water before the addition of the dye.

The eosines require to be dyed in a faintly acid bath, one of the two following methods being pursued:—(1) The bath receives an addition of 2–10 per cent. of acetic acid (or alum) according to the hardness of the water and the intensity of the dyeing; (2) the goods to be dyed are first boiled in a bath containing 5 per cent. of alum, 5 per cent. of acetic acid, and 5 per cent. of potassium bitartrate, the solution of the dye-stuff being added after the bath has been cooled down to 50° C. The temperature is afterwards again raised to boiling-heat. This second method gives the more brilliant dyeings. In either case less boiling is required than with the other acid dyes, a quarter of an hour to half an hour being sufficient.

For combination dyeings the selected dye-stuffs should be similar in their behaviour during the process, the choice therefore generally falling on such as equalise well and are able to stand a strongly acid bath.

Shading off is effected at boiling-heat in the case of dyes that equalise well; in other cases the bath must first be cooled by an addition of cold water.

Dyeings that have come out too dark or patchy may be corrected by a treatment with hot soda solution.

Finally, it may be mentioned that dyes generally equalise better in old bath liquors, *i.e.* such as have already been used several times over. The cause of this is of a twofold character; in the first place, the bath contains a larger quantity of Glauber salt (from previous dyeings); and, secondly, the repeated boiling of different parcels of wool has extracted a larger amount of wool substance, which, like the bast of silk, helps to retard the absorption of the dye.

An older method of dyeing with acid dyes, especially scarlets, consisted in using a small percentage of stannous chloride and potassium bitartrate. The resulting dyeings are faster to milling than those obtained by the aid of Glauber salt and sulphuric acid.

The alkali blues, which also belong to the acid class of dyes, are dyed in a special manner, owing to the fact that the corresponding dye acids are insoluble in acidified water. The goods are first entered in an alkaline bath (boiled for three-quarters of an hour to an hour) wherein the wool takes up the dye in a colourless form. Borax is the most suitable alkali for this purpose, 5–10 per cent. being used; soda, though sometimes employed, is disadvantageous for the fibre on account of its strong alkalinity. After this preliminary treatment the wool must be very thoroughly washed, and is then entered for about twenty minutes in a second bath, containing 5 per cent. of sulphuric acid. Here the colour is developed, coming out greener in shade, it may be stated, in proportion as the developing bath is cooler. If greater milling fastness is desired, the colour is developed with alum instead of sulphuric acid.

These alkali blue dyeings, which unfortunately are of only very low fastness to alkali and light, are, however, characterised by good milling fastness (provided they are well washed after the first bath) and considerable beauty. Shading, when desired, is effected by means of acid dyes applied in the second (acid) bath. Dyeing to pattern is a more difficult operation with these dyes, owing to the fact that the colour is only developed in the second bath.

Application to Silk.—Here also, and for the same reasons as in the case of wool, the dyeing is performed in an acid bath, sulphuric acid being most generally used. In some cases—eosines, for instance—such a strong acid bath is unfavourable, and should be replaced by acetic acid or tartaric acid. The silk draws the dye even in the cold, and—just as in the case of wool—it is possible to accelerate or retard the absorption to suit the equalising powers of the dye by regulating the temperature, degree of acidity, and the use of more or less bast soap, which here replaces Glauber salt. Instead of bast soap, a 2½ per cent. solution of Marseilles (olive oil soap) and a 0·4 per cent. solution of gelatine may be used —at least for dyeing on the small scale.

The acidified bast soap bath is prepared by boiling with the required quantity of acid; the silk is entered and then lifted, and then only is the necessary quantity of water added, along with a portion of the dissolved dye. In this method the fat separated from the bast soap remains in a state of very finely divided emulsion, which is not the case when the whole of the water and acid are added together. According to the equalising power of the dye, the amount of bast soap solution taken ranges from one-third to one-fourth of the entire bath, one-third part of bast soap solution and two-thirds water being generally used for starting. A larger proportion of bast soap is used when uneven dyeing is anticipated or when the silk has acquired a dusty appearance, due to defective treatment in process of weighting with sodium silicate.

The dissolved dye is added by degrees during the operation. The silk is entered at 30–40° C., well worked about whilst the temperature is being raised to near boiling-point, and is finished at a temperature of about 90° C. Actual boiling-heat should be carefully avoided. In the case of the eosines brighter colours are obtained at temperatures somewhat lower than the foregoing. Raw silk must be dyed lukewarm, souple silk at a lower temperature than fully scoured silk. Very delicate colours, being dulled by sericin, must be dyed without bast soap.

After dyeing, the silk is washed, then livened or brightened by treatment in a lukewarm to hot bath (more or less strongly acidified by the same acid[1] that was used for dyeing), and is afterwards drained and dried without rinsing. This treatment brightens the colour and improves the feel of the silk, *i.e.* makes it more brittle and harder to the touch, as well as giving out a crunching sound when compressed. The degree of "feel" produced is varied according to the purpose for which the silk is intended, and is the greater in proportion as the bath is hotter and more strongly acid. To entirely remove the feel, the silk is immersed for several hours in a lukewarm bath containing 25–30 per cent. of fuller's earth, calculated on the weight of the silk; the same softening effect is also obtained by treatment with the so-called "two oils" (*see under* Oleic Acid). The goods so treated are employed for producing a "moiré" finish, silk with scroop being unsuitable for this purpose.

Shading with another dye is sometimes practised in the brightening bath. In order to obtain fastness to washing, the dyed goods are put through a solidifying treatment (*q.v.*).

Dyeings that have come out too dark or patchy are corrected in a bath very rich in bast soap, which extracts part of the dye.

As in the case of wool, the alkali blues are first applied in an alkaline bath, and the colour developed in an acid bath. The first bath is charged with 10–15 per cent. of Marseilles soap for light

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[1] A few grams of acid per litre (parts per mil.), the quantity of water being thirty times the weight of the silk.

shades, or 20–30 per cent. for dark shades, together with the requisite amount of dye, the silk being entered hot and finished by boiling. It is next well washed—otherwise the colours will come out dirty—and the colour is developed in a bath containing sulphuric acid; stannous chloride and hydrochloric acid being used instead when greater fastness is desired.

Application to Cotton.—The acid dyes are not well adapted for dyeing cotton, their affinity for cellulose being almost *nil.* Nevertheless they have been used for this purpose in the absence of more suitable dyes—previous to the introduction of Congo red—and are still, though only to a limited extent, viz. for the production of a vivid scarlet by means of croceines and similar azo dyes. The *modus operandi* is as follows:—The cotton is first steeped for some time in a fairly concentrated solution of basic alum, and then dyed in a lukewarm dye-bath containing a minimum of water; or else the dyeing is effected in a single bath containing an addition of alum and common salt. Brighter colours are, however, obtained when the cotton is first treated with a cold (about 4° B.) solution of sodium stannate, for one to one and a half hours, previous to the alum bath. The eosines also can be applied to cotton in a lukewarm bath with a large proportion of common salt. All these dyeings, however, are so poorly fixed that they must not even be rinsed afterwards.

Some acid dyes, *e.g.* marine blue, produced by sulphonating strongly basic dyes, can be applied to cotton after the manner of the basic dyes, *i.e.* subsequent to the treatment of the material with tannin. (See later.)

2. Application of the Basic Dye-Stuffs.

The basic dyes are mostly salts of colour bases with hydrochloric acid or with zinc chloride. To this class belong several azo dyes, such as chrysoidine and Bismarck brown, also auramine, the rosaniline dyes, and such of the malachite green series as are not sulphonated, the rhodamines and pyronines, acridine dyes, methylene blue, most of the oxazines, such as new blue and Nile blue, the safranines, indoines, eurhodines; finally, also the indulines and nigrosines, in so far as they are not sulphonated compounds. The use of these dyes is chiefly for dyeing and printing cotton.

Application to Wool.—Wool takes up the basic dyes in a very uniform manner, without the use of any adjuncts in the dye-bath, and the absorption begins at a temperature of 30–40° C. Hard water should be corrected with acetic acid until the reaction is slightly acid, since otherwise the colour bases separate in resinous masses and cause streakiness, which is impossible of removal. A slight addition of acid is also desirable, because the wool mostly retains some alkali from the washing process, and this, by forming the colourless colour base, would retard the absorption of the dye. Moreover, these dyes draw more slowly in a faintly acid bath, a condition recognised as favourable in dyeing operations generally. Too much acid hinders the absorption of the dye. The goods are entered lukewarm, and the operation is continued for about an hour, the temperature not being allowed to exceed about 80° C. Dyeings performed at boiling-heat are less brilliant in colour. Nevertheless, gentle boiling is admissible in the case of dark shades, and of a few dyes of this class, such as methyl-violet. Auramine must be dyed in a neutral bath.

The brightest colours are obtained by adding a little Marseilles soap to the neutral dye-bath, and avoiding higher temperatures, about 50° C. being the limit. In this case, however, in order to avoid stains, the water must first be boiled with soap, and the resulting scum removed. This method is very seldom used in practice.

The necessary quantity of wool is added in two or three portions during the operation, and not all at once. Wool that has been sulphured is not, as a rule, fit for dyeing with basic dyes.

As far as possible the combination of basic dyes with those of acid character should be avoided, since in many cases it leads to the formation of insoluble precipitates which may produce spotting. Frequently, however, basic dyes are used for topping dyeings produced from other groups of dyes, the object of this treatment being to shade or enliven the colours. The operation is generally performed in a fresh bath.

A very special process is employed for dyeing with many of the green dyes, such as brilliant green, methyl-green, malachite green, etc. The wool is entered in a boiling hot bath containing 7½ per cent. of sodium hyposulphite, 2 per cent. of sulphuric acid, and 5 per cent. of alum (or zinc acetate), in a wooden vat, and is worked about in this bath for three-quarters of an hour after steam has been shut off; it is then drained in the hydro-extractor, rinsed, and dyed at about 50° C. in a bath containing about 3 per cent. of acetic acid, in addition to the dye. The bath liquors should be kept for use over again; the oftener they are used the finer the colours obtained.

In the above process sulphur is precipitated on the fibre, and assists in fixing the dye. These dyes can, however, be applied in a simpler manner by passing the wool through a hot soap bath (1–2 per cent. of soap), and then dyeing in a fresh, lukewarm dye-bath. This method is seldom used, though occasionally resorted to for the production of a brilliant green of greater fastness than is afforded by the use of the various acid greens.

Basic dyeings on wool are characterised by lustre, good equalisation, fastness towards alkalis, and milling fastness. They are, however, fugitive to light, rub off under friction, and bleed into any adjacent undyed portions when washed.

Application to Silk.—The basic dyes are rapidly taken up by silk, even in the cold. The process is conducted at temperatures up to about 50° C. in presence of acid dyes, and at higher temperatures in a bast-soap bath slightly qualified with acetic acid or tartaric acid, the dye being added in several portions during the operation.

These dyes play only a small part in silk-dyeing. The most generally used members of the group are rhodamine, methyl violet, malachite green, Magdala red, and fuchsine.

Application to Cotton.—This is the main sphere of usefulness of the basic dyes. They dye cotton direct, producing very handsome, light shades, which, however, cannot be utilised in practice, owing to their fugitive character. Only in the case of several soluble indulines, such as indamine, methylene grey, etc., can somewhat more stable dyeings be produced by the aid of alum, provided a medium temperature be not exceeded.

It must not, however, be forgotten that a variety of dyeings can be produced with basic dyes on cotton that is to be spun into half-wool vicuna yarns, by the aid of alum and medium temperatures. The fastness of the dye is improved by entering the cotton first in a hot soap bath, then in a cold bath of stannous chloride, and finally in the dye-bath. In some cases the cotton is first steeped for a short time in a solution of basic alum, then treated in a chalk bath, followed by a weak tannin bath, and finally by the dye-bath proper. In this manner, methylene blue, for example, will furnish purer blue dyeings than when fixed with tannin and antimony.

The only rational method of dyeing cotton with basic dye-stuffs consists in first preparing the material with tannin or a fatty acid salt of alumina, and then dyeing by gradually heating the bath to about 60° C. during half an hour or an hour. Some dyers prefer to dye without heat, since brighter colours are then obtained; these however, are not so well fixed as those furnished by the hot process, and consequently the method is only advisable for light and medium shades. In a few instances, *e.g.* indoine blue and several fast blues, the dye-bath must be heated to boiling.

Dyeings performed on cotton prepared with tannin are faster, but less handsome, than those obtained with the aid of fatty acids. A remarkable example of this is afforded by the rhodamines, a dull lilac being produced by tannin, whereas fatty acids give a handsome rose-red.

As already mentioned in the case of wool, hard water should be corrected before use for dyeing basic dyes; and here also an addition of acetic acid is essential when light shades or badly equalising dyes are in question. Some of the latter, *e.g.* those used to imitate indigo dyeings, viz. induline, indoine blue, etc., must receive an addition of alum, since otherwise uniform dyeing will be a result difficult of attainment.

In many instances the goods dyed with basic dyes are put through a supplementary treatment; some colours, *e.g.* fuchsine, are brightened by a treatment with hot alum solution; others are rendered faster by passing the goods through a bath of tannin. Finally, the fastness of the above-mentioned blue dyes is improved by a supplementary treatment with potassium bichromate, this "after-chroming" being effected by treating the goods for some time in a solution of the salt in question (1 per cent. for dark colours) at a temperature of 30–60° C.

Thanks to their great affinity for the fibre, the basic dyes may also be used for shading and topping cottons that have been dyed with dyes belonging to other groups.

3. Application of the Direct or Substantive Cotton Dyes.

To this group belong the benzidine, diamine, and Congo dyes, their principal employment being in the direct dyeing of cotton. Their introduction produced a revolution in the cotton-dyeing industry, the simplicity and cheapness of the process, and the non-necessity for using tannin or mordants, quickly raising these dyes to a position of high importance. However, they are surpassed in brilliance by the basic dyes and in fastness by the adjective dyes; moreover, they are more susceptible than the basic dyes to impurities in the material and to injury during the gassing process—on which account they should be gassed in a plate machine and in a moist condition. Some of the dyes of this class, *e.g.* cloth brown, anthracene red, carbazol yellow, the sulphone dyes, etc., are more suitable for wool-dyeing than for cotton.

The subject of these dyes has been treated in an excellent manner by A. Kertesz, in a book issued by L. Cassells & Co.

Application to Cotton.—The adjuncts used in the dye-bath comprise common salt, Glauber salt, soda, potash, sodium phosphate, and soap. The two first named help to precipitate the dye, and therefore accelerate absorption, whilst the others, being alkaline, exert a solvent action and therefore retard the process.

Here, therefore, just as in the case of dyeing animal fibres with acid dyes, we have the means of controlling the rate of absorption, in accordance with the equalising power and drawing of the dye, and the quality of the material to be dyed. Of the foregoing adjuncts, common salt, Glauber salt, and soap alone are used by themselves, the others being always employed in combination.

Common salt or Glauber salt can be used singly for dyeing any of the members of this group of dye-stuffs, though in practice they are confined to the slow-drawing dyes. In most instances, and in all combination dyeings, an alkaline reagent retarding the absorption of the dye, and a precipitant, are used in conjunction. When it is necessary to reduce the rate of absorption, as is the case with light shades and stuffs that are difficult to dye through, the alkaline reagent alone is added at the outset, the precipitant being added at the end of about half an hour; were it not for this latter, too much of the dye would be left behind in the bath. This method is also recommended for dyeing mixed shades.

Soap is preferably employed for light shades or difficult mixed colours, and it has also the advantage of softening the material in yarn-dyeing. In all other instances, soda is generally preferable to soap as the alkaline adjunct; the latter smears the dye vats.

As a general thing, the yellow dyes are applied in a neutral bath, the blues in a neutral or alkaline bath, and the reds in a strongly alkaline bath. Some dyeings—mainly yellows and some reds—come out brighter when sodium phosphate has been added; and in many red dyeings the same effect follows the use of Turkey-red oil.

The usual adjuncts are employed in the following proportions and with the following dye-stuffs:—

1. Common salt or (calcined) Glauber salt. These are chiefly used for slow-drawing dyes and dark shades, the proportions taken being 10–15 per cent. for light shades, and 20–30 per cent. for dark shades, calculated on the weight of the cotton. In a few cases (Mikado dyes, Nyanza and Tabora blacks, etc.) as much as 50–100 per cent. is taken. This adjunct is suitable for the Mikado and Hessian dyes, for primuline, diamine golden yellow, Titan rose-red, diamine green, various cotton browns, benzo grey, etc. For the most part, purity is not an essential feature in these salts, ordinary

Glauber salt and rock salt being quite suitable for the purpose, except in the production of delicate light colours, for which crystallised Glauber salt or ordinary common salt should be used.

2. Soda and Glauber salt. For dark shades, 5 per cent. of soda and 15 per cent. of Glauber salt are taken, the quantities being halved in the case of light shades.

This method is applicable to nearly all these dyes, especially for most of the diamines, Chicago and Zambesi blues, many mixed shades, etc.

3. Soap (2–5 per cent.) and Glauber salt (2–15 per cent.), the proportions varying according to the depth of the colour, are used for light shades, difficult mixtures, and materials that are hard to dye. This adjunct is specially recommended for geranine and for chloramine yellow.

4. A mixture of 5 per cent. of potash and 2 per cent. of soap is frequently used for dark shades of the various red dyes of this group—Congo, benzopurpurine, etc.,—as also for several blues, *e.g.* benzo-black blue. The highly important benzopurpurines, however, give fuller shades with sodium phosphate and soap, and brighter colours with sodium silicate and soap.

5. With 10 per cent. of sodium phosphate and 2 per cent. of soap (for dark shades) advantageous results can be secured in dyeing many yellow shades, such as chrysamine, chrysophenine, thioflavine S., thiazol yellow, Congo and toluylene orange, as well as others such as benzazurine, Congo-corinth, and many mixed shades.

When a number of substantive cotton dyes are used together for the production of mixtures, it is advisable to select such as are of similar behaviour. The adjuncts used will then depend on the properties of the predominating components of the mixture; and in these cases soda and Glauber salt, or soap and sodium phosphate, will be used almost exclusively.

The chief point to be considered in the selection of the adjuncts is the drawing property of the dye; and the influence of the adjunct on the shade of the colour must not be overlooked. Thus, for example, diamine green is dulled by alkalis, and must therefore be dyed in a neutral, or, at most, faintly alkaline bath.

As regards the temperature to be maintained in dyeing with this group, the following observations apply:—For light shades the goods are entered at 30–40° C., and the bath gradually heated to 50–60°, he dyeing process occupying about half to three-quarters of an hour.

For medium and dark shades the initial temperature is 50–60° C., the bath being then slowly raised to boiling-point and kept thereat for about an hour. For deep shades, however, it is generally preferable to boil for only half an hour at first, then shut off the steam and continue to dye in the slowly cooling bath.

The quantity of bath water plays an important part in the dyeing with substantive cotton dyes. Most of them draw badly, and consequently it is necessary to work with a minimum of water when dyeing dark shades. The maximum quantity of water is 20–25 times the weight of the cotton; for dyeing piece goods in the jigger (*q.v.*) a 5–6-fold quantity of water will be sufficient.

In any event, a portion of the dye will remain behind in the bath; consequently the baths from the dyeing of dark shades should be preserved. When using these over again, a correspondingly smaller quantity of dye is added, together with only one-third to one-half the original amount of the adjunct used. In using up an old bath previously employed for the production of a mixture, and therefore containing a number of dye-stuffs, it must not be forgotten that, in consequence of the varying drawing power of the constituent dyes, their proportion will be different from what it was at the outset. Hence, in order to ascertain what proportions of fresh dyes should be added, it will be necessary to make a trial dyeing with the bath as it is, the appearance of the resulting colour giving the requisite information.

The bath is prepared by adding to the water an amount of soda proportionate to the lime content, then boiling up the water with the dissolved dye-stuff, and afterwards running in the necessary quantity of the adjunct required.

After dyeing, the goods are washed, except in the case of light shades produced in a neutral bath. This washing must be performed with particular thoroughness in the case of the blues dyed in strongly alkaline baths, since otherwise the colours will be too dull. The goods must be dried at a moderate temperature, and in a plentiful supply of air; otherwise (especially in the case of benzazurine, congocorinth, etc.) irregularities may appear.

Reds are frequently livened up by means of Turkey-red oil, the goods being passed through an emulsion of the oil, and afterwards centrifugalised and dried.

Dyes diazotised and developed on the Fibre; so-called Ingrain Dyes.—The cotton is first dyed with a substantive dye containing a free amido group, capable of diazotisation, the absorbed dye being then diazotised by treatment in a bath containing sodium nitrite, and finally treated in a developing bath, a phenol, or an amine, to convert the dye into a complex azo compound.

This method was first applied to primuline, and subsequently extended to diamine black, diazo black, etc., and at the present time plays a very important practical rôle.

The dyeings produced in this manner are deeper and faster to washing, many of them also faster to light, than those produced in the first bath without any further treatment. In addition, the diazotisation and development of the colour are accompanied by an entire modification of tone,—primuline, for instance, when dyed direct with common salt, giving a yellow, which, though pure, is too unstable to be of any practical value; whereas when diazotised and developed with β-napthol, it furnishes a red; with ethyl-β-naphthylamine (Bordeaux developer), a Bordeaux: both distinguished for washing fastness, and far superior to primuline yellow in point of fastness to light. The different diamine blacks furnish a grey and a blue, which are also used *per se*. To produce darker shades of greater washing fastness, the dyes are mostly diazotised—with phenylenediamine, or toluylenediamine, for black; with β-naphthol for dark blue, and with naphthylamine ether for lighter and more brilliant blue. Diazo brilliant black gives a Bordeaux shade, which is converted, by diazotisation, into greyish blue, with β-naphthol, and into brown with phenylenediamine.

A modification of this method consists in developing the diazotised dye with soda, thus producing, not a complex diazo dye, but probably merely replacing the diazotised amido group by hydroxyl. This method chiefly serves for the production of bright browns with the assistance of diamine-catechu, diazo brilliant black, etc., these dyeings being intended to replace catechu.

The processes of diazotisation and development on the fibre are therefore mainly employed for the production of dark blues, browns, and blacks, also for red and Bordeaux (with primuline).

The *modus operandi* is as follows:—The cotton is first dyed with the requisite dye-stuff, then well washed and drained, and afterwards entered in the diazotising bath. This contains $2\frac{1}{2}$ per cent. of sodium nitrite and $7\frac{1}{2}$ per cent. of 20° B. hydrochloric acid, for dark shades, or $1\frac{1}{2}$ per cent. of sodium nitrite and 5 per cent. of 20° B. HCl for light shades, and is prepared by stirring the dissolved nitrite, and afterwards the (diluted) hydrochloric acid, slowly into a sufficient quantity of water—which depends on the weight of cotton to be treated—in a wooden vat. In this bath the cotton is treated for a short time, *e.g.* five minutes for primuline, or fifteen minutes for diamine black,[1] after which it is rinsed in acidified water (1 vol. of hydrochloric acid per 500 vols. of water) and immediately

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[1] Only in exceptional cases is the diazotising process incomplete at the end of this time, *e.g.* diazo blue (By.), which takes about three-quarters of an hour.

entered in the developing bath. After the diazotising bath the dye is contained in the fibre in the state of a readily decomposible diazo compound, and consequently the cotton must not be left to stand in this condition.

The developing bath contains a solution of some suitable developer, the most important of which have already been mentioned above. The bath must be cold, and the cotton treated therein (a few minutes to a quarter of an hour) until the colour ceases to become darker. Finally, the goods are washed, though in some cases a good soaping is needed to fully develop the colour.

Both the diazotising and developing baths must be brought up to the original strength before being used over again.

When soda is used as the developer, the goods are diazotised as usual, and then entered, without being washed, in a warm bath (40–50° C.) containing three parts, by weight, of calcined soda per thousand, where they are worked for a quarter of an hour, after which they are soaped or washed.

The process of diazotising and developing on the fibre is also adopted in the production of mixed colours, either by the combination of two or more diazotisable dyes, or by the combination of diazotisable dyes with other kinds of dyes that are not affected by the diazotising process; or, finally, by mixing different developers.

Topping Developed and Undeveloped Dyes with Basic Dyes.—The colours furnished by the substantive cotton dyes are inferior in beauty to those obtainable with basic dyes; neither are they so easy to dye exactly to pattern. For this reason they are frequently topped with basic dyes in small proportion, by treating the dyed and washed goods in a bath containing 1–2 per cent. of alum or acetic acid, together with the necessary amount of dye, at the ordinary temperature. The statement, often found in the literature of the subject, to the effect that the fixation of the basic dyes is a special faculty of the substantive cotton dyes, is erroneous, since all dyeings on cotton—indigo blue, alizarine colours, manganese bistre, etc.—possess the property of absorbing basic dyes or their colour bases.

Fixing Substantive Cotton Dyes by Subsequent Treatment with Metallic Salts.—In many instances the fastness to washing or light (or both) of substantive cotton dyes may be improved by immersing the dyed goods in hot solutions of metallic salts. Unfortunately, however, this treatment is accompanied by a change of shade, which renders the process unsuitable for general employment. It is advantageously used for blues intended to replace indigo, among which special mention may be made of Cassella's diamine blue RW, which when "coppered" (treated with copper sulphate) approximates very closely to indigo blue.

The method itself was first applied to Bayer & Co.'s benzazurine, which gives greenish shades very fast to light.

The salts employed in this treatment are—copper sulphate, chromium fluoride, and potassium bichromate, the first named in particular, the mode of application being as follows:—The dyed cotton is worked about for a quarter to half an hour in a bath containing 3–5 per cent. of copper sulphate (according to the depth of the colour) and kept at a temperature of about 80° C. When piece goods are in question, the bath contains 1½–3 parts of copper sulphate per 1000.

Application to Wool.—Of late this application of the substantive dyes has begun to receive the attention it deserves.

Mention should first be made of those dyes which, although belonging to the cotton dyes, are yet more suitable for dyeing wool; these include sulphonazurine, brilliant sulphonazurine, sulphonecyanine, fast diamine red, anthracene red, carbazol yellow, cloth brown, etc. They may all be dyed with 10 per cent. of Glauber salt—the acid-resisting fast diamine red also with bisulphate—and, except the two first named, all may be fixed with chrome mordants, thus yielding faster colours. This is done either by mordanting in advance, or, in the case of the reds, by after treatment with chromium fluoride. (*See* Mordant Dyes.)

The sulphone dyes (Bayer) must not be dyed at boiling-heat, neither is the customary addition of Glauber salt suitable in this case. According to the instructions given by the Elberfeld Farbenfabriken, these dyes must be used with an addition of ammonium acetate, though inequalities readily occur when this salt is used. In such event the following procedure should be adopted:—The goods are entered for some little time—about a quarter of an hour—in the dye-bath containing a small percentage (5 per cent. for light shades) of soap, after which about 2 per cent. of acetic acid is added by degrees, to facilitate the absorption of the dye, and boiling is then practised for twenty to thirty minutes. In this manner and by combining sulphonecyanine, sulphone brown, and chrysophenine, for example, perfectly uniform drab shades can be readily obtained, which are far superior in point of fastness to the corresponding colours furnished by acid dyes.

As regards the true cotton dyes, some of these exhibit, in wool-dyeing, properties which seem to render them more suitable, for many purposes, than the acid dyes. They are dyed at boiling-heat, with an addition of 10–20 per cent. of Glauber salt—according to the depth of shade required,—and, should more complete extraction be desired, 2–3 per cent. of acetic acid can be added as well. Moreover, in contrast to the case of cotton, these dyes draw very well for the most part when applied to wool. For some of them—the reds mainly—better results are obtained with acetic acid, whilst bisulphate is preferable for others, such as diamine scarlet, diamine blue, etc. The most suitable adjunct, however, for many of these dyes is 10 per cent. of common salt and ½ per cent. of potash—soda is altogether unsuitable here,—better extraction being obtained by this means.

As in the case of cotton, these dyes can be put through an after treatment with metallic salts.

The red and yellow substantive dyes are the best adapted for wool, the browns and violets least of all. Their superiority over the acid dyes is expressed in their greater power of withstanding milling and sulphuring. Thus, for instance, none of the many ponceau reds is suitable for dyeing loose wool and yarns for producing parti-coloured fabrics, which will have to be milled or require sulphuring in the piece, in order to clean any white that may be present. More on this point will be given in Section IV.

Finally, it may be remarked that the substantive dyes also play an important part in the dyeing of half-wool fabrics (*q.v.*).

The Application of the Substantive Dyes to Silk is exceedingly restricted, only a few—chrysamine, chrysophenine, Mikado yellow, etc.—being used, and that by reason of their fastness. The dye-bath for these is a bast soap bath qualified by the addition of acetic acid, and the brightening process is carried on in the usual manner. The dyes may be diazotised as in the case of cotton, and developed or treated with metallic salts. The substantive dyes are also of considerable importance in the dyeing of half-silk goods.

Supplementary Remarks.—In addition to the substantive dyes and several basic dyes, there are also a few others possessing the property of dyeing cotton direct. These are—rhodamine S, cachou de Laval, canarine, a few natural dye-stuffs like curcuma, safflower, and Orleans, though none but the two first are now in use for this purpose.

Rhodamine S is dyed at about 40° C. in presence of a small percentage of acetic acid, and furnishes a handsome rose-red.

Cachou de Laval is dyed for about half an hour at first, without any adjuncts, after which time 6 per cent. of soda is added—to soft water, or correspondingly more to hard water—and the operation continued for half an hour longer at about 70° C. By reason of their cheapness and fastness these dyes are still frequently used for bottoming dark colours; they may be shaded by a treatment with metallic salts, iron, chromium, or copper.

4. Application of the Mordant Dyes.

To this class belong a large number of very differently constituted dyes, all of which possess an acid character, and are indebted to the presence of hydroxyl or carboxyl groups for their capacity of forming lakes with mordants.

Their pigmentary character differs considerably in degree. Some of them, formerly entitled "adjective dyes" are such weak pigments that they are incapable of furnishing utilisable colours when used alone, and require to be combined with mordants, with which substances they produce strongly coloured insoluble compounds known as "lakes." To these belong alizarine and the dye-woods. Others, again, are themselves highly coloured, notwithstanding which they cannot be used for dyeing unless in conjunction with mordants; this section includes galleine and many alizarine dyes. Finally, there are a number of acid dyes and substantive dyes than can either be used alone or fixed on the fibre by means of mordants, this sub-group comprising anthracene yellow, carbazol yellow, fast diamine red, brilliant alizarinecyanine 3 G, chromotrope, etc.

It is, however, impossible to draw any strict line of demarcation between these dyes, their divergences being gradual and not fundamental. Only in the case of the first-named adjective dyes is it perhaps feasible to constitute a separate group; and even here there are individual dyes, *e.g.* santal wood, that possess intermediate properties.

One characteristic possessed by all these dyes in common is that of fastness to milling.

In dyeing with mordant dyes, the nature of the bath water plays an important part, and therefore the water used must have been corrected with acetic acid, otherwise a partial precipitation of the colour, in the form of lime and magnesia lakes, may occur. In some cases organic impurities have an unfavourable effect, *e.g.* in presence of cochineal or alizarine blue.

Application to Wool.—This is the most important use of mordant dyes, and, in fact, most of them are suitable for this purpose alone.

The methods of fixing that may be employed in this case are varied, and for convenience of treatment will be described in groups.

1. **Dyeing previously mordanted Wool.**—This is an import-

ant process in wool-dyeing, and is applicable to all the mordant dyes. The temperature, duration of boiling, and the addition of acetic acid to the bath, all depend on the nature of the dye; and, from this point of view, the mordant dyes may be divided into three classes:—

(*a*) *Alizarine Dyes.*—These require the greatest care in dyeing, and are, for the most part, very susceptible to the influence of impurities in the goods to be dyed. The *modus operandi* is as follows:—The mordanted wool is first treated for a quarter of an hour in a cold bath of dye; the temperature is then gradually raised to boiling, in about an hour, and maintained in this condition for one and a half to two and a half hours, the goods being well worked. Should the initial temperature be unduly high, or the heating proceed too rapidly, unequal dyeing may easily result. Only in the case of loose wool is less care necessary, the initial temperature in that case being up to 40° C. The prolonged boiling is necessary to ensure the proper fixing of the dye.

A neutral bath is the most favourable for some of the alizarine dyes: alizarine red, alizarine orange, anthracene brown, and galleine, that come on the market in paste form. In other instances, especially for the powdered alizarine red, alizarine brown, and galleine, which are sodium salts of dye-stuff sulpho-acids, the liberation of the dye acid entails the addition of an excess of acetic acid (750 c.c. of 8° B. acetic acid per kilo—0·082 gal. per lb.—of dye, when the water has been previously corrected). The different marks of alizarine blue, cœruleine, alizarine yellow, etc., require in addition about 2 per cent. of 8° B. acetic acid to facilitate extraction, this addition being made by degrees at intervals during the process.

In mixed shades of different alizarine dyes it will always be possible, by exercising a little care, to work in a weak acetic acid bath, the acid being added gradually and not until the bulk of the dye has been absorbed.

Delicate light colours and materials that are difficult to dye through, such as felt hat bodies, are preferably dyed in a slightly ammoniacal bath at the start; and after boiling has proceeded for some time, the acetic acid is added until the reaction becomes slightly acid.

To shade dyeings made with alizarine dyes, the bath is neutralised with ammonia, the shading dye is added, and after a short time the acetic acid is run in by degrees.

(*b*) *Dye-Woods.*—These are easier to manipulate than the alizarines.

The mordanted wool may be entered at 50°–60° C, and the period of boiling may be shorter, an hour and a half being sufficient for dark colours. A neutral bath is employed.

(*c*) *All other mordant dyes* can be dyed by entering the mordanted wool at 40° C., gradually raising the temperature to 100°. and boiling for an hour to an hour and a quarter—longer boiling being only required in the case of chrome blue and chrome violet, for example, in order to complete the formation of the lake. They are all applied in a weak acetic acid bath, the amount of acid (1 to 1¼ per cent. of 8° B. acetic acid) depending on how the dye draws. In some instances, *e.g.* cloth red, or goods that are difficult to dye, a little sodium acetate is added at first, followed by acetic acid.

Dyeings that have a tendency to dust off, *e.g.* logwood black, are often returned to the mordanting bath for a short time, after dyeing, to improve the fixation of the dye. This treatment occasionally induces a slight modification of the shade, alizarine cyanine, for instance, becoming a little bluer and darker.

2. Dyeing in a Single Bath.—This method has the advantage over the previous one of being quicker, simpler, and therefore cheaper, since the mordanting and dyeing are here combined into one operation. Herein, however, resides the drawback of the process, inasmuch as the formation of the lake in the bath results in a loss of both mordant and dye, and in most cases the dyeings are not so full or so well fixed as in the first method. There are three variants of this process:—

(*a*) *Dyeing in a Single Bath containing both the Dye and the Metallic Salts used as Mordants.*—In this case, therefore, the formation of the lake proceeds in the bath itself, and for this reason an acid substance (oxalic acid or potassium bitartrate) must be added, in order that the colour lake may be presented in a soluble form to the fibre. At the same time it is thus evident that this method, which gives the brightest of all the mordanted dyeings, can only be employed when the colour lake is correspondingly soluble. Its chief uses are in the production of cochineal scarlet, dyeing with yellow dye-woods (especially quercitron), and in a few logwood dyeings which will be dealt with more fully later on.

Latterly, also, this method has been applied to dyeing light shades with alizarine dye-stuffs. The dye-bath is charged with 3 per cent. of alum, or an equal quantity of chrome alum, 2 per cent. of oxalic acid, and the requisite quantity of dye, the wetted goods being entered at 30° C.; the temperature is then gradually raised to 100° C., and is maintained thereat for an hour. Similar alizarine single-bath dyeings can be performed with the assistance of tin or iron mordants, some alizarines even giving dark shades on materials that equalise well, *e.g.* a dark red, with alizarine S, alum, and Glauber salt. The only single-bath alizarine dyeings of any practical importance, however, are those produced by the aid of chromium fluoride. The bath is charged with the dye and 3 per cent. of chromium fluoride, the damped goods are entered cold, then slowly raised to boiling and maintained there for an hour or an hour and a half. A number of pale blue, grey, and drab shades are produced on worsteds by this means, with or without vat bottoming.

(*b*) *The Deepening Method.*—This is used in the production of a number of drabs and blues by the aid of fustic, santal, madder, logwood, and sumach. The red dye used in the case of light shades is madder, the more powerful pigment, santal-wood, being employed for dark shades.

Used alone, without mordants, the above dye-stuffs furnish only light shades; light drab, for example, being obtained by the help of fustic, madder, sumach, and potassium bitartrate. The addition of logwood furnishes greyer tints.

In most cases, however, these dyeings must be darkened by the aid of mordants. Thus, for example, the goods are first dyed with fustic, madder, sumach, and logwood; the dye-bath is then cooled down by an addition of cold water, a little ferrous sulphate is added, and the whole is boiled up again for an hour.

Dark browns are produced by this method in the following manner:—The goods are first boiled for about an hour in a bath containing fustic, santal, logwood, and sumach; then cooled as above, treated with copper sulphate, boiled for another hour,—and when required to be still darker, cooled again as before, treated with ferrous sulphate, and boiled one hour longer.

It is impossible to give further details, the procedure depending entirely on the shade and depth of colour. For dark browns in general, 3 per cent. of copper sulphate and 1–10 per cent. of ferrous sulphate are employed; occasionally, for light shades, only a few hundredths to tenths of 1 per cent. of ferrous sulphate are taken, the copper sulphate being omitted altogether. Iron gives darker, copper brighter, shades.

(*c*) *After-Chroming; Developing with Mordants.*—Many acid dyes and substantive dyes, such as chromotrope, Victoria violet 4 BS and 8 BS, patent blue, cloth red, milling blue (Kalle & Co.), flavazol (Berliner Actiengesellschaft), anthracene yellow, anthracite black, fast diamine red, anthracene red, etc., can be improved in point of fastness to milling by a hot after-treatment with mordants. This treatment has been styled "after-chroming," because only chrome mordants, *i.e.* chromium fluoride or potassium bichromate, are used.

It has been discovered (at the Hoechst Farbwerke) that acid alizarine dyes also can be applied by this method, both with alum as well as with the aforesaid chrome mordants.

In the case of acid dyes the advantages of this method are, that the fastness of the dyes, particularly with regard to milling, is greatly improved, better equalisation and more thorough permeation of the material being also ensured.

The after-treatment with chrome mordants renders the colours somewhat darker, but otherwise their appearance undergoes little alteration as a rule. In the case of Victoria violet, purer blues are obtained; but with the chromotropes, to which this method was first applied, a complete change of colour ensues, the red shades produced in an acid bath being converted by this treatment into dark blue to black.

The chemical reaction proceeding in the after-chroming treatment consists chiefly in the formation of a chrome lake of the corresponding dye; in a few instances, especially with several chromotropes (F.B., S.), chrome brown and chromogene I. (M.L.Br.) the reaction is one of oxidation, and consequently potassium bichromate is the only means that can be employed for after-chroming these dyes; in other instances the operation is performed partly with chromium fluoride and partly with bichromate. Some dyes, like the aforesaid Victoria violet, are decomposed by bichromate, and must therefore be treated with chromium fluoride. For all others, preference is given to whichever of these two chrome mordants furnishes the best results, chromium fluoride being most frequently selected, since it also renders the wool less harsh than the bichromate.

For the acid dyes the following method is employed:—The goods are dyed first in an acid bath as usual, after which chromium fluoride is added—in the proportion of 3–4 per cent. for dark shades, or less for light shades—and the bath is boiled for half an hour to an hour longer. When bichromate is used the bath must be first cooled down by adding cold water, and in this case also an addition of a little oxalic acid towards the end of the operation is usually beneficial.

Shading can be effected in the same bath, either before or after chroming, dyes of good equalising power being preferably used. When bichromate has been employed, the shading dyes selected must be such as are able to resist the action of this reagent, *e.g.* patent blue, many acid violets, azoflavine, orange IV, fast acid violet A2R, etc. Darkening with dye-woods, *e.g.* logwood, must be performed in a separate bath.

For the acid alizarine dyes and several other mordant dyes, the after-chroming treatment has the additional advantage that difficult materials are more thoroughly penetrated by the dye, and better equalisation is secured.

The goods are first dyed in an acid bath, to which the chrome mordant is then added. Here the actual colour is developed by the addition of the mordant, on which account the method has been termed "developing with mordants." The bath is charged with 4–6 per cent. of sulphuric acid—it should be noted that many alizarine dyes draw badly when much sulphuric acid is used,—10–50 per cent. of Glauber salt, and the requisite quantity of dye. As can be seen, the proportion of Glauber salt fluctuates only within remarkably narrow limits, the amount depending entirely on the material to be dyed, and being larger in proportion as the material is more difficult to dye through and uniformly.

For easily penetrable yarns 10 per cent. is taken; for heavy close goods, 20 per cent. and over. Nevertheless, the above limit of 50 per cent. is rarely exceeded in practice. The previously damped goods are entered at 50° C., or even hotter in the case of easily dyed goods, and boiled for an hour and a half, then cooled down to 50–60° C. by cold water, and, after the addition of the chromium fluoride or bichromate, boiled again for an hour to an hour and a half. The quantity of chromium fluoride taken varies from 2 to 6 per cent., and depends on the dye-stuff used; in most instances 3 to 4 per cent. will be sufficient. Bichromate is used in the proportion of 1 to 3 per cent.

Though alum and other mordants can be used for developing, only the above-mentioned chrome mordants are used in practice. With regard to the choice between the two, the observations already made in dealing with the after-chroming of acid dyes also apply here.

Finally, it should be mentioned that, according to the recipes of the manufacturers of dye-stuffs, these dyeings can also be performed in two baths. The goods are dyed in the first acid bath as already described, and, after development, are finished in a second bath by boiling with bichromate (about 1 per cent.) and sulphuric acid, or with chromium fluoride alone, or this latter in conjunction with about 1 per cent. of oxalic acid. This method has the advantage over the single-bath process that the two baths can be used over again.

Other mordant dyes for which the method of developing with mordants is of practical importance are—alizarine black, WR (B. A. S. F.) and diamine black (F. Bayer & Co.). For the first of these the method has the advantage of cheapness, whilst by this means the usual difficulty encountered with regard to the equalising of diamine black on mordanted wool is entirely obviated.

Both are dyed in a bath containing acetic acid—first with ammonium acetate and then with acetic acid, in the case of piece goods difficult to dye through, and afterwards developed in the same bath with 1 to 1½ per cent. of bichromate.

In the case of diamine black, when the goods are not difficult to dye through, Glauber salt is added, together with a little sulphuric acid to ensure more complete extraction; after adding the bichromate the goods are boiled for three-quarters of an hour, or an hour in the case of alizarine black.

Special interest attaches to dyeing with cochineal and a few of the logwood dyeings, which will therefore now be dealt with in detail.

Dyeing with Cochineal.

Cochineal furnishes a red with tin mordants, and an amethyst (bluish red) with aluminium mordants. The first of these, cochineal scarlet, is one of the oldest, handsomest, and best colours known, and formerly played a very important part in wool-dyeing. Even at the present time the cochineal scarlet shade is highly esteemed, though nowadays it is produced by the aid of various ponceau reds. Nevertheless, when a fast scarlet is required, as is most frequently the case with smooth cloths, it must still be produced by means of cochineal. Frequently the colour is bottomed with cochineal and topped with ponceau, a dyeing of this kind being termed "semi-fast scarlet," whilst the cheaper colour obtained with ponceau alone is called "fugitive scarlet," though the actual difference in fastness between the cochineal and ponceau scarlets is confined to their behaviour during washing and milling, the latter bleeding whereas the former are fast. Cochineal scarlet, however, will not stand treatment with soap or alkalis without undergoing a change of shade and turning a bluish tinge, whilst ponceau scarlet remains free from appreciable alteration. In point of fastness to light the best ponceaus are little inferior to cochineal.

There are two ways of testing the fastness of scarlet—by sulphuric acid and by stannous chloride solution. When touched with the former reagent, a cochineal dyeing gives a pure yellow stain, but in the case of ponceaus the colour is more or less brownish. When treated with a solution of stannous chloride of a certain strength—which can be determined by a few tests with the two colours—and heated, the ponceau dyeings are bleached entirely, whilst the cochineal dyeings are less affected. Semi-fast scarlet can also be easily detected by this means.

For the most part, cochineal scarlet is produced with cochineal and lac dye, the resulting colour being somewhat less sensitive to the action of alkalis. In point of fastness to light these two dyes are about on a par; the handsomest shade, however, is that obtained from cochineal alone.

Cochineal requires no preliminary treatment to fit it for use, whereas lac dye must first be mixed into a paste with water, left to stand for several weeks, incorporated with a solution of stannous chloride, and again left for some time, since fresh lac dye will not give a handsome colour, the beauty of the dyeing increasing with the duration of the preparatory treatment. The method of dyeing is the same whether the cochineal is used alone or in conjunction with lac dye; consequently, for the sake of brevity, cochineal alone will be mentioned in describing the process.

Before entering on this description it should be stated that cochineal scarlet may be of various shades—full or thin, and more or less tinged with blue or yellow, as desired. It may be produced by mordanting and subsequent dyeing, or in a single bath. The latter method gives a more handsome red, of yellowish cast, whilst the other method furnishes more intense bluish red, and the material is dyed through better. Occasionally the two processes are combined, either by adding part of the dye to the mordant bath, or *vice versâ*.

The mordants used are stannous chloride ("tin salt") with oxalic acid, or "acid for scarlet" with potassium bitartrate. By taking a small quantity of tin salt, a dull red, of bluish cast, is obtained, whilst an excess of tin salt or bitartrate gives a yellower scarlet, the latter salt furnishing a handsomer shade than is obtainable with oxalic acid. Scarlet produced with tin salt and oxalic acid is less sensitive to alkalis than that furnished by the other mordant mixture, though, on the other hand, the latter colour undergoes less alteration when heated.

In any case, pure soft water must be used for dyeing scarlet, and the operation must not be too protracted, the colour being rendered muddy by prolonged boiling. It is impossible to obtain a pure scarlet in a copper pan, and tin vessels must therefore be used. Strangely enough, the colour obtained by dyeing in wooden vessels, where there is no metal to cause muddiness, is less handsome than that produced in tin vessels.

The dye should, as far as possible, lie on the surface of the cloth, since under these circumstances the underlying white throws up the colour more brightly. The white section of the dyed goods is a characteristic indication of fast scarlet, the goods being always dyed further through when ponceau has been used.

The best method of procedure to adopt for obtaining a handsome scarlet is as follows:—The bath is prepared in a tin vessel, and contains only a part of the necessary cochineal and acid for scarlet, together with (purified, semi-crystal) bitartrate. The goods are entered very hot, so as to deposit as much as possible of the scarlet on the surface, the temperature being then raised to boiling, and the rest of the scarlet acid and cochineal added after awhile. The whole operation should not take longer than an hour and a quarter. About 15 per cent. of cochineal is required; but the amount of the mordant cannot be definitely given, owing to its very variable concentration.

In the second method, 3 per cent. of tin salt and an equal quantity of oxalic acid are used.

After dyeing, the goods are rinsed with water, slightly acidified with sulphuric acid to prevent the scarlet being tinged blue by the action of the bicarbonate in the water. The baths are not fully exhausted, and can be used over again with advantage.

By topping the scarlet with rhodamine a very vivid appearance is imparted to the colour. For producing a yellow tinge flavine is generally used, this being added to the cochineal in the dye-bath. Buckthorn berries, and occasionally fustet wood, are also taken for this purpose.

Scarlet occasionally exhibits a number of small black specks, so-called "tin stains" (tin sulphide?), in which event the goods must be steeped in a solution of oxalic acid.

Finally, it may be mentioned that very pale scarlets are also produced for pink shades.

To obtain amethyst shades with cochineal, alum is used, with or without tin mordant. In this case the single bath method is inapplicable on account of the considerable precipitate that would form in the bath owing to the low solubility of the alumina lake. Moreover, lac dye is unsuitable, this dye giving ugly brown shades with alumina mordants. The goods are mordanted with alum, bitartrate, and scarlet acid, and dyed in a fresh bath containing a little bitartrate and scarlet acid in addition to the cochineal. It is advisable to add a portion (about 1 per cent.) of the dye to the mordanting bath in order to ensure the goods being dyed through better.

Cochineal dyeings are often darkened by topping with archil; madder or alizarine being also employed for brownish red tones.

Occasionally the so-called "scouring" process is employed for blueing cochineal dyeings, the dyed goods being treated in a lukewarm bath to which ammonia is added by degrees. The operation must proceed slowly, and the goods must always be somewhat