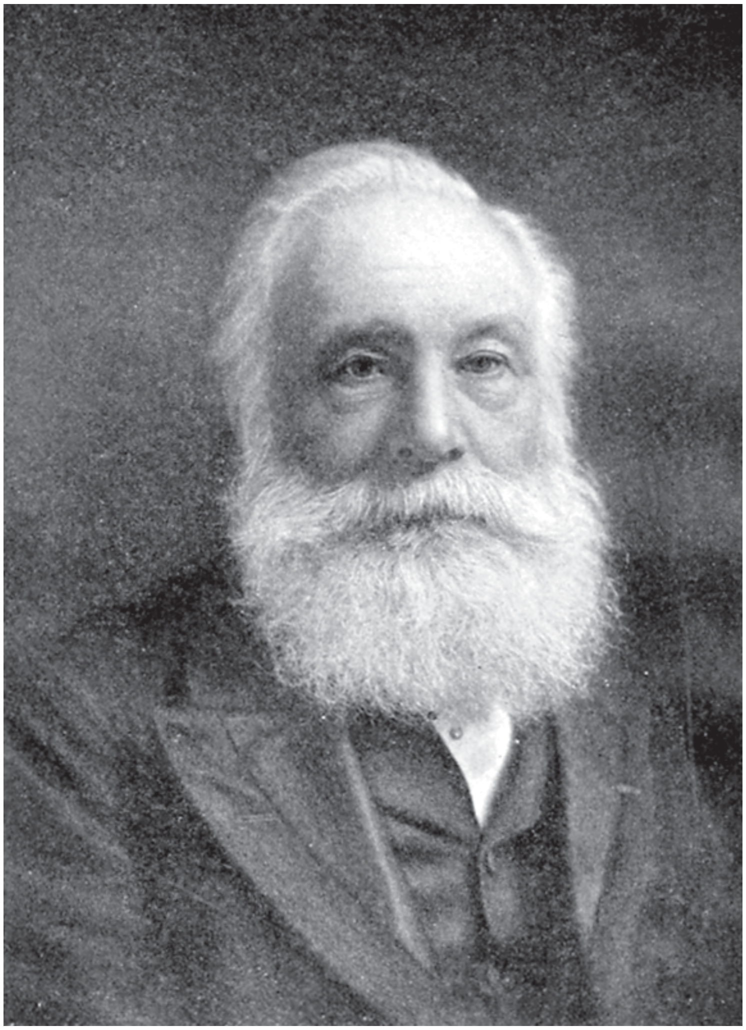


SIR WILLIAM HENRY PERKIN
Discoverer of Mauve, the First Coal Tar Coloring Matter

Cyclopedia
of
Textile Work

A General Reference Library

ON COTTON, WOOLEN AND WORSTED YARN MANUFACTURE, WEAVING, DESIGNING, CHEMISTRY AND DYEING, FINISHING, KNITTING, AND ALLIED SUBJECTS.

Prepared by a Corps of

TEXTILE EXPERTS AND LEADING MANUFACTURERS

Illustrated with over Two Thousand Engravings

SEVEN VOLUMES

CHICAGO
AMERICAN TECHNICAL SOCIETY
1913

Authors and Collaborators

FENWICK UMPLEBY

Head of Department of Textile Design, Lowell Textile School.

◆

LOUIS A. OLNEY, A. C.

Head of Department of Textile Chemistry and Dyeing, Lowell Textile School.

◆

M. A. METCALF

Managing Editor, "The Textile American."

◆

H. WILLIAM NELSON

Head of Department of Weaving, Lowell Textile School.

◆

JOHN F. TIMMERMANN

Textile Expert and Writer.
Formerly with Central Woolen Co., Stafford Springs, Conn.

◆

WILLIAM R. MEADOWS, A. B., S. B.

Director, Mississippi Textile School.

◆

MILES COLLINS

Superintendent of Abbott Worsted Co., Forge Village and Graniteville, Mass.

◆

CHARLES C. HEDRICK

Mechanical Engineer, Lowell Machine Shop.

◆

OTIS L. HUMPHREY

Formerly Head of Department of Cotton Yarn Manufacturing, Lowell Textile School.

C. E. FOSTER

Assistant Superintendent, Bigelow Carpet Co., Clinton, Mass.

Authors and Collaborators—Continued

WILLIAM G. NICHOLS

General Manufacturing Agent for the China Mfg. Co., the Webster Mfg. Co., and the Pembroke Mills.
Formerly Secretary and Treasurer, Springstein Mills, Chester, S. C.
Author of "Cost Finding in Cotton Mills."

◆

B. MOORE PARKER, B. S.

Head of Department of Carding and Spinning, North Carolina College of Agriculture and Mechanic Arts.

◆

I. WALWIN BARR

With Lawrence & Co., New York City.
Formerly Instructor in Textile Design, Lowell Textile School.

◆

EDWARD B. WAITE

Head of Instruction Department, American School of Correspondence.
American Society of Mechanical Engineers.
Western Society of Engineers.

◆

WALTER M. HASTINGS

Assistant Agent, Arlington Mills, Lawrence, Mass.

◆

GEORGE R. METCALFE, M. E.

Head of Technical Publication Department, Westinghouse Elec. & Mfg. Co.
Formerly Technical Editor, Street Railway Review.
Formerly Editor of Text-book Department, American School of Correspondence.

◆

ALFRED S. JOHNSON, Ph. D.

Editor, "The Technical World Magazine."

◆

HARRIS C. TROW, S. B.

Editor of Text-book Department, American School of Correspondence.
American Institute of Electrical Engineers.

◆

CLARENCE HUTTON

Textile Editor, American School of Correspondence.

Authorities Consulted

THE editors have freely consulted the standard technical literature of Europe and America in the preparation of these volumes and desire to express their indebtedness, particularly to the following eminent authorities, whose well known treatises should be in the library of every one connected with textile manufacturing.

Grateful acknowledgment is here made also for the invaluable co-operation of the foremost manufacturers of textile machinery, in making these volumes thoroughly representative of the best and latest practice in the design and construction of textile appliances; also for the valuable drawings and data, suggestions, criticisms, and other courtesies.

WILLIAM G. NICHOLS.

General Manufacturing Agent for the China Mfg. Co., the Webster Mfg. Co., and the Pembroke Mills.
Formerly Secretary and Treasurer, Springstein Mills, Chester, S. C.
Author of "Cost Finding in Cotton Mills."

❧

THOMAS R. ASHENHURST.

Head Master Textile Department, Bradford Technical College.
Author of "Design in Textile Fabrics."

❧

J. MERRITT MATTHEWS, Ph. D.

Head of Chemical and Dyeing Department, Philadelphia Textile School.
Author of "Textile Fibers," etc.

❧

J. J. HUMMEL, F. C. S.

Professor and Director of the Dyeing Department, Yorkshire College, Leeds.
Author of "Dyeing of Textile Fabrics," etc.

❧

WILLIAM J. HANNAN.

Lecturer on Cotton Spinning at the Chorley Science and Art School.
Author of "Textile Fibers of Commerce."

❧

ROBERTS BEAUMONT, M. E., M. S. A.

Head of Textile Department, City and Guilds of London Institute.
Author of "Color in Woven Design," "Woolen and Worsted Manufacture."

❧

JOHN LISTER.

Author of "The Manufacturing Processes of Woolen and Worsted."

Authorities Consulted—Continued

W. S. BRIGHT McLAREN, M. A.

Author of "Spinning Woolen and Worsted."

CHARLES VICKERMAN.

Author of "Woolen Spinning," "The Woolen Thread," "Notes on Carding," etc.

WILLIAM SCOTT TAGGART.

Author of "Cotton Spinning."

HOWARD PRIESTMAN.

Author of "Principles of Wool Combing," "Principles of Worsted Spinning," etc.

H. NEVILLE.

Principal of Textile Department, Municipal Technical School, Blackburn.
Author of "The Student's Handbook of Practical Fabric Structure."

FRED BRADBURY.

Head of Textile Department, Municipal Technical Schools, Halifax.
Author of "Calculations in Yarns and Fabrics."

E. A. POSSELT.

Consulting Expert on Textile Manufacturing.
Author of "Technology of Textile Design," "Cotton Manufacturing," etc.

H. A. METZ.

President, H. A. Metz & Co.
Author of "The Year Book for Colorists and Dyers."

T. F. BELL.

Instructor in Linen Manufacturing, etc., City and Guilds of London Institute.
Author of "Jacquard Weaving and Designing."

M. M. BUCKLEY.

Head of Spinning Department, Halifax Municipal Technical School.
Author of "Cone Drawing," "Worsted Overlookers Handbook," etc.

FRANKLIN BEECH.

Author of "Dyeing of Woolen Fabrics," "Dyeing of Cotton Fabrics," etc.

Authorities Consulted—Continued

WALTER M. GARDNER, F. C. S.

Professor of Chemistry and Dyeing in City of Bradford Technical College.
Author of "Wool Dyeing," etc.

❧

ALBERT AINLEY.

Author of "Woolen and Worsted Loomfixing."

❧

G. F. IVEY.

Author of "Loomfixing and Weaving."

❧

ERNEST WHITWORTH.

Formerly Principal of Designing and Cloth Analysis Department, New Bedford Textile School.
Author of "Practical Cotton Calculations."

❧

DAVID PATERSON, F. R. S. E., F. C. S.

Author of "Color Printing of Carpet Yarn," "Color Mixing," "Color Matching on Textiles," etc.

Introductory Note

THE Cyclopedia of Textile Work is compiled from the most practical and comprehensive instruction papers of the American School of Correspondence. It is intended to furnish instruction to those who cannot take a correspondence course, in the same manner as the American School of Correspondence affords instruction to those who cannot attend a resident textile school.

¶ The instruction papers forming the Cyclopedia have been prepared especially for home study by acknowledged authorities, and represent the most careful study of practical needs and conditions. Although primarily intended for correspondence study they are used as text-books by the Lowell Textile School, the Textile Department of the Clemson Agricultural College, the Textile Department of the North Carolina College of Agriculture and Mechanic Arts, the Mississippi Textile School, and for reference in the leading libraries and mills.

¶ Years of experience in the mill, laboratory and class room have been required in the preparation of the various sections of the Cyclopedia. Each section has been tested by actual use for its practical value to the man who desires to know the latest and best practice from the card room to the finishing department.

¶ Numerous examples for practice are inserted at intervals. These, with the test questions, help the reader to fix in mind the essential points, thus combining the advantages of a textbook with a reference work.

¶ Grateful acknowledgment is due to the corps of authors and collaborators, who have prepared the many sections of this work. The hearty co-operation of these men — manufacturers and educators of wide practical experience and acknowledged ability — has alone made these volumes possible.

¶ The Cyclopedia has been compiled with the idea of making it a work thoroughly technical, yet easily comprehended by the man who has but little time in which to acquaint himself with the fundamental branches of textile manufacturing. If, therefore, it should benefit any of the large number of workers who need, yet lack, technical training, the editors will feel that its mission has been accomplished.

Contents

VOLUME VI.

---

* For Page numbers see foot of pages.

CHEMISTRY AND DYEING.

TEXTILE CHEMISTRY AND DYEING.

1. One needs but a limited knowledge of the subject of textile coloring to readily see that, no matter how much the numerous processes may differ in principle or vary in detail, they all involve two fundamental factors.

First: The Material to be colored.
Second: The Substances to be used as coloring agents.

2. To acquire a knowledge of the first, one must carefully study the chemical and physical properties of the various fibres together with their action toward the different chemicals with which they may come in contact during the process of manufacture, and the subsequent dyeing and finishing. A thorough knowledge of the second is necessary to the dyer, but it is only when this knowledge is combined with a thorough acquaintance with the first that proficiency is attained in the art of textile coloring.

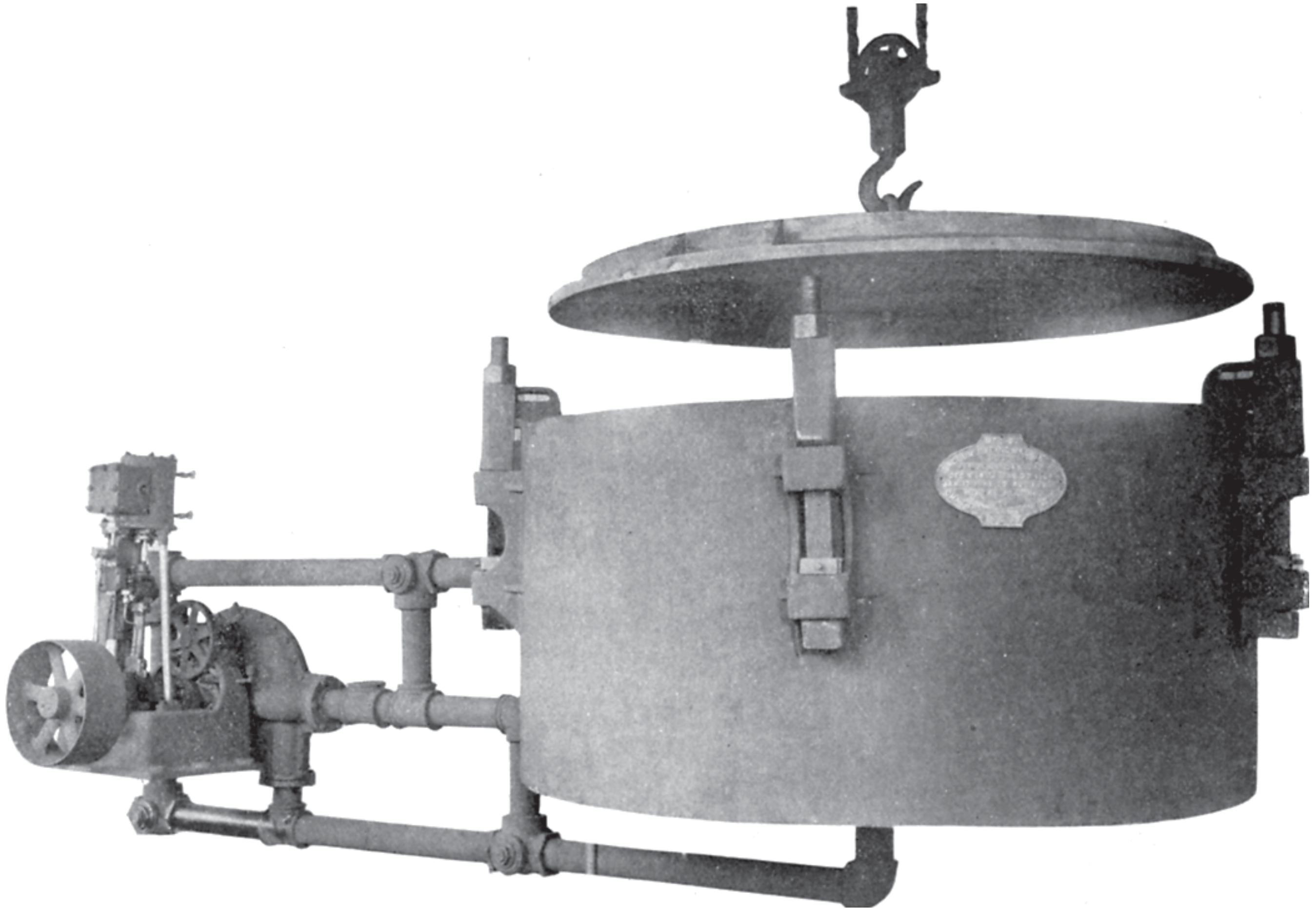
3. A thorough conception of these factors can be obtained only after a careful preliminary study of Chemistry, and when thus prepared the student is ready to take up the Study of Textile Chemistry and Dyeing, which should include the following subjects:

1. Technology of the Fibres.
2. Operations Preliminary to Dyeing.
3. Water and its Application in the Textile Industry.
4. Mordants and other Chemical Compounds used in the Textile Industry.
5. Theories of Dyeing.
6. Natural Coloring Matters.
7. Artificial Coloring Matters.
8. Machines used in Dyeing.

TECHNOLOGY OF FIBRES.

4. For convenience, fibres are divided according to their origin into the following classes:

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



IMPROVED VACUUM DYEING MACHINE WITH CAST IRON BOWL AND PLATES

Vacuum Dyeing Machine Co.

The third class, however, is of minor importance in the Textile Industry.

5. Members of Each Class. Of *vegetable fibres*, cotton is by far the most important, then follows linen, hemp, jute, China Grass, or ramie, and a few others of less importance, such as Manilla hemp, Sunn hemp, New Zealand flax and the fibre obtained from various palms.

The other vegetable substances with which the dyer may have to deal are straw for hats, vegetable ivory used for buttons, wood fibre, and paper pulp which may consist of almost any vegetable fibre or mixture of vegetable fibres.

The only *animal fibres* of great importance are wool, and a few varieties of hair, and silk. To this class also belong such substances as leather, feathers, horn and bone, all of which are sometimes colored.

Under the head of *mineral fibres* are included such substances as glass wool, slag wool, asbestos, etc. These are used in certain chemical operations, and in covering steam-pipes, boilers, steam-jacketed kettles and stills, on account of being non-conductors of heat, but for practical purposes they are never colored, and need not be further considered.

Under the head of *artificial fibres* are included all fibres produced artificially from chemical products. The only one of importance, however, is artificial silk, and this will be considered later. (See Art. 24.)

COTTON.

6. Cotton is the downy, fibrous material that covers the seeds of several species of plants known botanically as *Gossypium*. The fibre and seeds are enclosed in a three to five valved capsule or cotton boll, which when ripe bursts open. The cotton is then picked and separated from the seeds by a process known as ginning, the products being cotton, ready to be baled, and cotton seed.

7. Cotton Seed Industry. Formerly, cotton seeds had no commercial value, but in recent years they have become a source of great income, owing to the large amount of oil which can be pressed from them, and also for the various animal feeding products obtained therefrom. Certain portions of the seeds are also valuable as fertilizers.

Considering the annual product of the United States as 10,000,000 bales of cotton, the corresponding amount of seed is 5,000,000 tons, with an average value of $10 a ton as a raw product.

8. Motes. The complete removal of the fine particles of broken seed from the fibre is not always possible, and they are visible in the unbleached cloth as small specks, technically known as motes.

9. Under certain conditions these motes give up a portion of the tannic acid which they contain. Tannic acid has a great affinity for some dyestuffs (particularly that class known as basic colors), and unless these motes are completely removed from the cloth before the dyeing, it is likely that more color will be deposited in their immediate neighborhood than on any other portions of the cloth, thus producing dark spots and uneven dyeing.

10. A typical cotton fibre is a long tubular vegetable cell varying in diameter from .0004 to .001 of an inch, and from .75 to 1.5, and in extreme cases nearly 2 inches in length. (See Fig. 1.)

When examined under the microscope, matured cotton fibres present the appearance of long flattened tubes, thicker at the edge than at the center, and spirally twisted, thus resembling a twisted ribbon, the edges of which are thick and rounded. This spirally twisted appearance is most marked in fully ripened fibres and is probably due to the drying and contraction of the sap which fills the central opening of the partially ripened fibre.

Fig. 1.

In cross-section, cotton fibres present a variety of shapes, as shown in Fig. 2, but all have the appearance of flattened tubes with comparatively thick walls and a small central opening. This opening runs from the end of the fibre attached to the seed almost to the opposite end, which appears to be closed.

It is the special character of the fibre which renders it suitable for the manufacture of very fine yarns. Its hollow and twisted condition makes it light and elastic as compared with linen, which, although having a longer fibre, is stiff and straight.

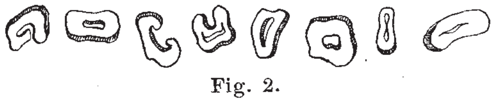


Fig. 2.

11. The value of the microscope in the detection and examination of the various fibres cannot be overestimated, and when used in conjunction with various chemical tests it is, in most cases, an easy matter to identify the various fibres, and also the constituent fibres of mixed material.

Fig. 3.

12. Dead Fibres. Under microscopic examination one often finds cotton fibres which present no indication of a hollow central opening but on the contrary show a broad ribbon-like structure, almost transparent and with irregular folds. (Fig. 3.) These are young or unripe fibres, technically known as *dead fibres.* They are very difficult to dye as compared with ripe cotton fibres, and with certain colors, especially indigo and alizarine, may appear in the dyed material as white specks.

13. The principal substance of cotton fibre is cellulose, and the remainder chiefly water and certain natural impurities.

The approximate composition may be given as follows,

Cellulose	87 to 90 per cent.
Water	5 to 7 per cent.
Natural Impurities	4 to 6 per cent.

14. Cellulose constitutes the foundation or frame work of plant life, but in most cases it is accompanied by a large proportion of resinous material, - coloring matter, dried sap, etc. It occurs in cotton in a comparatively pure state.

Considered chemically, it has a formula, $C_6 H_{10} O_5$, and belongs to the class of organic compounds known as the carbohydrates. It is, when pure, a snowy white solid substance, insoluble in ordinary solvents, such as water, alcohol and ether, but dissolves in concentrated sulphuric acid and also in an ammoniacal solution of cupric hydrate, known as Schweitzer's Reagent, from which it is precipitated by acids.

15. Hygroscopic Moisture. The moisture present in raw cotton is of hygroscopic nature, and this is the reason why the percentage may vary to such an extent.

By hygroscopic moisture we mean moisture that is not chemically combined as a constituent of the main substance of any material, but mechanically held in its pores. Hygroscopic substances are usually more or less porous. A hygroscopic substance, when placed in a very dry atmosphere, will gradually give up its moisture, and if heated any length of time to a temperature just above the boiling point of water, it will be almost entirely removed. By application of this principle it is possible to determine the percentage of moisture in the various fibres. This will be discussed more fully under Silk, which is a very hygroscopic fibre.

On the other hand, if a hygroscopic substance is placed in a very moist atmosphere it will absorb moisture and increase in weight. Thus certain fibres, more particularly animal fibres, if stored in a damp place will contain a higher percentage of moisture than when stored in a very dry place.

16. Natural Impurities. Investigations that have been made in regard to the natural impurities of cotton indicate at least five different constituents, enumerated as follows :

(1) A waxlike body, commonly known as *cotton wax*, which is insoluble in, and lighter than water, and having a comparatively high melting point. The fact that raw cotton or material made of raw cotton is so difficult to saturate with water or wet out, is probably due to a thin but impenetrable coating of this wax upon the surface of the fibre.

(2) A fatty matter that melts at 55° C and appears to be either margaric acid or a mixture of palmitic and stearic acids.

(3) Certain nitrogenous, non-crystalline coloring matters of a brownish color.

(4) A light amorphous substance of an acid character, resembling certain gums and known as *pectic acid*.

(5) Albuminous matter in small quantities.

Of the five constituents mentioned above, the pectic acid is present in the largest proportion, the coloring matters next, while the others are present in very small quantities.

17. Bleaching. The chief object of bleaching cotton is to remove the natural impurities and coloring matters, and to leave the fibre as nearly pure cellulose as possible. This, however, will be discussed in detail under that head.

18. Absorbent Cotton. By successively treating cotton with various solvents, such as alcohol, ether, etc., it is possible to remove from cotton the last traces of impurities and leave behind, except for the moisture it may contain, practically pure cellulose. This is known as absorbent cotton, and is largely used in surgery.

ACTION OF COTTON TOWARD ATMOSPHERIC CHANGES AND CHEMICAL REAGENTS.

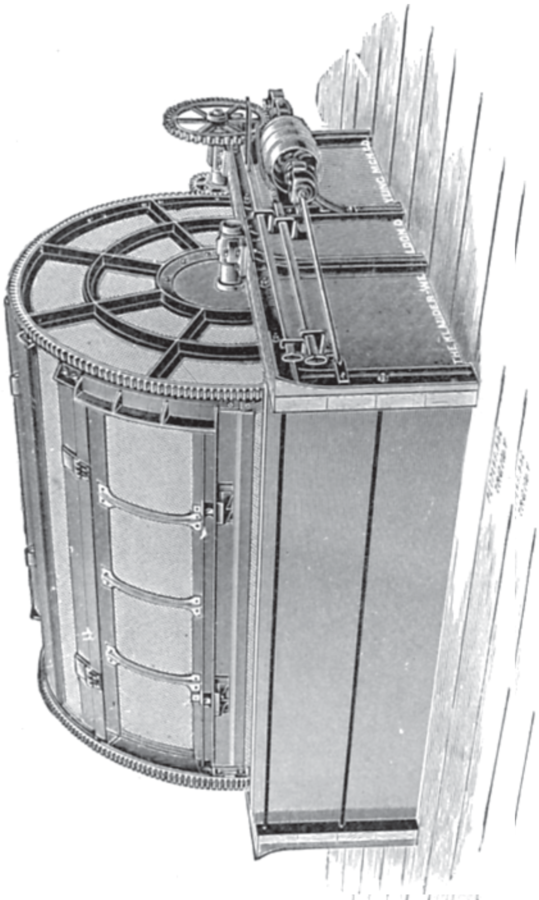
19. Mildew. Cotton material that is contaminated with organic matter, such as starch, gum, etc. (for instance, finished calicoes, or any heavily sized cotton cloth, particularly if stored in a warm, moist atmosphere), is likely to be acted upon by a certain low order of vegetable organism or mold, known as mildew. A sort of fermentation of the sizing material sets in, and eventually the fibre itself is attacked and becomes tendered.

Little trouble, however, is experienced with raw cotton, and even less with bleached cotton, owing to the comparative freedom from impurities.

20. Frost. No definite information can be given in regard to the action of frost on cotton fibre and material. It has been thought by some that cotton, being hollow, would, if cooled below the freezing point, when in a moist condition, become stiffened by the formation of a core of ice, and when handled in this condition become easily broken.

21. Acids. The action of various acids on cotton is an extremely important consideration, for under certain conditions many of the acids used in the various textile processes will seriously affect, and in some cases entirely destroy the fibre.

In general, concentrated mineral acids will seriously corrode, and in many cases completely destroy cotton fibre, the results



e acid, its degree of con-

e or no action on cotton if
llowed to dry on the fibre
centrated to corrode and
complete destruction.
getic, the physical appear-
ut a change in chemical
is converted more or less
known as oxy-cellulose.
ellulose, the fibre has no
ast friction or mechanical
. Upon this fact depends

ght in contact with concen-
ls into a gelatinous mass,
a substance known as

ion of *artificial parchment.*
Heavy unsized paper is
c acid for a few seconds,
substance called amyloid.
ct, and when washed and
dried is extremely hard. The result is a good imitation of natural parchment.

Warm concentrated sulphuric acid completely dissolves cotton, converting the cellulose into a soluble substance known as *dextrin* or *British gum.*

Hot dilute sulphuric acid is likely to tender cotton, if it comes in contact with it any length of time, but cold dilute sulphuric acid has no perceptible action unless the fibre is dried before the acid is washed out.

23. Nitric Acid. The action of nitric acid on cotton is of extreme importance, since through its action many valuable articles, such as gun-cotton, celluloid and artificial silk, are produced.

When heated with concentrated nitric acid, cotton is entirely decomposed, producing oxy-cellulose and oxalic acid, but when acted upon by cold concentrated nitric acid, or, better, a cold mixture of nitric and sulphuric acid, the cellulose of the cotton is changed into nitro-cellulose.

Depending on the strength of the acid and length of duration of the action, different products may be formed, such as

$C_{12}H_{16}(NO_3)_4O_6$	Tetra Nitro-cellulose.
$C_{12}H_{15}(NO_3)_5O_5$	Penta Nitro-cellulose.
$C_{12}H_{14}(NO_3)_6O_4$	Hexa Nitro-cellulose.

The first two are soluble in alcohol and ether, and are known as soluble gun-cotton. Such a solution is known as collodion and is largely used for photographic and other purposes. Gun-cotton is also known as pyroxylin.

The Hexa nitro-cellulose is insoluble in alcohol and ether, and is a violent explosive and a constituent of many modern explosives.

The other cellulose nitrates are explosive, but not to as great an extent as the Hexa products.

Celluloid is made by properly mixing soluble gun-cotton with camphor.

Artificial silk is made from soluble gun-cotton.

Dilute nitric acid has little if any action on cotton if thoroughly washed from the fibre, but if allowed to dry upon the fibre it gradually becomes concentrated enough to convert the cotton into oxy-cellulose.

24. Artificial Silk. Several different processes, and many modifications of these processes, have been tried, having as the object the production of artificial silk, but the majority have proved of no practical value.

The oldest and probably most successful is the one introduced by Chardonnet in 1884. The principle of this process depends upon the fact that a solution of Tetra nitro-cellulose solidifies when brought into contact with cold water. This solution of Tetra nitro-cellulose, commonly known as pyroxylin, is forced, under pressure, through a tube A, (Fig. 4), which ends in a very fine capillary orifice O. The inner tube A is surrounded by an outer tube T, through which there is a constant flow of cold water. Upon coming in contact with the cold water at O the pyroxylin solidifies and can be drawn out, dried and reeled in the form of a continuous fibre.

When made from pure pyroxylin the fibre is so inflammable as to be extremely dangerous. In order to reduce its great inflammability, certain metallic chlorides may be added to the pyroxylin solution, and sometimes the fibre is treated with ammonium phosphate. Colored effects are often produced by adding the proper dyestuffs directly to the pyroxylin solution. In brilliancy artificial silk even surpasses the natural.

Its use is limited to cases where great durability is not essential and where it is not likely to come in contact with water. It is said that the demand is greater than the supply, and that in some cases it brings a price greater than some grades of silk.

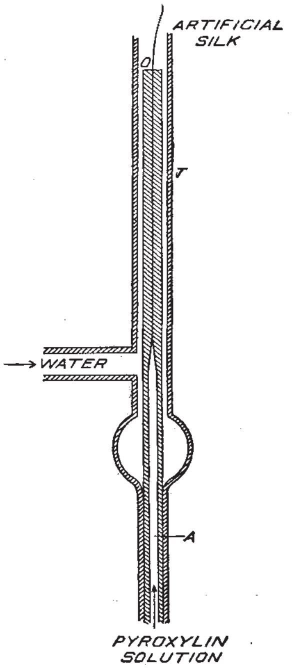


Fig. 4.

25. Hydrochloric Acid. Hydrochloric acid, whether concentrated or dilute, has the mildest action on cotton of any of the so-called mineral acids, but if allowed to dry upon the fibre tendering follows, and if dried at a high temperature the fibre is completely disintegrated.

26. Other Acids. Phosphoric acid acts similarly to hydrochloric acid.

Acetic acid has no noticeable action on cotton.

Solutions of oxalic, tartaric, and citric acids have no apparent action, but if the cotton is saturated with a 2 per cent solution of these acids, and dried at 100° C. for an hour, it becomes slightly tendered, and when saturated with a 5 per cent solution and dried for an hour at 100° C., there is a decided destructive action. If, however, the acids are mixed with certain thickening agents, such as starch, gum, etc., and the dry heat replaced by steaming, there is little fear of serious tendering. These facts are of importance since in the production of calico prints it is sometimes necessary to use as high as 3 to 4 per cent of these acids in a printing paste.

27. Alkalies. The action of alkalies on cellulose, and consequently on the vegetable fibres, is entirely different from that of acids.

The alkaline carbonates, including the carbonates of potassium, sodium and ammonium, borax and soap, have no action under ordinary conditions. Dilute caustic alkalies, and lime water even at a boiling temperature do not tender cotton fibre if air be entirely excluded, but if allowed to come in contact with the air at this high temperature the oxygen gradually converts the cellulose into oxy-cellulose, thus greatly reducing the strength or even destroying the fibre.

MERCERIZATION.

28. The action of strong caustic soda, or caustic potash solution, on cotton is not only remarkable, but the practical application of this action has proved of great interest and value to the textile industry.

If a piece of cotton cloth is steeped for a few minutes in a solution of caustic soda (50° to 60° * Tw. Sp. Gr. 1.25 to 1.30), it assumes a gelatinous appearance, and when taken out and washed it is found to have shrunk considerably in surface area, and become of much closer texture.

Should a single fibre of this cloth be examined under the microscope it will be found to have lost the appearance of a perfectly normal cotton fibre. The spirally twisted appearance has disappeared and it has no superficial markings, but has become thick, straight, rod-shaped and transparent. (See Fig. 5.) The sectional appearance is entirely changed also. It has no longer the appearance of a flattened tube, but is cylindrical, while its walls have thickened until the central opening has become a mere point.

Fig. 5.

Cotton treated in this way not only increases in strength, but has a greater attraction for coloring matters.

This peculiar action of caustic soda was discovered by John

---

* NOTE. To find the specific gravity or density of liquids, hydrometers are used. There are various forms such, as Baumé, Twaddle, etc. The Twaddle (abbreviated to Tw.) is used for liquids denser than water. This subject will be taken up later. (See page 39.)

Mercer, a Lancashire calico printer, more than fifty years ago, while attempting to filter a concentrated caustic soda solution through a piece of cotton cloth. Later he patented a process for treating cotton cloth with caustic soda, and hence the term mercerization.

Mercer's process consisted in simply passing the cloth through a caustic soda solution, when the action already mentioned took place. The results were that cloth counting 200 threads to the inch would become so compact as to count 270. The increase in strength for a given width was 50 per cent, or even more, and a given amount of cloth would increase in weight 4.5 to 5.5 per cent. It also assumed a finer superficial appearance, and an increased lustre, and affinity for dyestuffs.

At one time it was thought that an application of this process to cotton cloth would be of great value to the textile industry, as will be seen by the fact that Mercer was offered $200,000 for his patent in 1852, which he refused to accept. The cloth, however, shrank from 20 to 25 per cent in length as well as in width, and this, together with the fact that its increase in durability would tend to make the call for fresh supplies less often, led to its abandonment.

It has proved of value for other purposes, and the principal use at the present time, and undoubtedly the most important application ever made, is in the production of a silk-like gloss on cotton yarn by mercerizing it in such a way that it cannot shrink.

It is still an open question, in this country at least, as to the legal claimant to the process of producing lustre on yarn by mercerization. The most aggressive claimants are Horace Arthur Lowe, who took out certain patents about 1891, and Thomas and Prevost, who took out others in 1895.

The various processes for obtaining this silky lustre differ mechanically in the method of preventing the shrinkage, but the general principles involved are the same in all, and are as follows:

The mercerizing bath consists of a caustic soda solution kept commonly at a Sp. G. between 50° and 60° Tw.

Solutions of a Sp. G. less than 15° Tw. have but slight mercerizing action. For the best results the temperature should remain low, about 15° C. and not over 20° C.

The time of immersion is of little consequence as long as the yarn is thoroughly saturated. Ten minutes is usually long enough. The yarn is commonly under tension when it enters the mercerizing bath, but in some methods it is subjected to tension upon being taken from the bath. In either case, however, it is necessary that the lye be washed from the yarn before the tension is relieved.

Although all cotton receives a silky lustre upon mercerization under tension, up to the present time it is only long staple cotton, such as Egyptian and Sea Island, that appears to receive enough lustre to make its mercerization practical for this purpose. The gassing of the yarn before it is mercerized also seems to add materially to the lustre of the finished product. Gassing consists in rapidly passing the yarn through a gas flame for the purpose of singeing the projecting superficial fibres.

At least two other applications of mercerization have proved of importance.

First, the production of seersucker effects by printing on a cotton cloth a narrow stripe of strong caustic soda paste. The cloth shrinks where the caustic soda comes in contact, and when washed and finished, a seersucker effect results.

Second, the production of two-color designs by printing a figure on cotton cloth with a caustic soda paste, and then dyeing in a bath containing a direct cotton color. If the color be a blue, the result will be a light blue ground and a darker blue figure, and similarly with other colors.

This effect is due to the increased affinity for dyestuffs of that portion of the cotton fabric that has been acted upon by caustic soda.

Other reagents, such as strong sulphuric acid and a concentrated solution of zinc chloride, if properly used, produce an effect similar to caustic soda, but they have never been introduced on a practical scale.

As to the chemistry of mercerization, the accepted theory at the present time is similar to that proposed by Mercer, that is, that the change is due to the formation of a hydrate of cellulose. When cotton is mercerized, a reaction represented by the following equation probably takes place:

$$2\,C_6H_{10}O_5 + 2\,NaOH = (C_6H_{10}O_5)_2Na_2O + H_2O$$

Cellulose Caustic Soda

and when mercerized cotton is washed the sodium compound is converted into a cellulose hydrate:

$$(C_6H_{10}O_5)_2Na_2O + 2\,H_2O = (C_6H_{10}O_5)_2H_2O + 2\,NaOH.$$

The chemistry of the subject has not been studied as thoroughly as the physical side, and the above is merely the accepted theory of the present time.

29. *Lime.* Milk of lime even at a boiling temperature has little or no action on cotton material as long as it remains below the surface of the liquor, but if it comes in contact with the air, at a boiling temperature, tendering takes place, through the oxidation of the fibre. Such exposure must be avoided in cotton bleaching.

30. *Chlorine and Hypochlorites.* Cotton is quickly tendered if exposed to gaseous chlorine, especially in the sunlight.

The action of bleaching powder or calcium hypochlorite on cotton varies between the following limits according to its concentration and temperature. A cold dilute solution has scarcely any action, but a hot concentrated solution will tender the fibre seriously. Hypochlorite solutions, if too concentrated or too warm, convert cellulose into oxy-cellulose. For this reason particles of bleaching powder must not remain in contact with cotton cloth any length of time, for the cloth will become so tendered in the immediate neighborhood as to cause holes. Very dilute and cold solutions of bleaching powder or hypochlorites are universally used for bleaching cotton material.

31. *Oxy-cellulose.* The tendency of all oxidizing agents is to convert cellulose into oxy-cellulose, a substance containing a higher percentage of oxygen than ordinary cellulose. Oxy-cellulose has a decided affinity for the basic dyestuffs, while cotton does not. Use is made of this fact in detecting its presence.

32. Metallic Salts. Cotton fibre has little or no affinity for ordinary neutral salts, such as alum, copper sulphate and ferrous sulphate, but when they are present in a basic condition it has the power of decomposing them; the metallic oxides or hydroxides formed during decomposition becoming loosely fixed upon the surface and in the pores of the fibre. In this condition the cotton has a greater affinity for certain coloring matters. This will be considered more fully under Mordants.

33. Action of Cotton with Coloring Matters. Until within the last twenty years the only dyestuffs of importance for which cotton showed a direct affinity were indigo and turmeric. All others had to be applied through the use of an intermediate product called a *mordant*.

Some of the basic dyestuffs may be said to have had a slight affinity, but with the discovery of Congo red, in 1884, a new class of artificial dyestuffs known as the direct cotton colors came into use, and these at the present time are capable of producing on cotton, without the use of a mordant, almost any shade except very bright blues and very bright greens.

FLAX AND LINEN.

34. Next to cotton, linen is the most important vegetable fibre. It is the product of the flax plant, the variety commonly cultivated being known botanically as Linum Usitatissimus.

Flax grows best in a temperate climate, and is cultivated in nearly all parts of Europe, and to a considerable extent in the United States. It is an herbaceous plant, with long, narrow, smooth leaves, and bearing bright blue flowers, which ripen into the seed valuable for the production of linseed oil.

In order to produce a product satisfactory for textile purposes, great care is necessary. The production of good linseed and valuable fibre from the same plant, is said often to be impossible, but facts established in other countries as well as in our own, indicate otherwise. In Belgium, for instance, the finest linen of Europe is grown, and the seed from the same plant is not only saved, but a portion used for the production of the next year's crop. It is a fact, however, that if the flax is allowed to grow beyond a certain point, the fibre becomes stiff and coarse ; and the double result can be obtained only when the flax-grower has had experience, and the conditions are favorable. Many flax-growers of the United States sacrifice the value of their crops, as far as the fibre is concerned, for the purpose of producing large quantities of rich seed.

35. Removal of the Seed. The process known as rippling has for its object the removal of the seeds, and is accomplished by drawing the flax stalks through a series of iron combs. In this country the seeds are often removed by passing the flax through threshing machines, but this renders the flax worthless so far as the production of the fibre is concerned.

The seeds, if ripe enough, are used in the preparation of linseed oil, the most valuable of the common drying oils.

36. Retting. Whereas cotton is ready for the textile manufacturer immediately after it has been ginned, flax has to undergo a series of operations, involving both mechanical and chemical principles, before workable linen fibre can be obtained. This is necessary because after rippling, the air-dried flax contains less than 30 per cent of actual linen fibre, the remainder being wood, pith and rind, which cling to the fibre with great tenacity. The process of separating the fibre is thus rendered difficult. It involves several operations, and is commonly called retting.

Retting is carried out in a number of different ways, but in every case the object is to decompose by fermentation and otherwise, the pulpy and resinous matter that holds together the woody material and actual fibre, and thus render the two separable.

The different methods of retting may be classified as follows:

Natural retting.
  (1) By steeping in stagnant water.
  (2) By steeping in running water.
  (3) Dew retting.

Artificial retting.
  (1) Retting with warm water.
  (2) Retting with steam under pressure.
  (3) Retting by the use of mineral acids.

Retting in stagnant water is carried out mainly in Russia and Ireland. The flax is steeped in pools or tanks of soft water. In the course of a few days fermentation sets in and the resinous and pulpy matter becomes more or less soluble, thus facilitating the separation of the fibre from the woody material. The retting is completed by exposing the flax in the fields to the action of the sun and atmosphere for a few days.

Retting in running water is accomplished by packing the flax in crates, and immersing these crates in streams of water, so that there is a slow but constant flow of water through them.

Fermentation soon begins, and the retting is completed in from ten to twenty days. The flax is sometimes removed during the process, exposed to the sun for several days, and returned to the water. This form of retting is used chiefly in France and Belgium, and gives a lighter colored linen than the previous method.

Dew retting is accomplished by exposing the flax in a moist condition to the action of the dew and sun, by keeping it spread in a field during a period of ten weeks. This takes longer than either of the previous methods, but produces a whiter linen. This form of retting is used largely in Germany and Russia.

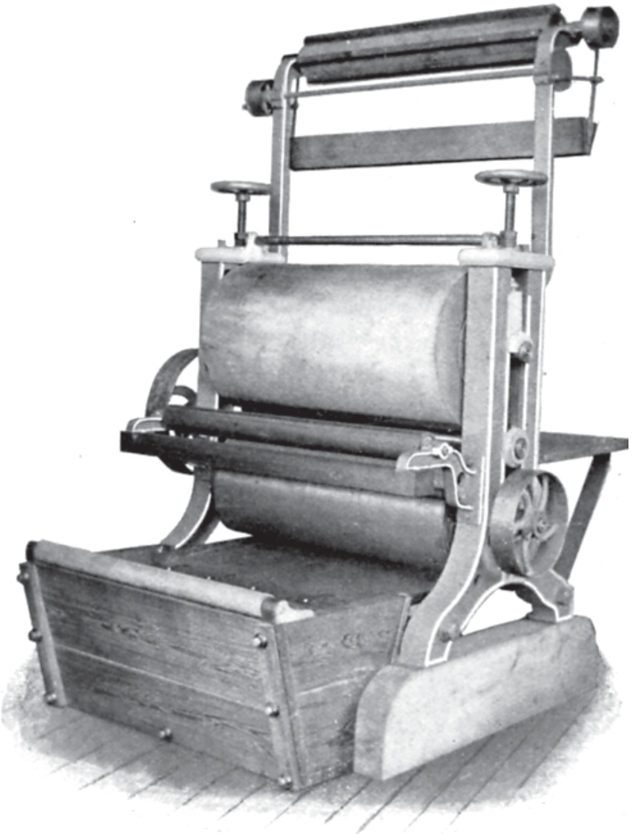
The artificial methods of retting are of less importance than the natural, since they are at present in a more or less experimental stage. The object of all artificial methods is to shorten the extended period of time, and reduce the territory needed to carry out the natural, and in some cases to prevent the obnoxious odor arising from the fermentation.

Warm Water Retting. This is accomplished by steeping the flax in warm water at 30° to 35° C. for two or three days; when the resinous material becomes so softened as to readily squeeze out when the stalks are passed between squeeze rollers.

Retting with Hot Water and Steam. This is the quickest of all retting processes. The flax is first exposed in strong iron cylinders to the action of water at 150° C., under pressure, for 30 to 40 minutes, and then to the action of high pressure steam at the same temperature for 30 minutes. Under these conditions the resinous material of the flax becomes soluble and is removed during a subsequent washing. The whole process takes but a fraction of a day.

Retting with Mineral Acids. Under this head might be included a number of methods by which small quantities of different acids, such as sulphuric and hydrochloric, are added to the retting bath. The addition of acid not only lessens the time as compared with the natural fermentation method, but prevents the disagreeable smell.

37. Breaking. After retting, the flax is subjected to several mechanical operations, the object of which is to remove the woody portions of the stem as completely as possible. The first of these



PRESSURE-HYDRO-EXTRACTOR FOR EXTRACTING WATER FROM CLOTH

Rodney Hunt Machine Co.

operations is known as breaking, and its object is to break up the woody portion of the stalks, so that it may be removed from the fibre.

This was formerly done by hand with indented wooden mallets, but at present is generally accomplished by passing the stalks through a series of fluted rolls.

38. Scutching is the next operation, and consists in the removal of the broken particles of wood either by hand or machinery, thus leaving the fibre in a more or less free condition.

39. Hackling or Heckling. The last of the series of mechanical operations is known as hackling or heckling. It has for its object the separation of the fibres into an individual state and laying them parallel to each other. This is accomplished by drawing the flax through several combs; the first are coarse, and then finer and finer, until it is in a suitable condition for being spun.

Two products are the result of this operation:

First: Flax line, which consists of the long, straight and more valuable fibres; and

Second: The tow, which includes the short and more or less tangled fibres.

40. Linen Fibre. Flax line commonly has the appearance of a long, fine, soft and lustrous fibre, varying in color from a yellowish buff to a greenish gray. When examined under the microscope, what appeared to the naked eye to be a single fibre will often prove to be composed of a number of smaller fibres cemented together. If these are separated, the ultimate single fibre appears as a long transparent tube, often striated longitudinally, possessing thick walls and a minute central canal. At irregular intervals faint transverse markings may be detected, and these are often pronounced in the larger fibres. (See Fig. 6.) Flax line varies considerably in length and diameter, since it is composed of a varying number of constituent fibres, but the ultimate fibres are approximately 25 to 30 millimeters in length, and .02 to .025 millimeters in diameter.

Linen is stronger than cotton, possesses greater lustre, and is a better conductor of heat. It is for the latter reason that it makes cooler clothing. Linen is hygroscopic to about the same extent as cotton, containing 6 to 8 per cent of moisture.

41. Chemical Composition. Like cotton, linen consists for the most part of cellulose, but in the raw and unbleached state it is mixed with from 15 to 30 per cent of natural impurities. Among these natural impurities, pectic acid is the most abundant, and this is accompanied with smaller amounts of fatty and coloring matters.

42. Action of Reagents. In general, linen acts like cotton with reagents. Schweitzer's Reagent dissolves pure linen as readily as it does cotton.

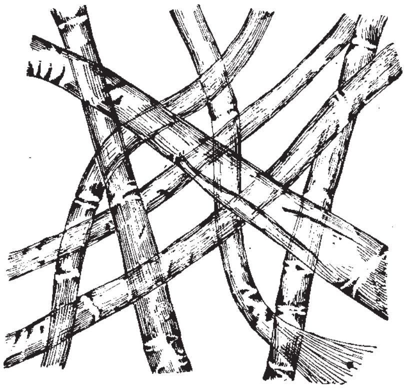


Fig. 6.

The action of mineral acids on bleached linen is almost identical with their action on cotton, but in the case of raw and unbleached linen the action is a little more energetic, owing to the large percentage of natural impurities present. For this reason, linen is also rendered much more difficult to bleach than cotton.

The action of mordants and dyestuffs on linen is very similar to their action on cotton, but linen is usually more difficult to dye, not being as easily penetrated as cotton.

JUTE.

43. Jute is the most important vegetable fibre after linen. Its principal source is India. The processes of its treatment are very similar to those of linen, but it differs from both cotton and linen in its composition. It contains no cellulose in the free state, but instead is composed chiefly of a combination of cellulose and bastose, the latter being a compound intermediate between the carbohydrate and aromatic compounds, and possessing to some extent the properties of both.

Bastose is much more easily acted upon by chemical reagents than cellulose, and for this reason the action of various chemical reagents on jute is entirely different from their action on linen and cotton, jute being much more sensitive to the action of acids and not standing as much treatment, even with water. When treated with hypochlorites, the liberated chlorine forms a chlorinated compound, and when treated with alkalies, bastose is decomposed into cellulose and an insoluble tannin product.

For these reasons, jute cannot be easily bleached in the same way as cotton and linen, and in fact is seldom bleached.

44. Action of Dyestuffs. Jute may be said to be a naturally mordanted fibre, since it contains a certain amount of tannin material, which acts as a mordant for certain dyestuffs. This is the reason why it takes up many basic dyestuffs directly. Jute may be dyed with the direct cotton colors, but it is largely used in making bagging, burlap, backs of carpets and in upholstery, where there is no necessity for dyeing.

HEMP.

45. Hemp resembles flax in nearly every way, and its treatment is similar. It is, however, much coarser than linen, and is seldom bleached or dyed.

It is used chiefly in making rope, twine and bagging.

RAMIE.

46. Ramie fibre or China grass is the fibre obtained from a form of nettle grown in China, India, and in an experimental way in the United States. In the best samples of ramie the individual fibres are 20 centimeters long, with a diameter varying from .04 to .08 millimeter. When purified and cleansed, ramie possesses a characteristic and silk-like lustre which surpasses that of linen.

In composition it consists mainly of cellulose, accompanied in the unbleached state with about the same percentage of natural impurities as cotton.

Although easily bleached, some difficulty is experienced in dyeing full and bright shades without injuring its lustre.

The great drawback to its extensive use and cultivation is the difficulty experienced in separating by mechanical means the individual fibres from the stem and bark in a condition satisfactory for spinning. Several processes have been devised for retting and separating the fibre, but as yet, neither the European nor the American product can compete either in price or quality with the ramie imported from China, the latter being separated entirely by hand, where labor is valued at only a few cents per day.

The Chinese are also far ahead of all other nations in the spinning and weaving of ramie, but experiments along this line performed of late in this country have proved very encouraging.

47. The other vegetable fibres of importance are Manila hemp, sunn hemp, New Zealand flax, and the products of the leaves of different palms, and the fibrous material that surrounds the cocoanut. These fibres, however, are seldom dyed, and will not be further discussed.

WOOL.

48. The most important animal fibre is wool. This term is applied to the hairy covering of a number of animals. In the strictest sense it is the hairy covering of sheep, but for practical reasons the hair of certain goats, as the cashmere, mohair and alpaca, and of camels is generally classified under the same head.

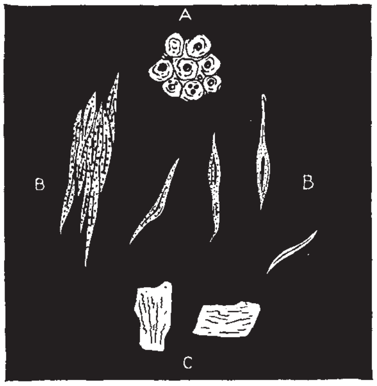


Fig 7.

According to the authorities, there are no less than thirty varieties of sheep, nearly half of which are natives of Asia, one-third coming from Africa, and only four from Europe and two from America. All the different varieties give different qualities of wool, which are distinguished from each other by length, fineness, strength, elasticity, color, etc. Different portions of the same animal also give a varying quality of fibre; that from the shoulders and upper portion being finer than that from the lower.

It is necessary that these different qualities be separated by hand, and the process is known as *wool sorting.*

According to the average length of fibre, wool is divided into two general classes: long and short staple. The former is commonly carded, combed and spun into worsted yarn, while the latter is generally carded and spun into woolen yarn.

49. Diseased Wool and Its Action toward Dyestuffs. The wool of diseased sheep, especially if taken from the hide after death, is of a very inferior quality, and experiments show that its action toward dyestuffs is different from that of perfectly healthy wool; the diseased wool when dyed lacking the brilliancy characteristic of the normal wool.

50. Wool Fibre. Wool has a characteristic physical structure which distinguishes it from other fibres. Undoubtedly no one has made a more thorough study of the physical structure of wool fibre than Dr. F. H. Bowman, and according to his authority wool is a product of the epidermal layer of the skin and is built up of innumerable individual cells; when examined carefully under the microscope it will be found to consist always of two and sometimes of three portions.

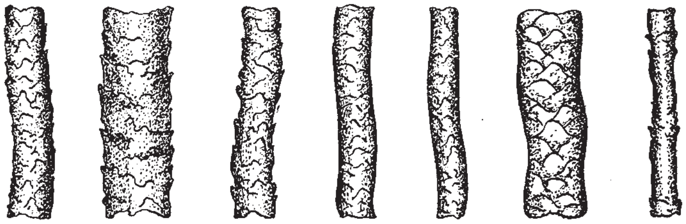


Fig. 8

These three portions are:

(1) External or horny covering.
(2) Cortical or underlying body of fibre.
(3) Medullary or central portion.

Under the microscope wool fibre appears as a solid rod-shaped substance, the surface of which is covered with broad horny plates, all projecting in the same direction, and much resembling the scales of a serpent or fish, as shown in Figs. 8 and 9.

The cortical comprises the body of the wool and sometimes the entire portion of the fibre underlying the outer horny covering. It is built of a large number of spindle-shaped cells of a more or less horny character.

The medullary or central portion of the wool (see Fig. 10) appears to be wholly lacking in the finest grades of wool. When noticeable, it seems to be composed of larger cells than the surrounding cortical, which are more or less rhombic, or cubical, and of a marrowy nature. Under the microscope, this portion of the fibre appears darker than the rest, but may be rendered nearly transparent by boiling with glycerine or turpentine.

Wool is a very elastic fibre; much more so than any of the vegetable fibres. The average length of wool varies with the different grades from 1½ to 20 inches, and the diameter from .004 to .0018 inch.

51. Hygroscopic Moisture. Wool fibre is much more hygroscopic than any of the vegetable fibres. The amount present may vary from less than 10 per cent to more than 30 per cent, depending mainly upon the conditions of the atmosphere where the wool has been stored.

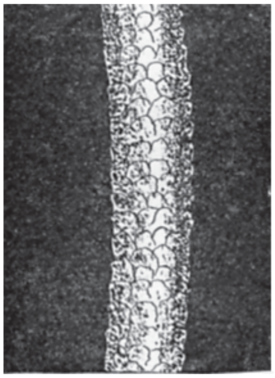


Fig. 9.

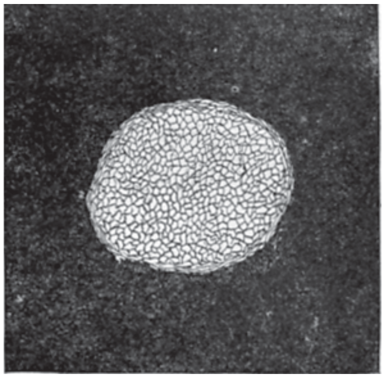


Fig. 10.

The process of determining the quantity of moisture present is known as *conditioning*, and will be considered more fully under Silk. The wool-conditioning establishments of Europe take 18.25* per cent moisture as the standard, while the percentage accepted in this country may be a trifle lower.

52. Felting. The characteristic superficial structure of wool plays an important part in its felting properties.

When a large number of wool fibres are pressed together, especially in the presence of hot water, soap and an alkali, which soften the external horny scales, the opposing scales gradually

---

*NOTE. For worsted tops. Raw unscoured wool may be as low as 10%.

work themselves together, and when the wool has become cooled and dried the softened scales harden, the fibres set are tightly held together, and the wool is said to be felted. This principle is of valuable application in the finishing of certain classes of wool goods.

53. Affinity of Cortical for Dyestuffs. The cortical appears to have a greater attraction for dyestuffs than the exterior scaly covering. This may account for the fact that an acid bath is sometimes advantageous in certain wool mordanting and dyeing processes, the acid having a tendency to open the exterior scales and cells, thus exposing the interior. This also explains why carbonized wool may be dyed deeper shades and more rapidly than ordinary wool.

54. Kemps. Here and there in wool are sometimes seen fibres that appear almost like ivory. If examined under the microscope, they will be found to be void of any of the characteristic structure of wool. These fibres come from portions of the sheep where the wool has merged into hair. They cannot be felted, are difficult to dye, and often appear in the dyed goods as light specks. They are technically known as kemps.

55. Composition of Wool Fibre. A careful chemical examination of raw wool will show that the foreign matter present is often far in excess of the actual wool fibre. When properly cleansed and freed from all accompanying substances, the fibre is found to possess a chemical composition similar to that of horn and feathers, and consists of what is termed *keratin* (horny substance).

The elementary composition varies somewhat in different qualities of wool, but the following may be taken as representative:

Carbon	49.25 per cent.
Hydrogen	7.50 per cent.
Oxygen	23.75 per cent.
Nitrogen	15.75 per cent.
Sulphur	3.75 per cent.

56. Foreign Matter in Raw Wool. The foreign matter enveloping the actual wool fibre possesses a special interest to the dyer, for on its entire removal depends, to a great degree, the success with which pure, even and fast colors may be obtained. To the manufacturer and merchant it is also of great importance, since the amount present in raw wool varies considerably and effects its commercial value.

57. *Wool Suint or Perspiration.* By extracting raw wool with warm water until all matter soluble in this reagent is removed, and then evaporating the extract to dryness, a residue is obtained which consists essentially of the potassium salts or soaps of certain fatty acids, particularly oleic, stearic, palmitic and acetic acid, together with the potassium salts of some mineral acids, such as hydrochloric and phosphoric. Small quantities of certain ammonium compounds are also present. This extract is known as wool suint or perspiration and is essentially that portion of the impurities soluble in water.

58. *Wool Yolk.* If, after all the water-soluble matter has been removed, the wool is extracted with alcohol and ether, and the extract evaporated to dryness, the residue will be found to consist of a mixture of various fatty compounds. For the most part they are not glycerides, but compounds of the alcohols chloresterin and isochloresterin with certain fatty acids, and this accounts for the difficulty sometimes experienced in their removal by mild scouring agents.

59. Mechanical Impurities and Dirt. When all the extractive matter has been removed, there remains a varying amount of insoluble mineral and organic matter, which was held mechanically to the wool through the adhesive nature of the yolk.

60. Composition of Raw Wool. Taking an average of the results of various investigators on different grades of raw wool, the following may be given as fair limits:

Moisture	4 to 30 per cent.
Combined Yolk and Suint	12 to 47 per cent.
Actual Wool Fibre	15 to 72 per cent.
Mechanical Impurities and Dirt	3 to 24 per cent.

As a rule the best grades of wool contain the highest percentage of combined yolk and suint.

Some authorities include suint under the head of yolk, but this does not draw a sharp dividing line between that portion of the impurities soluble in water and the portion that is insoluble.

61. Influence of Sulphur. The amount of sulphur in wool varies considerably, and whether or not it is an essential constituent of wool has been much discussed. It seems, however, to occur in all wool in some form or other, and its presence may be considered an advantage in some respects and a disadvantage in others.

Certain dyestuffs, particularly naphthol green and malachite green, have a greater affinity for wool that has been mordanted with sulphur, and when dyeing with these and similar colors its presence would naturally be an advantage. On the other hand, wool containing much sulphur is likely to become spotted if it comes in contact with certain metals or their salts, especially lead and copper.

ACTION OF DIFFERENT REAGENTS ON WOOL.

62. Heat. If wool is heated to 100° C. in a moist atmosphere, it becomes plastic, may be worked or bent in any shape, and when cooled this shape is retained. This is of great advantage in wool finishing.

If heated above 100° C. in a dry atmosphere, wool loses all its hygroscopic moisture and becomes harsh, but when exposed to ordinary atmosphere it takes up moisture and resumes its natural feel. At a temperature of 130° C. it commences to decompose, giving up ammonia and water vapor, and at 145° C. it gives up sulphur vapor. In a direct flame it burns with difficulty, emitting the disagreeable odor characteristic of burning feathers.

63. Acids. Dilute mineral acids, such as sulphuric, hydrochloric and nitric, may be said to have no appreciable effect upon wool fibre, although they are absorbed and retained with great tenacity and are not readily extracted even with boiling water.

Nitric acid, if sufficiently concentrated, gives a yellow color to wool. The color produced by certain dyestuffs may be stripped from wool by boiling with dilute nitric acid Care should be taken that the acid is not too strong, and the boiling should not last over three or four minutes.

In the case of concentrated acids, the fibre soon begins to disintegrate, but in no case is the action so destructive as on cotton fibre. Dilute acids may be dried upon the fibre even at high temperatures without any noticeable tendering, and this fact is made use of in carbonizing.

64. Sulphurous acid, $H_2 SO_3$, or sulphur dioxide, SO_2, has the power of removing the natural yellow color of ordinary wool, and is the commonest, and all things considered, probably the best bleaching agent employed for this fibre.

Wool treated in this way is very persistent in retaining the sulphur dioxide, and this should always be removed previous to dyeing, especially in the case of light colors. This may be effected by steeping the wool in a very dilute solution of sodium carbonate or bleaching powder. When the first reagent is used, the acid is merely neutralized, but in the second case the sulphurous acid is oxidized to sulphuric acid.

Should the removal of the sulphur dioxide be neglected, the dyed wool is likely to be decolorized by the bleaching action of the portion remaining in the fibre.

65. Alkalies. Alkaline solutions in general have a noticeable action on wool, but the effects produced vary considerably according to their nature, concentration, temperature and period of the action. Caustic alkalies—sodium hydroxide and potassium hydroxide—act injuriously on wool fibre under nearly all circumstances. Even when applied in cold and dilute solutions they act injuriously, and for this reason they cannot be used as scouring agents.

It should be noted, however, that cloth composed of cotton and wool is sometimes passed through a concentrated solution of caustic soda to produce a mercerizing action on the cotton. In this case the caustic solution is cooled with ice, and the cloth passes directly through the bath into an excess of water.

It should also be noted that experiments with solutions of the caustic alkalies of different concentration show that a very strong solution has far less action upon wool fibre than one moderately dilute.

Hot solutions of caustic alkalies, even when dilute, dissolve wool to a soapy liquid, from which a white amorphous mass is precipitated by the addition of acids.

Solutions of the alkaline carbonates and of soap have little or no injurious action if they are not too concentrated and the temperature is not higher than 50° C.

Soap and carbonate of ammonia have the least injurious effect, while the carbonates of potassium and sodium tend to give the wool a yellowish color and render it slightly harsh and less elastic.

The different action of the various alkalies under different conditions is of the utmost importance in wool scouring, and will be considered more fully under that head.

66. *Chlorine and Hypochlorites.* The action of chlorine and hypochlorites on wool is ordinarily harmful, although used to advantage in the production of chlorinated wool.

A hot solution of bleaching powder will entirely destroy the fibre, liberating nitrogen. Dilute solution, when cool, will turn wool yellow. For this reason hypochlorite solutions, so extensively used in the bleaching of vegetable fibres, cannot be used in wool bleaching. Even the very dilute solution sometimes used to destroy the sulphur dioxide in bleaching is deleterious to a certain extent.

CHLORINATED WOOL.

Wool readily absorbs chlorine gas, and under certain conditions may take up 30 per cent of its own weight. If the chlorine is dry and the wool not too moist, this absorption of chlorine seems to impart a decided lustre and the scroopy feel of silk to the fibre without seriously tendering it. Wool treated in this way is known as chlorinated wool, and is produced commercially. Chlorinated wool also has an increased affinity for dyestuffs, and this fact is used in the production of two-color effects in a single dye bath. This increased affinity for colors is probably due to a partial oxidation of the fibre.

Chlorinated wool may also be produced by the following, which is recommended by W. J. Matheson & Co.

For 100 pounds of wool either in the loose state or form of yarn, treat as follows:

First enter the material for a half hour in a cold bath containing 1½ pounds concentrated hydrochloric acid per 10 gallons of water. Then squeeze gently and work in a bath made up as follows:

For Hard Wools.

15 to 20 pounds of Bleaching Powder.
350 gallons of water.

For Soft Wools.

20 to 25 pounds of Bleaching Powder.
475 gallons of water.

In either case the Bleaching Powder solution when made up should have a strength of between .6° and 1° Tw.

After working in the above bath for a half hour, add to the same bath 3 ounces hydrochloric acid per 10 gallons of bath and work for another ten minutes.

Then re-enter the first acid bath, to which has been added 8 ounces of hydrochloric acid per 10 gallons of bath, work fifteen minutes, and wash thoroughly in cold water. If after the final washing a decided smell of chlorine is still perceptible, it is advisable to treat the material for another fifteen minutes in a bath containing 5 per cent (weight of wool) of sodium thiosulphate at 86° F. and then rinse again.

The chlorinated wool is then ready for use, and if woven with ordinary scoured yarn, will produce a plain cloth which will give a two-color effect when dyed.

67. Metallic Salts. There seems to be no chemical action between wool and solutions of salts which are neutral in reaction, such as sodium chloride, sodium sulphate and calcium chloride, but when boiled for some time with such metallic salts as aluminium sulphate, ferrous sulphate, chromium sulphate, chrome alum, etc., which are slightly acid in reaction, there is more or less absorption of these metallic compounds by the wool. The fibre apparently decomposes the salts during the boiling in such a manner that a basic salt, oxide, or hydroxide of the metal is precipitated in the pores of the fibre, and free acid remains in solution.

Taking the case of aluminium sulphate as an example, the following reaction probably takes place:

$$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3H_2SO_4$$

the aluminium hydroxide being absorbed by the fibre, and the sulphuric acid remaining in solution.

The basic compounds deposited in this way seem to have a great attraction for certain coloring matters, forming with them permanent lakes. Upon these facts depend most cases of wool mordanting. This method of mordanting is not applicable to the vegetable fibres, since they do not possess the power of decomposing salts in this way.

68. Coloring Matters. Wool may be said to exert the greatest affinity for coloring matters of any of the textile fibres. It combines directly with all the substantive colors, and has a tendency to combine with a number of the adjective colors, if the bath is in the proper state of neutrality or acidity. Being somewhat porous, wool is readily penetrated by solutions, especially when heated, and this contributes to the easy manner in which it takes up coloring matters.

69. Quantitative Separation of Wool from Cotton. At this point it might be well to emphasize the marked difference between the action of acids and alkalies toward cotton and wool. Acids completely destroy cotton, with little, if any, destructive action on wool, while alkalies will destroy wool, and have no destructive action toward cotton.

Upon these facts are based two methods for determining quantitatively the amount of cotton and wool present in a piece of union material.

(1) If the cloth is saturated with dilute sulphuric acid, and dried, without washing, at a temperature of 100° C., and then briskly rubbed between the hands, the cotton, which has become carbonized, will fall out as a grayish-white powder. If the material is weighed before and after this treatment, the loss of weight will be the amount of vegetable fibre present. This method, however, can be used with only certain classes of goods, and is not as accurate or satisfactory as the following:

(2) Weigh carefully a small piece of material, and boil it for four or five minutes in a 4 per cent solution of caustic soda.

At the end of this period the wool will be completely dissolved by the caustic soda, and if the weight of the dried residual textile material is subtracted from the original weight of the cloth, the loss will represent the percentage of wool or similar fibre present.

SILK.

70. Among the animal fibres, silk is next in importance to wool. Silk is the light yellow, white or buff-colored fibre that the silkworm spins and uses as a covering when it passes from the *caterpillar* into the pupa or chrysalis state. It differs from the vegetable fibres as well as from wool in that all cellular structure is absent.

71. Varieties and Sources. Silk may be divided into two classes, wild and cultivated.

Wild silk is the product of certain wild moths which are natives of India, China and Japan. It is of minor importance as compared with the cultivated.

Cultivated or artificially reared silk is the product of the common silk moth (Bombyxmori), which has been studied and cultivated for a period of several thousand years. The important sources of cultivated silk are southern Europe, particularly France and Italy, Turkey, China, India and Japan.

72. Rearing Silkworms. Eggs of the common silk moth are of a yellowish to gray color, and about the size of poppy seeds; about 40,000 weigh an ounce. In Eastern countries, China and Japan, the eggs are hatched and the worms raised in the open air, but in Europe, specially constructed buildings called magnaneries are used for these purposes.

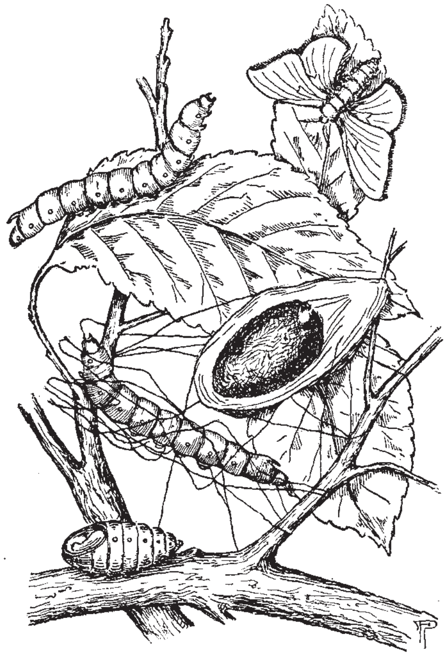


Fig. 11.

The eggs are laid out on sheets of white paper in these buildings, which are well lighted and ventilated. The atmosphere is kept at a constant degree of moisture, and the temperature is gradually raised from 18° C. to 25° C. during the period of from ten days to two weeks. At the end of this period the perfect eggs hatch, and the worms are transferred to a large, airy room, and fed at regular intervals on the leaves of the mulberry-tree for a period of from four to four and a half weeks, when they stop eating and are ready to spin.

At this time the worms, which have now grown to considerable size, weighing as much as five grams, are transferred to another room containing loose twigs, and upon these the silkworms immediately attach themselves and begin to spin. (See Fig. 11.)

73. *The Cocoon.* When the spinning operation begins, the silkworm builds about itself the cocoon, in which it lives during the chrysalis state. While spinning, the silk issues from the spinneret of the silkworm at the rate of from four to six inches per minute; the worm making during that time about sixty-five elliptical movements of the head, or a total of 300,000 in the average cocoon. The time taken by the worm in spinning the cocoon is three to five days.

The silk substance is secreted by a pair of glands, which are symmetrically located along the sides of the body. Each gland consists of three parts, as shown in Fig. 12: a small tube, which extends into the body; an enlarged continuation of this tube, C B, which comprises the main portion of the gland, and a contracted continuation, B A. The portion B A of both glands meet at the spinneret S, thus giving rise to the double structural formation of silk, which will be described later.

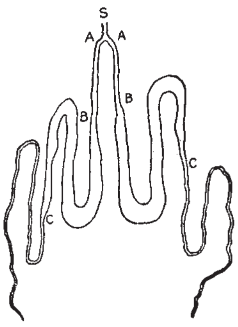


Fig. 12.

While the worm is spinning, the central portion of the large gland, C B, contains a clear, colorless, gelatinous liquid, which appears to merge into a slightly different liquid toward the walls of gland. When the silk substance arrives at A it solidifies and issues from the spinneret S as a double fibre. The central substance of the gland forms the actual fibre, while the outer liquid furnishes the silk gum that cements the two fibres together. It is this latter portion that is removed during the silk boiling, or degumming, as it is often called.

The cocoons are thus made of a continuous double fibre rarely broken, and from 1,200 to 4,000 feet, or even more, in length. They are generally of a white to yellowish color, and about three centimeters in length, and 1.5 to 2 centimeters in thickness.

74. *Treatment of the cocoons.* When the change from the caterpillar to the chrysalis state is complete, the cocoons are collected. A few are selected for breeding purposes and placed in a room kept at a temperature of about 20° C. At the end of three weeks the silk moth has been formed in the cocoon, and by emitting a peculiar saliva, which softens and separates the fibre of the cocoon, it forces its way out. In a few days the female moths lay their eggs. These are collected, slowly dried, and stored in glass bottles in dry, dark rooms until the following spring.

The cocoons which are to be used for the production of silk are either subjected to steam or heated to 60° to 70° C. to kill the pupæ contained within. This takes from ten to fifteen minutes.

When killed by steam, the cocoons are allowed to remain in the damp state for a short time, but after a few hours are placed in a dry room and moved about until they become dry.

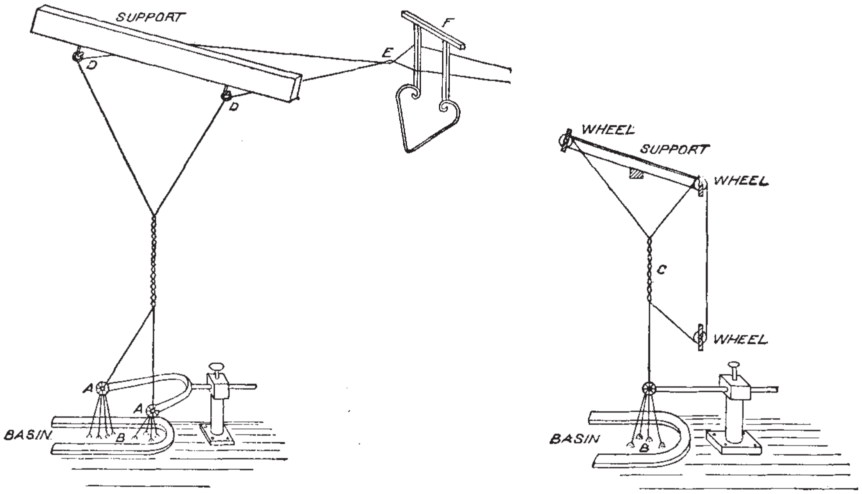


Fig. 13.

75. Raw Silk. The next step in the process of silk making is called reeling. The cocoons are sorted into grades of different quality. The best cocoons are selected for the preparation of warp thread, commonly called organzine, as that has to be strong, lustrous and tightly twisted. The poorer cocoons are commonly worked up for weft or filling, which contains fewer individual fibres, less twist than the organzine and is commonly known as tram.

In the reeling operation a number of cocoons are placed in a basin of warm, soapy water, and a skilled operative is able by the aid of a little brush or broom, often made of briar twigs, to catch the outer end of the fibre. When this has been done with the proper number, which may vary from three to as many as twenty, the ends are placed together, passed through a smooth guide, sometimes made of agate, and then twisted several times about a thread of similar structure to give it twist and make it smooth. This twisted thread then passes through another guide and on to a large reel. The accompanying cuts (Fig. 13) will give an idea of the process.

Silk reeled directly from the cocoon is of the most valuable quality, and constitutes the raw or net silk of commerce.

The tangled and fine loose ends of the cocoon, as well as that obtained by degumming the broken and injured cocoons, are combed like flax and spun similar to worsted into what is known as spun or floss silk.

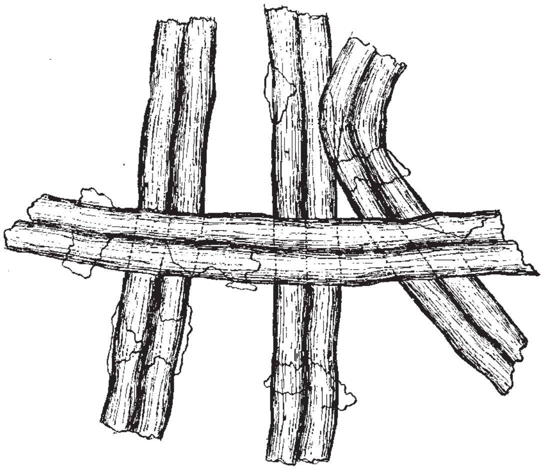
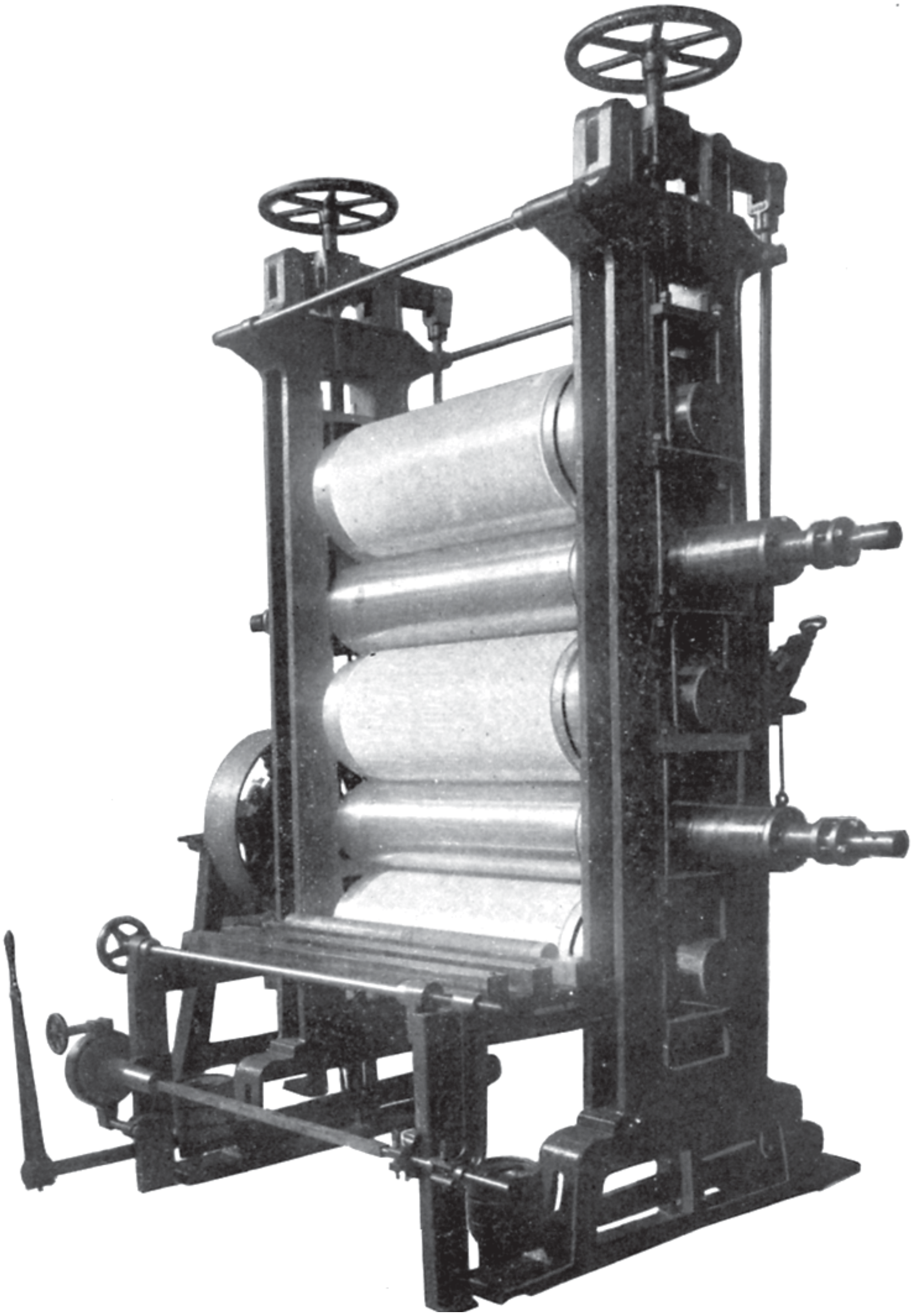


Fig. 14.

76. Silk Fibre. Silk is characterized by its lustre, strength, elasticity and remarkable avidity for moisture. Another characteristic property of silk is the peculiar crisp, crunching sound, or rustling, produced when it is handled, known as the *scroop* of silk. It is a poor conductor of heat and electricity, but is easily electrified. This latter fact is one of the drawbacks in silk manufacturing, but can be overcome to a certain extent by keeping the air at the proper degree of moisture. Silk can be stretched $\frac{1}{7}$ to $\frac{1}{6}$ its length without breaking.



FIVE-ROLL CALENDER FOR COTTON AND LINEN GOODS

Textile Finishing Machinery Co.

A microscopical examination of raw silk shows it to be a double fibre. Occasionally the double fibre separates for a short distance into its components, and at these places the appearance is that of two solid cylindrical fibres. These two fibres are gummed or glued together by what is termed silk glue, or sericin.

77. Hygroscopicity. As already mentioned, silk-like wool is very hygroscopic, absorbing more than 30 per cent of moisture without feeling the least moist.

Owing to the high price of silk it is necessary that the seller as well as the buyer should know the percentage of actual silk they are handling. This fact has resulted in the establishment throughout the silk districts of what are known as "conditioning establishments." At these establishments the amount of moisture in excess of 10 per cent, which is considered normal, is determined. The commonest form of apparatus for this purpose is the Talabot Persoz Rogeat, shown in Fig. 15. In this apparatus the silk is kept constantly at 221° F. until constant weight is attained, it being possible to determine the weight of the silk at any time without its removal from the apparatus.

78. Composition. Chemically, raw silk may be said to be composed of two entirely different substances.

First:—An outward envelopment of gummy material, which is quite readily soluble in such reagents as water, alcohol and ethers.

Second:—An inner portion, the true fibre, which withstands the action of all ordinary reagents.

The first to make an extensive study of the composition of silk was Mulder, and he assigned the name of fibroin to the inner insoluble portion, and to the outer gummy portion the name sericin has been given.

The fibroin constitutes about 65 per cent of raw silk. It is insoluble in water, but soluble in strong acids, alkalies and Schweitzer's reagent.

Sericin, or silk glue, is a gelatinous substance, soluble in water, from which it can be precipitated by lead acetate. Investigations lead to the conclusion that sericin is a product of fibroin through oxidation and hydrolysis.

For all practical purposes we may consider the fibroin as the actual silk fibre, and the sericin the silk glue or gum which envelops it and holds the two constituent fibres of the raw silk together. It is the sericin that is removed during the silk boiling or degumming process.

Commercial, or boiled-off, silk usually gives .7 to 1 per cent of ash, consisting mainly of the oxides of calcium, magnesium, aluminum and iron.

ACTION OF DIFFERENT REAGENTS.

79. Water. Water, either cold or boiling, has no action on silk other than to remove the sericin from raw silk.

80. Acids. In general, silk is readily attacked and dissolved by concentrated mineral acids, while dilute mineral acids and solutions of the organic acids are much milder in their action.

Concentrated hydrochloric acid will dissolve more than its own weight of silk. Upon addition of water to this solution the silk separates as a flocculent precipitate. If applied in the gaseous state, hydrochloric acid will rapidly disintegrate silk. Even when somewhat diluted, boiling hydrochloric acid has an action on silk, but when very dilute has little action other than to remove the sericin. The action of hydrochloric acid on silk is valuable in its detection.

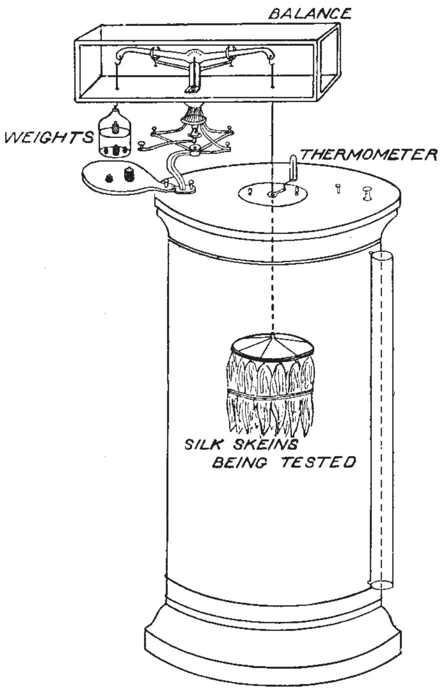


Fig. 15.

Concentrated nitric acid rapidly destroys silk, dissolving it to a yellow solution, but dilute acid simply colors the fibre yellow. This latter reagent may be used for distinguishing silk from vegetable fibres.

Concentrated sulphuric acid dissolves silk to a brown viscous solution. Warm dilute sulphuric acid, however, simply dissolves the sericin of the raw silk and may be used in the degumming process.

Most other acids, as phosphoric and arsenic, act as dilute mineral acids. Dilute acetic acid, even when hot, has no injurious action, and is in fact used to brighten dyed silk. Silk, however, will completely dissolve when heated under pressure with glacial acetic acid.

Sulphur dioxide, either gaseous or dissolved in water, destroys the yellow color of silk, and is consequently sometimes used to bleach it.

81. Alkalies. Concentrated solutions of the caustic alkalies, especially when hot, dissolve silk rapidly, but at a low temperature the action is slight. Very dilute solutions of the caustic alkalies, potassium and sodium, dissolve the sericin without attacking the fibroin, but as the tendency is to diminish the whiteness and brilliancy of the fibre, they cannot well be used in the degumming process.

The alkaline carbonates, potassium and sodium, have a similar action to caustic alkalies, but are less energetic. Ammonia has but little action. Soap and borax have no appreciable effect upon the true silk fibre, or fibroin, although they dissolve sericin. For this reason they are valuable in the silk-degumming process.

Lime renders silk brittle and impairs its lustre.

82. Oxidizing Agents. Chlorine or hypochlorites, if at all concentrated, will destroy silk. Very dilute solutions of these reagents give silk an increased affinity for certain coloring matters, but their action is nevertheless detrimental to the strength of the fibre.

Chromic acid destroys silk, bichromate of potash turns it yellow, and permanganate of potash gives it a brown color.

83. Metallic Salts. Silk behaves similar to wool in respect to its action toward such salts as those of aluminum, iron and tin. When silk is steeped in cold and not too dilute solutions of these salts, absorption takes place, which is probably due to the formation of metallic hydrates or insoluble basic salts, on or in the substance of the fibre.

The mordanting and weighting of silk depend upon this fact, but will be discussed more fully under their respective heads.

84. *Solvents of Silk Fibre.* The following may be mentioned as the best solvents of silk: Concentrated hydrochloric acid (see Art. 80). Zinc chloride solution 140° Tw. will dissolve silk to a thick, sticky liquid. Schweitzer's reagent also dissolves silk.

85. *Action of Coloring Matters.* Silk, like wool, has a strong affinity for, and can be dyed directly with, most of the artificial coloring matters except the true mordant dyestuffs. Silk has but little attraction for mineral coloring matters.

86. *Wild Silks.* There comes to the market, chiefly from India, fibres produced by silk moths other than the common silk moth already described. The most important of these are the Tussah, Eria, Muga, Atlas, and Yama Mai. Of these the Tussah silk is the most common, and is used in considerable quantity in the manufacture of plushes.

Physically, wild silks differ from the mulberry silk in that the fibre is commonly longer and of greater diameter, and each individual fibre is composed of a large number of fibres, which gives it a striated appearance when viewed under the microscope. It is also darker in color than the mulberry silk.

In general, Tussah silk is not as readily acted upon by reagents as the mulberry silk.

SPECIFIC GRAVITY OF LIQUIDS.

The specific gravity (commonly written Sp. G.) of any liquid is the ratio between the weight of a certain volume of that liquid and the weight of an equal volume of water at the same temperature.

Water at 4° C or 39.2° F is usually taken as the standard, this being one of the constants of water, namely, the temperature at which it is at its maximum density and minimum volume; but this is not strictly adhered to, for it is often convenient to use a temperature more easily obtained, namely, 15.5° C or 60° F.

As commonly used, the number expressing specific gravity represents the number of times heavier or lighter the liquid under consideration is than an equal volume of water at the same temperature, or to express it as a formula,

$$\text{Sp. G. of any Liquid} = \frac{\text{Weight of a Given Volume of that Liquid}}{\text{Weight of an Equal Volume of Water at same Temp.}}$$

Thus, if 15 cubic centimeters of a sample of sulphuric acid at 4° C weigh 26.85 grams, and 15 cubic centimeters of water at 4° C 15 grams, then the Sp. G. of the sulphuric acid equals

$$\frac{26.85}{15} = 1.79$$

If 50 cubic centimeters of alcohol at 4° C weigh 40.30 grams, and 50 cubic centimeters of water at 4° C weigh 50 grams, then Sp. G. of the alcohol equals

$$\frac{40.30}{50} = .806$$

When the highest degree of accuracy is desired, the Sp. G. of a liquid is determined by weighing equal volumes of the liquid and water, under the proper conditions, on a delicate balance, using for the container a small capillary stoppered flask, known as a specific gravity bottle, or picnometer. (See Fig. 16.) For ordinary purposes, however, instruments called hydrometers are used.

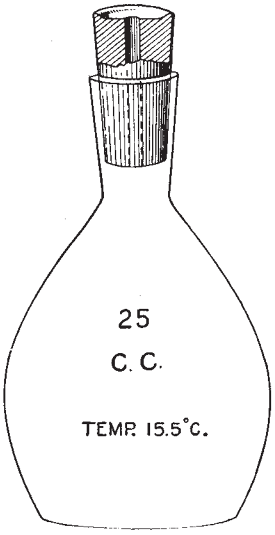


Fig. 16.

Hydrometers (see Fig. 17) are commonly made of glass and consist essentially of: a cylindrical bulb or sealed air-chamber, A (Fig. 18), which gives the instrument sufficient buoyancy to cause it to float in liquids; a long cylindrical stem, C, and a small spherical bulb, B, at the bottom, containing shot or mercury, which brings the center of gravity low enough to keep the stem, C, in an upright position when the hydrometer is placed in a liquid.

The buoyancy or weight-supporting power of a heavy liquid being greater than that of a lighter one, the stem of any particular hydrometer will always extend farther above the surface of a heavy liquid than it will of a lighter one, and the distance to which the stem is exposed will always remain constant for liquids of the same Sp. G. Upon this fact is based the usefulness of the hydrometer.

Hydrometers are graduated in such a way that the Sp. G., in some terms or other, can be read directly by observing the marking on the stem coinciding with the surface of the liquid.

Several different systems of graduation are used.

For scientific purposes the regular decimal scale is used, as

Water = Sp. G. 1.000
Concent. Sulphuric Acid = 1.845
Alcohol = .806

but in many industrial establishments, and in the chemical trade, the use of other scales which record the Sp. G. in degrees is common.

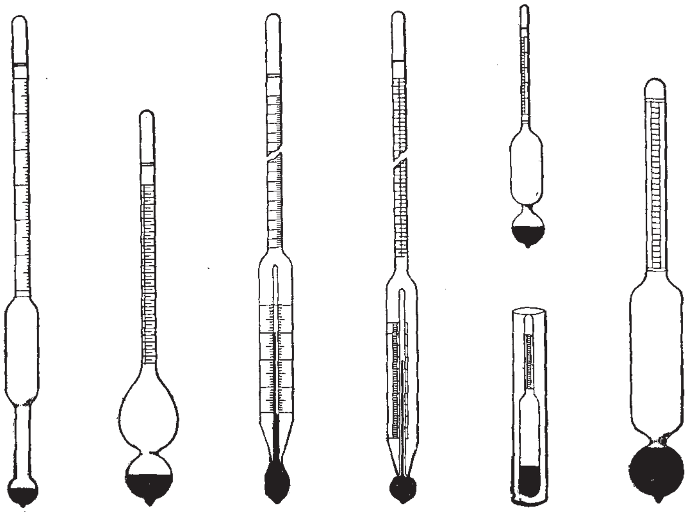


Fig. 17.

Of these scales the Beaumé and Twaddle are by far the most important in the United States. The former being used extensively in chemical works and by oil manufacturers, while the latter is in general use in dyehouses, bleacheries and print works.

The Beaumé scale, which is arbitrary as far as any exact expression of Sp. G. is concerned, assumes, for liquids heavier than water, the 0° on the scale as representing the Sp. G. of pure water, and 15° as the Sp. G. of a solution made by dissolving 3 parts of common salt in 17 parts of pure water. The space on the stem between these two points is divided into 15 equal divisions or degrees, and these divisions are continued as high as 70°.

For liquids lighter than water the length of the division or degree is established by calling the Sp. G. of a solution of 1 part common salt in 9 parts of pure water 0° and pure water 10°.

On hydrometers for liquids heavier than water, the graduation for pure water is at the top of the stem, while for liquids lighter than water it is at the bottom.

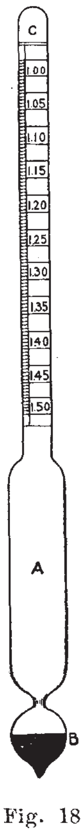


Fig. 18.

On the Twaddle scale, which is also expressed in degrees, one division or degree corresponds to .005 Sp. G.

Thus, water Sp. G. 1.000 = 0° Tw.
Sp. G. 1.005 = 1° Tw.
Sp. G. 1.010 = 2° Tw.
Sp. G. 1.015 = 3° Tw.
Sp. G. 1.250 = 50° Tw.
Sp. G. 1.500 = 100° Tw.

To convert ordinary Sp. G. to degrees Twaddle, subtract 1.000 and divide by .005.

Thus, Sp. G. 1.35 = 1.350
1.000
.005) .350
71° Tw.

To convert degrees Twaddle into Sp. G., multiply by .005 and add 1.000.

Thus, 71° Tw. = 71 × .005 = .355
1.000
1.355 = Sp. G.

For the conversion of Beaumé degrees into Twaddle degrees or actual specific gravity readings, or *vice versa*, a table is necessary.

Table A, see page 44, will be found handy for reference and conversion.

The great value of the hydrometer lies in the simplicity with which the instrument may be used for determining the strength of various acids and solutions of chemicals.

In general, the Sp. G. of a solution of a substance or mixture of an acid with water increases as the ratio of the amount of substance or acid to the amount of water increases.

For a given amount of any substance dissolved in a given amount of pure water, however, the Sp. G. remains constant.

Thus the Sp. G. of an 8 per cent solution of caustic soda = 1.091, and of a 40 per cent solution of caustic soda = 1.438.

These amounts remaining constant at the temperature at which they were determined, all that is necessary, if we wish to make up an 8 per cent or 40 per cent solution, is to add caustic soda to water, until the hydrometer registers the corresponding Sp. G.

Tables have been carefully prepared which give the Sp. Gravities corresponding to various percentage strengths of solutions of all the common chemicals and acids, and to determine the strength of such a solution it is only necessary to take the hydrometer reading and consult the table.

Many books containing Sp. G. tables exist, and one should be kept with the necessary hydrometers and cylinders in every well-regulated dyehouse.

Table B, see page 44 for caustic soda, will serve as a good example.

For a mixture of water with a liquid that is lighter, as alcohol, the Sp. G. diminishes as the ratio of the liquid to the water increases. The Sp. G. of the solutions of certain gases in water, as ammonia, also diminishes as the percentage of gas dissolved increases.

As already stated, the standard temperature for testing liquids by hydrometers is 60° F or 15.5° C. Hydrometers are graduated for this temperature, and for accurate work liquids should always be brought to the standard temperature. If the temperature of liquids heavier than water is above 60° F, the reading will be too low, and if below, the reading will be too high. For liquids lighter than water the reverse will be the case. The hydrometers supplied by the makers are often inaccurate, and should be tested by comparison with the specific gravity bottle or with hydrometers known to be correct.

The Beaumé hydrometer is founded on an arbitrary standard, which varies in Europe and America. The readings of the American standard are slightly below those of the English standard. This fact should be noted when using tables.

TABLE A.

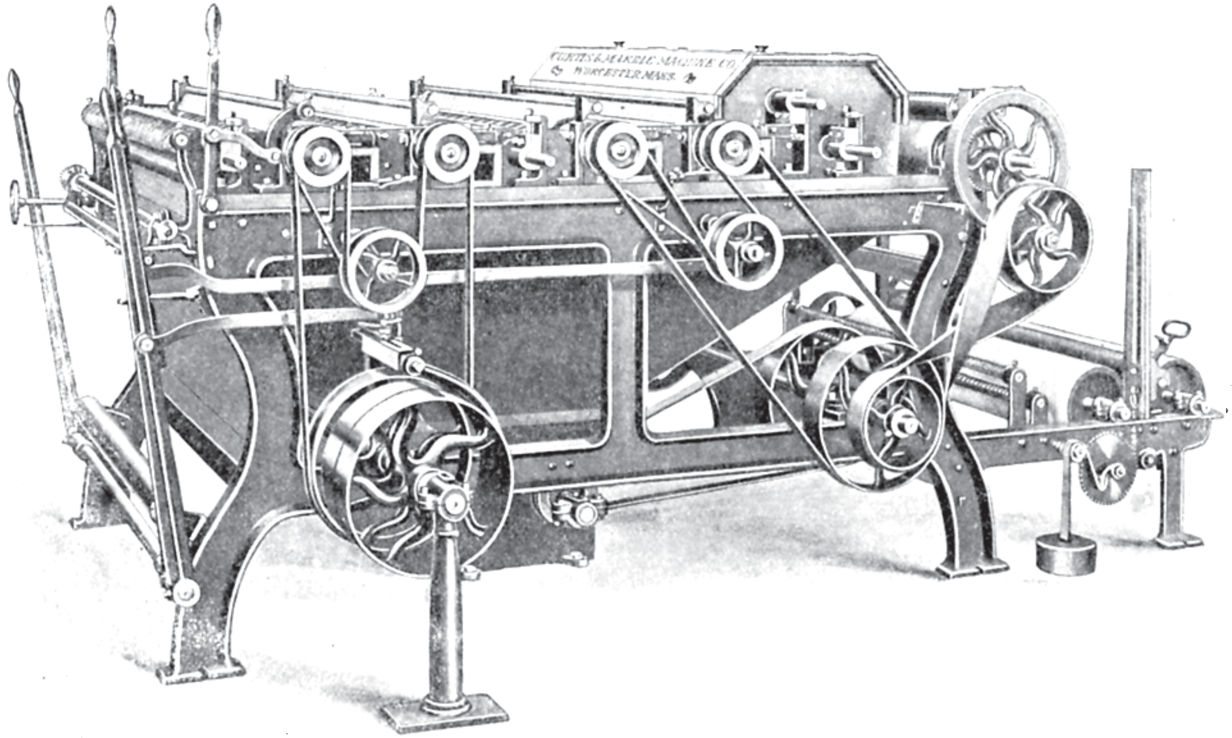
SPECIFIC GRAVITY, DEGREES TWADDLE AND DEGREES BEAUME.

Twaddle.	Beaumé.	Specific gravity.	Twaddle.	Beaumé.	Specific gravity.	Twaddle.	Beaumé.	Specific gravity.	Twaddle.	Beaumé.	Specific gravity.
0	0	1.000	44	26.0	1.220	88	44.1	1.440	132	57.4	1.660
1	0.7	1.005	45	26.4	1.225	89	44.4	1.445	133	57.7	1.665
2	1.4	1.010	46	26.9	1.230	90	44.8	1.450	134	57.9	1.670
3	2.1	1.015	47	27.4	1.235	91	45.1	1.455	135	58.2	1.675
4	2.7	1.020	48	27.9	1.240	92	45.4	1.460	136	58.4	1.680
5	[illegible]	1.025	49	28.4	1.245	93	45.8	1.465	137	58.7	1.685
6	4.1	1.030	50	28.8	1.250	94	46.1	1.470	138	58.9	1.690
7	4.7	1.035	51	29.3	1.255	95	46.4	1.475	139	59.2	1.695
8	5.4	1.040	52	29.7	1.260	96	46.8	1.480	140	59.5	1.700
9	6.0	1.045	53	30.2	1.265	97	47.1	1.485	141	59.7	1.705
10	6.7	1.050	54	30.6	1.270	98	47.4	1.490	142	60.0	1.710
11	7.4	1.055	55	31.1	1.275	99	47.8	1.495	143	60.2	1.715
12	8.0	1.060	56	31.5	1.280	100	48.1	1.500	144	60.4	1.720
13	8.7	1.065	57	32.0	1.285	101	48.4	1.505	145	60.6	1.725
14	9.4	1.070	58	32.4	1.290	102	48.7	1.510	146	60.9	1.730
15	10.0	1.075	59	32.8	1.295	103	49.0	1.515	147	61.1	1.735
16	10.6	1.080	60	33.3	1.300	104	49.4	1.520	148	61.4	1.740
17	11.2	1.085	61	33.7	1.305	105	49.7	1.525	149	61.6	1.745
18	11.9	1.090	62	34.2	1.310	106	50.0	1.530	150	61.8	1.750
19	12.4	1.095	63	34.6	1.315	107	50.3	1.535	151	62.1	1.755
20	13.0	1.100	64	35.0	1.320	108	50.6	1.540	152	62.3	1.760
21	13.6	1.105	65	35.4	1.325	109	50.9	1.545	153	62.5	1.765
22	14.2	1.110	66	35.8	1.330	110	51.2	1.550	154	62.8	1.770
23	14.9	1.115	67	36.2	1.335	111	51.5	1.555	155	63.0	1.775
24	15.4	1.120	68	36.6	1.340	112	51.8	1.560	156	63.2	1.780
25	16.0	1.125	69	37.0	1.345	113	52.1	1.565	157	63.5	1.785
26	16.5	1.130	70	37.4	1.350	114	52.4	1.570	158	63.7	1.790
27	17.1	1.135	71	37.8	1.355	115	52.7	1.575	159	64.0	1.795
28	17.7	1.140	72	38.2	1.360	116	53.0	1.580	160	64.2	1.800
29	18.3	1.145	73	38.6	1.365	117	53.3	1.585	161	64.4	1.805
30	18.8	1.150	74	39.0	1.370	118	53.6	1.590	162	64.6	1.810
31	19.3	1.155	75	39.4	1.375	119	53.9	1.595	163	64.8	1.815
32	19.8	1.160	76	39.8	1.380	120	54.1	1.600	164	65.0	1.820
33	20.3	1.165	77	40.1	1.385	121	54.4	1.605	165	65.2	1.825
34	20.9	1.170	78	40.5	1.390	122	54.7	1.610	166	65.5	1.830
35	21.4	1.175	79	40.8	1.395	123	55.0	1.615	167	65.7	1.835
36	22.0	1.180	80	41.2	1.400	124	55.2	1.620	168	65.9	1.840
37	22.5	1.185	81	41.6	1.405	125	55.5	1.625	169	66.1	1.845
38	23.0	1.190	82	42.0	1.410	126	55.8	1.630	170	66.3	1.850
39	23.5	1.195	83	42.3	1.415	127	56.0	1.635	171	66.5	1.855
40	24.0	1.200	84	42.7	1.420	128	56.3	1.640	172	66.7	1.860
41	24.5	1.205	85	43.1	1.425	129	56.6	1.645	173	67.0	1.865
42	25.0	1.210	86	43.4	1.430	130	56.9	1.650			
43	25.5	1.215	87	43.8	1.435	131	57.1	1.655			

TABLE B.

SPECIFIC GRAVITY OF CAUSTIC SODA AT 15° (LUNGE).

Specific gravity.	Beaumé.	Twaddle.	Per cent Na_2O	Per cent NaOH	Specific gravity.	Beaumé.	Twaddle.	Per cent Na_2O	Per cent NaOH
1.007	1	1.4	0.47	0.61	1.220	26	44.0	15.18	19.58
1.014	2	2.8	0.93	1.20	1.231	27	46.2	15.96	20.59
1.022	3	4.4	1.55	2.00	1.241	28	48.2	16.76	21.42
1.029	4	5.8	2.10	2.71	1.252	29	50.4	17.55	22.64
1.036	5	7.2	2.60	3.35	1.263	30	52.6	18.35	23.67
1.045	6	9.0	3.10	4.00	1.274	31	54.8	19.23	24.81
1.052	7	10.4	3.60	4.64	1.285	32	57.0	20.00	25.80
1.060	8	12.0	4.10	5.29	1.297	33	59.4	20.80	26.83
1.067	9	13.4	4.55	5.87	1.308	34	61.6	21.55	27.80
1.075	10	15.0	5.08	6.55	1.320	35	64.0	22.35	28.83
1.083	11	16.6	5.67	7.31	1.332	36	66.4	23.20	29.93
1.091	12	18.2	6.20	8.00	1.345	37	69.0	24.20	31.22
1.100	13	20.0	6.73	8.68	1.357	38	71.4	25.17	32.47
1.108	14	21.6	7.30	9.42	1.370	39	74.0	26.12	33.69
1.116	15	23.2	7.80	10.06	1.383	40	76.6	27.10	34.96
1.125	16	25.0	8.50	10.97	1.397	41	79.4	28.10	36.25
1.134	17	26.8	9.18	11.84	1.410	42	82.0	29.05	37.47
1.142	18	28.4	9.80	12.64	1.424	43	84.8	30.08	38.80
1.152	19	30.4	10.50	13.55	1.438	44	87.6	31.00	39.99
1.162	20	32.4	11.14	14.37	1.453	45	90.6	32.10	41.41
1.171	21	34.2	11.73	15.13	1.468	46	93.6	33.20	42.83
1.180	22	36.0	12.33	15.91	1.483	47	96.6	34.40	44.38
1.190	23	38.0	13.00	16.77	1.498	48	99.6	35.70	46.15
1.200	24	40.0	13.70	17.67	1.514	49	102.8	36.90	47.60
1.210	25	42.0	14.40	18.58	1.530	50	106.0	38.00	49.02



COTTON SHEARING MACHINE DESIGNED FOR PRINTERIES, BLEACHERIES, ETC.

Curtis & Marble Machine Co.

TEXTILE CHEMISTRY AND DYEING.

PART II.

OPERATIONS PRELIMINARY TO DYEING.

87. Necessity of a Preliminary Treatment of Textile Material and the Three Stages of the Manufacturing Process during which this Treatment may be Performed. All fibers contain a varying amount of impurities both natural and foreign. These must be removed before the fibers are of such a character as to be used for the production of white goods or to be dyed delicate tints or light shades. This necessitates that most textile materials be given certain preliminary treatments before they can be used for the above purposes.

These preliminary treatments may be given: —

1st. When the fiber is in the loose or unspun state, as is customary with wool.

2d. When it has been spun and is in the form of yarn as is the case with silk.

3d. When it has been woven and is in the form of cloth, as is commonly the case with cotton.

COTTON BLEACHING.

88. Natural Impurities of Cotton. It has previously been stated (See No. 13) that the approximate composition of raw cotton is,

Cellulose	87 to 90%
Water	5 to 7%
Natural Impurities	4 to 6%

These natural impurities are for the most part insoluble in water, but may be removed by the use of certain acids and alkalies. If we boil unbleached cotton in a clear solution of soda ash, the solution gradually assumes a dark brown color. By adding sulphuric acid to this solution a dark colored flocculent precipitate is thrown down which contains the greater portion of natural impurities. (See No. 16.)

89. Foreign Impurities in Cotton. Beside containing natural impurities, cotton that has been made into yarn or cloth, picks up from the various machines through which it passes and from the hands of the operatives, a varying amount of foreign dirt and grease. Furthermore a varying amount of sizing material, composed largely of organic matter is added to the warp previous to the process of weaving, and the cloth when it arrives at the bleachery invariably has a grayish and dirty appearance, and the total amount of impurities may run as high as 30% of the weight of the cloth.

90. Object of Bleaching. Cotton bleaching has for its object the complete removal of these natural and foreign impurities, in order that the cloth may be sold in a pure white state and to prepare it for the dyeing of delicate tints or light shades, or the production of perfectly white grounds in calico printing. The bleaching of *back cloths* is also an important consideration. In calico printing it is customary to print on bleached cotton cloth, constantly keeping between this cloth and the padding blanket, a piece of unbleached or gray cloth which owing to the shrinkage in bleaching is several inches wider than the bleached piece that is being printed. This intermediate piece of cloth is known as the *back cloth* and serves to protect the blanket from any color that may strike through or lap over the printed cloth.

Three general principles are commonly involved in the accomplishment of these results; 1st, the removal of such impurities as are soluble in water, by simple washing; 2d, the conversion of others by the action of various chemical reagents into compounds soluble in water, which are then easily removed by subsequent washing, and finally the decolorization of any remaining impurities which have resisted previous treatment.

91. Three States in which Cotton may be Bleached. It is possible to bleach cotton in the three states, namely, raw or loose state, in the form of yarn, or as cotton cloth or piece goods. The latter will be considered first.

92. Bleaching of Cotton Piece Goods. General Consideration. By far the most important and extensively used form of cotton bleaching is that of woven cloth commonly called piece goods.

The bleaching of cotton cloth is rendered more complicated and laborious, than that of cotton yarn or raw cotton, for the two latter contain little other than natural impurities, while the cotton cloth contains a high percentage of foreign impurities introduced during the process of weaving, by oily machinery, greasy hands, and to a still greater extent in the form of warp sizing. The following are some of the substances that may be used in sizing; farina, starch, soap, tallow, paraffin wax, small quantities of copper and lime soaps, and certain inorganic compounds such as the sulphates of magnesium and barium and the chlorides of magnesium and zinc. The total impurities in the woven cloth may amount to as high as 25 to 30%. Not only do all these impurities have to be removed, but in many cases the back cloths (See No. 90), which may be daubed with any of the colors used in a print works, have to be bleached.

Different bleachers have different ideas in regard to bleaching and it is doubtful if two bleacheries, not under the same management, could be found using the same process in every detail. It is only the detail however that varies, for the principles involved have remained the same for more than a half century.

The almost universal bleaching agent for cotton is chlorine, it commonly being liberated from bleaching powder or calcium hypochlorite during the bleaching process.

The bleaching proper is usually preceded by boiling the material in one or more alkaline baths to facilitate the removal of those impurities which the chlorine would not destroy. In addition several treatments with dilute acid, and thorough washings are necessary at various stages of the process.

93. Grades of Bleaching. There are several grades of bleached cotton cloth which differ chiefly in the thoroughness with which the bleaching has been carried out. As examples we have,

(1). Madder Bleach, which is the commonest.
(2). Turkey Red Bleach.
(3). Market Bleach.
(4). Rapid Bleach, where the cloth is to be dyed a dark shade.

The bleach applied in any particular case, depends upon the manner in which the cloth is to be finished or subsequently used. Each will be treated separately beginning with the madder bleach, the process for which will be given in detail including a description of the apparatus used. The others will be given with only sufficient detail to show wherein they differ from the madder bleach.

94. The Madder Bleach. (Origin of Name and when used.) In the days when madder was so extensively used, it was customary to give cloth printed with that dye stuff an extremely thorough bleach. At the present time madder has been entirely replaced by other dye stuffs, especially the alizarines, but the name Madder Bleach is still used in many bleacheries, and we will use it to represent the most thorough form of bleaching in use to-day for cotton piece goods. The process has been changed but little since its introduction, about the year 1835.

In calico printing with alizarine colors, or in fact any colors, where a particularly clear and white ground is desired this form of bleach is used.

95. Outline of the Madder Bleach. The following may be taken as an outline of the steps in the Madder Bleach.

(1). Stamping and Stitching.
(2). Singeing and Shearing.
(3). Wash following singeing. (Gray Wash.)
(4). Lime Boil.
(5) Wash.
(6). Acid Treatment. (Sometimes called the Brown Sour.)
(7) Wash.

(8-9). Lye Boils. (Resin Soap and Alkali.)
(10). Wash.
(11). Chemicking or Bleaching Proper.
(12). Wash.
(13). Acid Treatment. (Sometimes called White Sour.)
(14). Final Wash.
(15). Finishing.

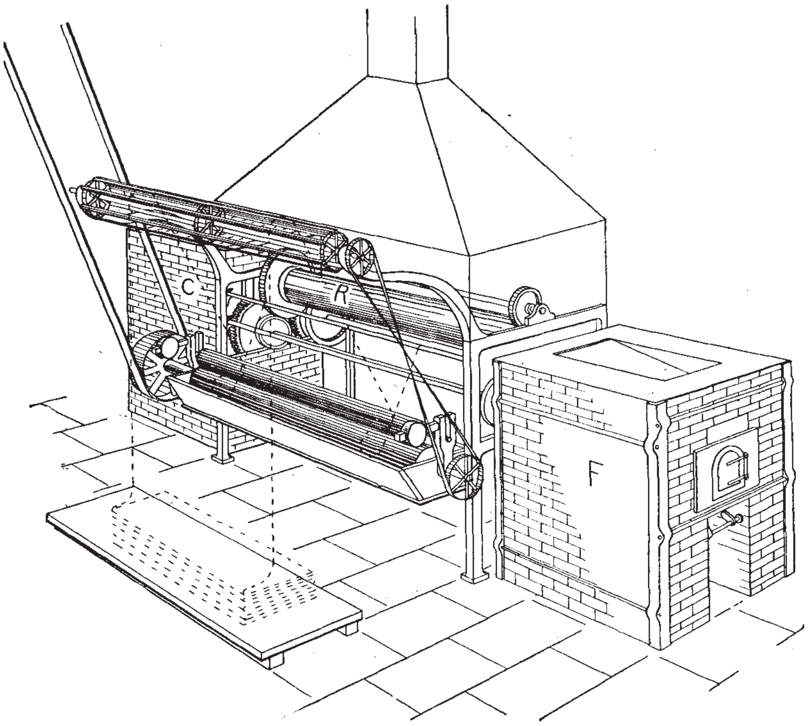
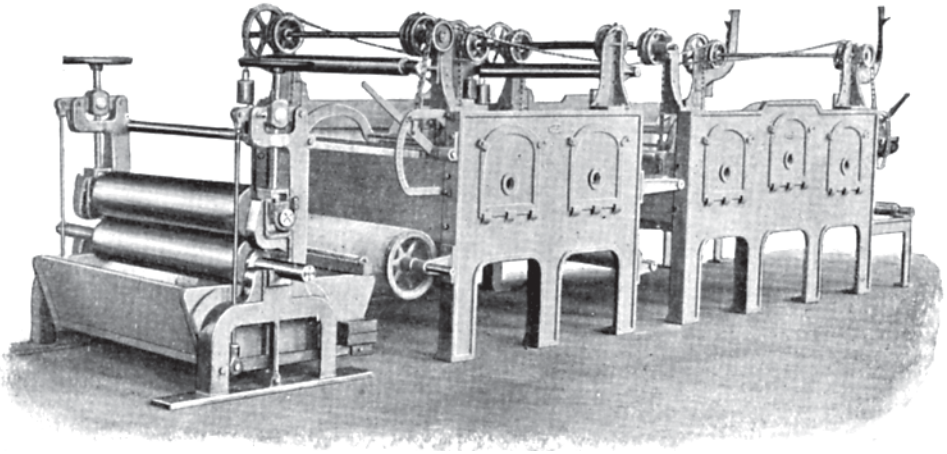


Fig. 19. Roller Singeing Machine.

96. Stamping and Stitching. Each separate piece of cloth as it is taken from the bale or roll, is stamped with a system of letters and figures, so that it can be identified at any time during the subsequent processes. In the stamping, some substance such as coal tar or aniline black must be used which will not be destroyed during the bleaching.

These pieces of cloth, which contain in the neighborhood of fifty yards each, are placed end to end and stitched together on a



SINGEING MACHINE, OIL FUEL

H. W. Butterworth & Sons Co.

portable sewing machine. As many as 800 pieces are sometimes fastened together in this way making a continuous strip 4,000 yards or nearly 25 miles long. Such a piece is called a "lot."

97. Shearing and Singeing. The surface of the gray cloth always possesses more or less unevenness owing to loose threads and projecting motes; also a fuzziness or nap, all of which must be removed before the surface possesses the necessary smoothness for printing. With this in view the gray cloth is always subjected to the singeing operation, and not unfrequently passed through a shearing machine. When both machines are used, the cloth passes through the shearing machine which removes the large threads and heavier nap and then through the singeing machine which takes off the lighter nap and clears the fabric. A combination machine to perform both operations is sometimes used.

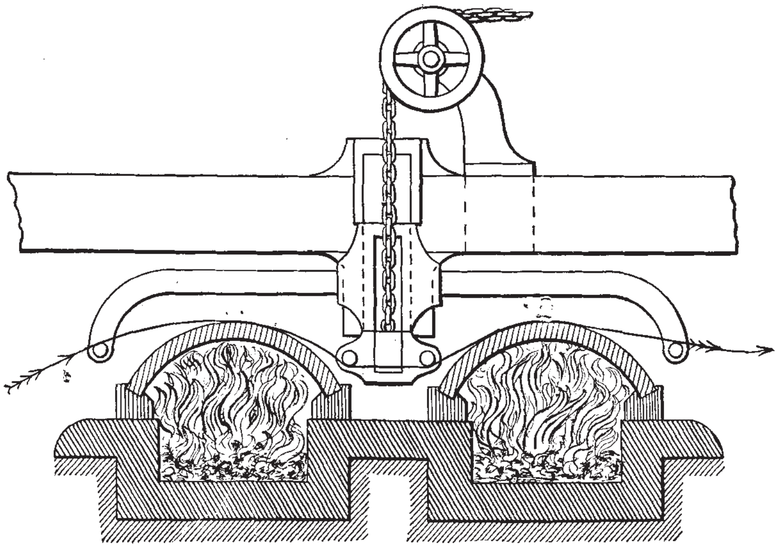


Fig. 20. Principle of Plate Singeing.

The principle of the singeing is to pass the cloth over heated metallic rolls or plates, or through a series of gas flames, at such a speed as to allow the surface inequalities and nap to be burned off without burning the body of the fabric.

In the roller singeing machine (See Fig. 19) the cloth is passed in the full width over a hollow roller R that is kept at a red heat by the passage of the flame from the furnace F, through it to the chimney C.

The principle of the plate singeing will be easily understood from Fig. 20. The plates are usually of copper and may be heated by coal, petroleum, or gas. Fig. 21 shows a plate singer in operation.

Gas singeing machines vary somewhat in construction, but (Fig. 22) will serve as a good illustration. The cloth is passed full width through one or more series of gas flames, coming from rows of Bunsen burners. The principle will be easily understood from Figs. 23 and 24. The flames come in contact with the cloth while the latter is being passed with considerable tension over the rolls N N. This causes the nap to stand out as much as possible. B in Fig. 23 represents the end burner of the series, and H a hood through which a draught is constantly passing.

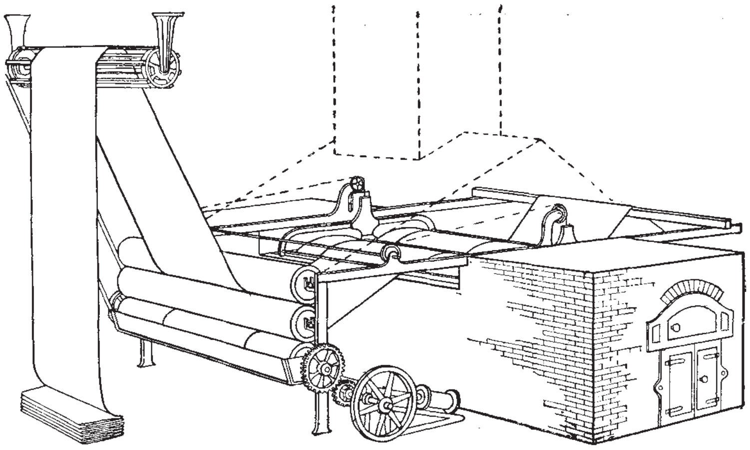


Fig. 21. Plate Singer in Operation.

Upon leaving the singeing machine the cloth is often passed rapidly through water, or a steam box, in order to extinguish any sparks that might remain upon the surface.

Concerning the relative value of plate and gas singeing, it may be said that with the former the surface is very thoroughly singed, with little if any singeing between the threads; while with gas singeing there is less action upon the surface, but greater penetration between the threads. By many, plate singeing is considered better for heavy goods, and gas singeing more desirable for light fabrics and those of comparatively open weave, and also raised figure goods, and corduroys on account of the unevenness of their surface. For some classes of sateens plate singeing is probably better as it gives a desirable rub finish to the goods.

Machines combining both gas and plate singeing are sometimes used. Fig. 25 represents a type of combination machine made by the Granger Foundry and Machine Co. of Providence. The plates in this machine are heated by petroleum, and rows of flames from the same fuel placed between the plates.

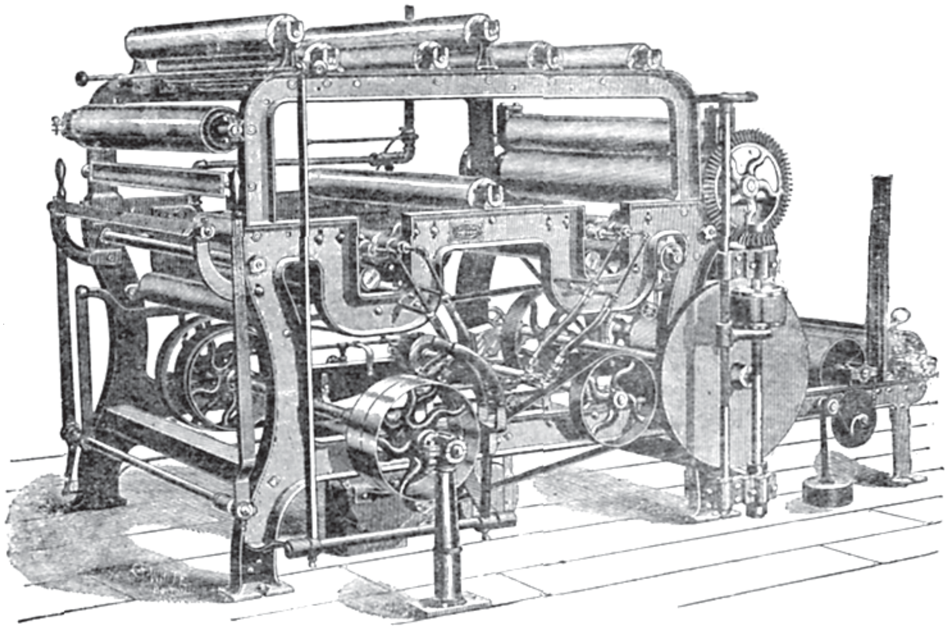


Fig. 22. Elevation of Singeing Machine.

The whole singeing room should be well ventilated, and it is advisable to furnish each machine with a separate hood and forced draught.

Any excess of nap remaining after the bleaching must be removed by shearing, since singeing can never be done successfully after bleaching, owing to the more or less scorched or brown color it imparts to the cloth.

The extent to which the shearing is carried out and the period of the operation at which it is performed, depends upon the nature of the cloth and the uses to which it is to be put.

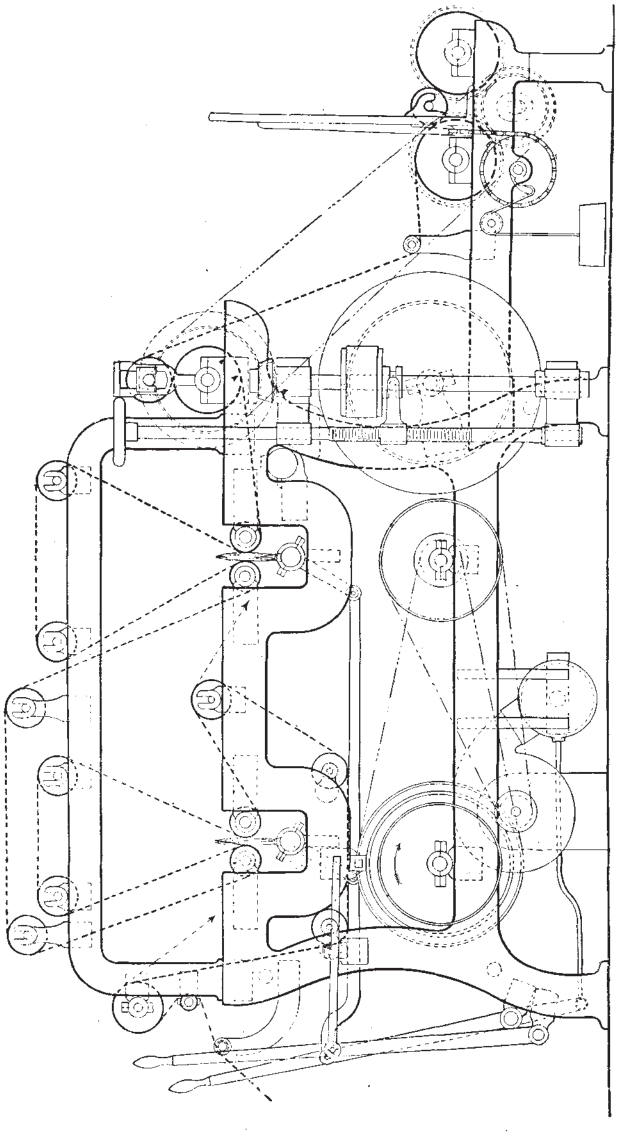


Fig. 22 A. Sectional View of Fig. 22.

The shearing machine consists of a set of very sharp steel blades spirally set into a roller which revolves rapidly, near and parallel to a stationary blade, the whole resembling an inverted lawn mower. (See Fig. 26 B.) The shearing is accomplished by passing the cloth full width between the stationary and the revolving blades. The shearing machines are also equipped with rapidly revolving brushes, which serve to bring out the nap before the shearing and remove the loose fuzz and dust that collects upon the surface of the cloth.

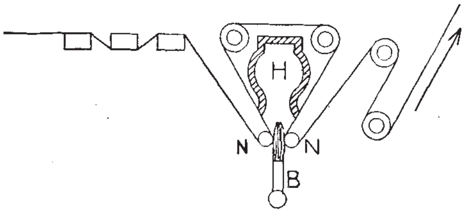


Fig. 23.

One of the standard types of Cotton Shearing Machines for bleacheries built by the Curtis and Marble Machine Co. is shown at Fig. 26. This is made with four sets of shear blades for the face and with brushes for the face and back of the goods; three for the face and one for the back. This machine applies especially to those cotton fabrics where but one side of the cloth is to be sheared. The one or more brushes which apply on the back of the goods are especially valuable since the face and back of the cloth comes in contact with each other when rolled up; so that if dirt or lint be left on the back it is liable to come off on the face when the goods are unrolled, thus giving trouble in the subsequent processes. Shearing machines are made with from four to six sets of shear blade for the face, and any number of brushes for both face and back, according to the requirements of the class of work in hand.

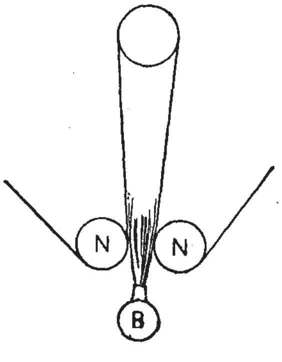


Fig. 24.

Fig. 26 A is a sectional view of this machine showing the threading of the cloth, swing cloth-rests and stop motion for the revolvers. It will thus be seen that the cloth-rests may be raised or the revolvers stopped in order to allow the seams to pass through. The exhaust fan underneath the machine provides means for carrying away dust and lint. This shear may be operated from either side as regards starting and stopping and the lifting of the cloth-rests or stopping of the revolvers. Spreader bars are attached to both the front and delivery ends for taking out wrinkles and turned edges ; these together with the horizontal rolling attachment, causes a smooth even roll to be delivered after shearing.

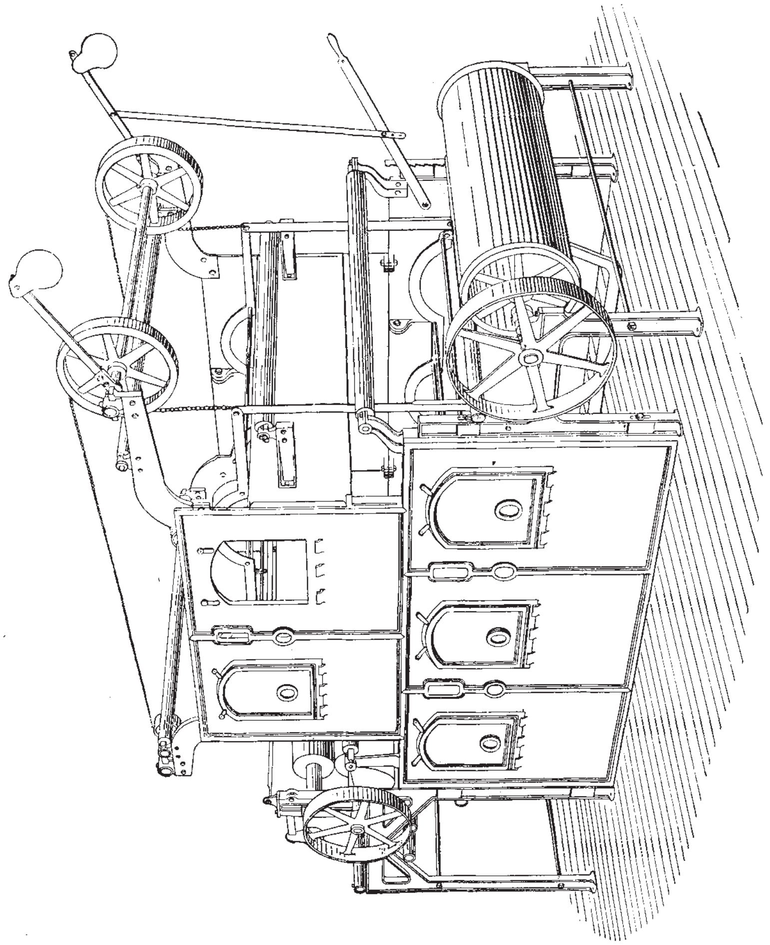


Fig. 25. Combination Plate and Gas Singer.

A simple form of English shearing machine made by Mather

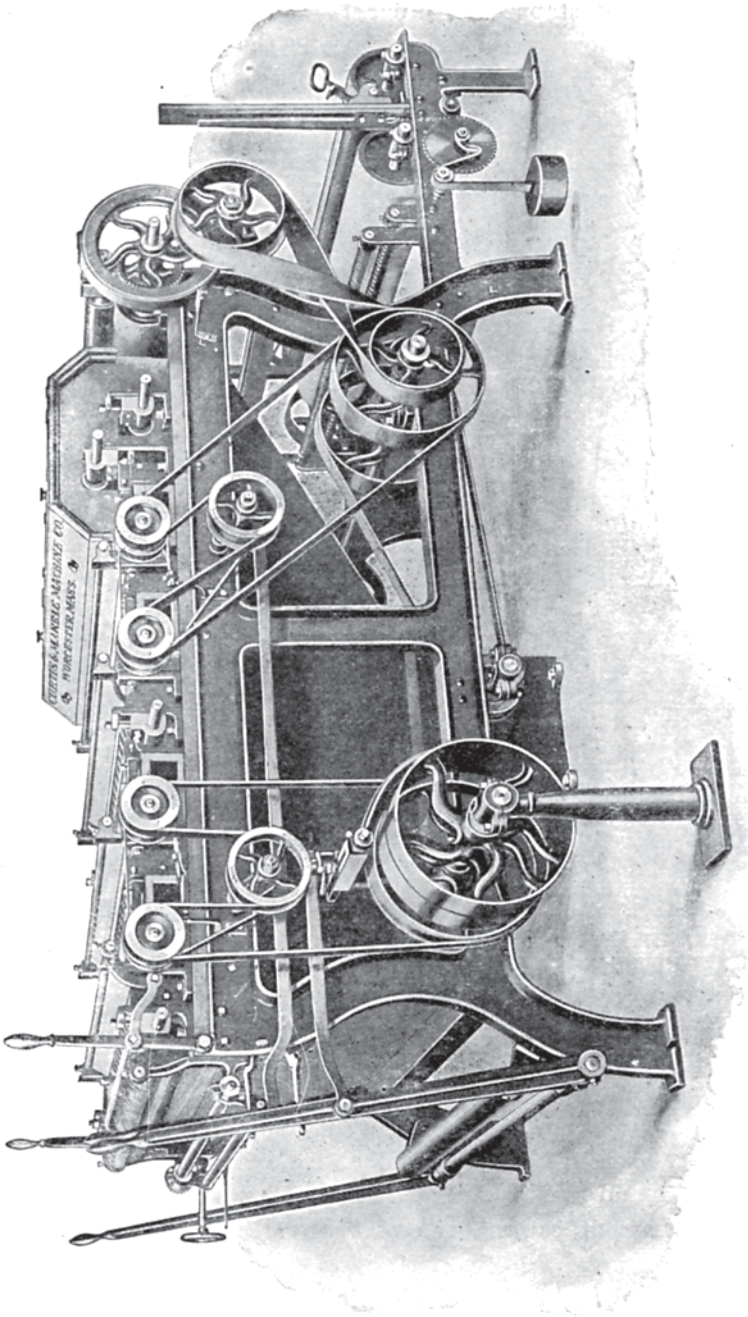


Fig. 26. Elevation of Cotton Shearing Machine.

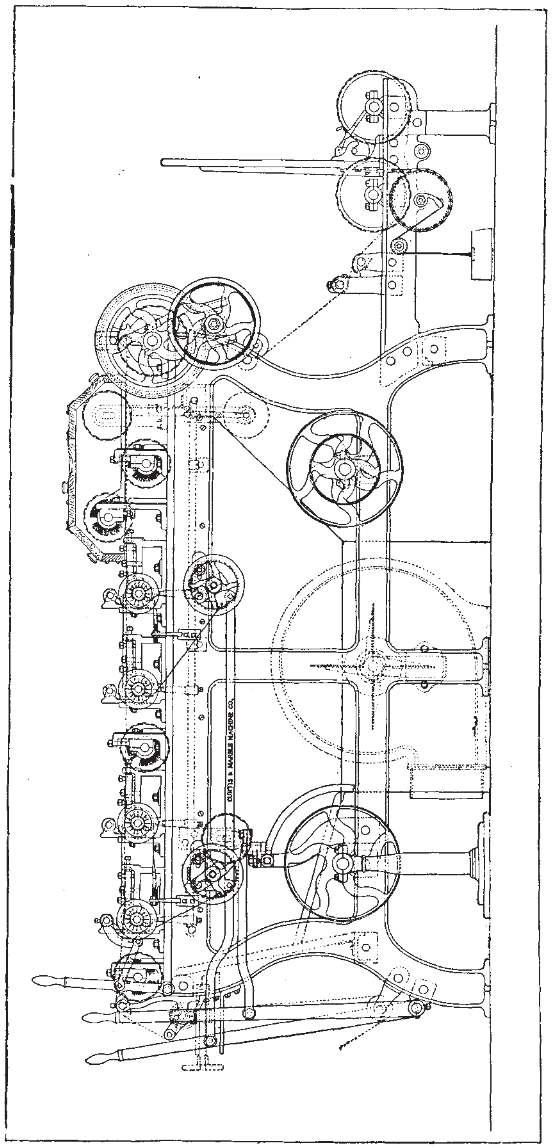


Fig. 26 A. Sectional View of Fig. 26.

& Platt is represented in Fig. 27. This machine is used in cotton print works and bleacheries, where it is necessary to shear but one side of the cloth.

98. The Gray Wash and its Chemistry. Upon leaving the singeing room the cloth is ready for the gray wash, the first step in the actual bleaching process. It is at this stage that the cloth passes from the full width to the rope or string form, as it is called, which form it retains until the bleaching process is completed. This is accomplished (See Fig. 28) by simply allowing the cloth to pass directly from the roll through a smooth porcelain or hard rubber ring (sometimes called a pot eye), about 6 inches in diameter.

The gray wash is usually accomplished by first running the cloth through water in an ordinary washing machine (See Figs. 29 and 30) and then allowing it to stand in the wet or at least damp condition for several hours or even over night.

The object of this washing is to remove everything present in the cloth that is soluble in water, and to attack the surface coating, so that the fiber may become thoroughly wet out and penetrable by liquids. When crowded for room or pushed for time, the cloth may be passed from the washing machine directly through squeeze rolls and into the kier in which the next step of the operation is performed, but it is an established fact than an exposure of cloth to the air in a moist condition for a number of hours renders the remaining impurities more easily removed in the subsequent operations. This is probably due to a mild fermentation of the sizing materials and some of the natural impurities present.

Some bleachers recommend a steeping process in which the water is warmed to between 50° and 60° C. (122° — 140° F.) for a number of hours. Under these conditions the surface coating of the fiber seems to be more energetically attacked. When the lime boil follows, this steeping process is scarcely necessary, but in such processes as the Mather and Platt (See No. 120) where the lime boil is entirely omitted, and in some forms of linen bleaching, it seems advantageous.

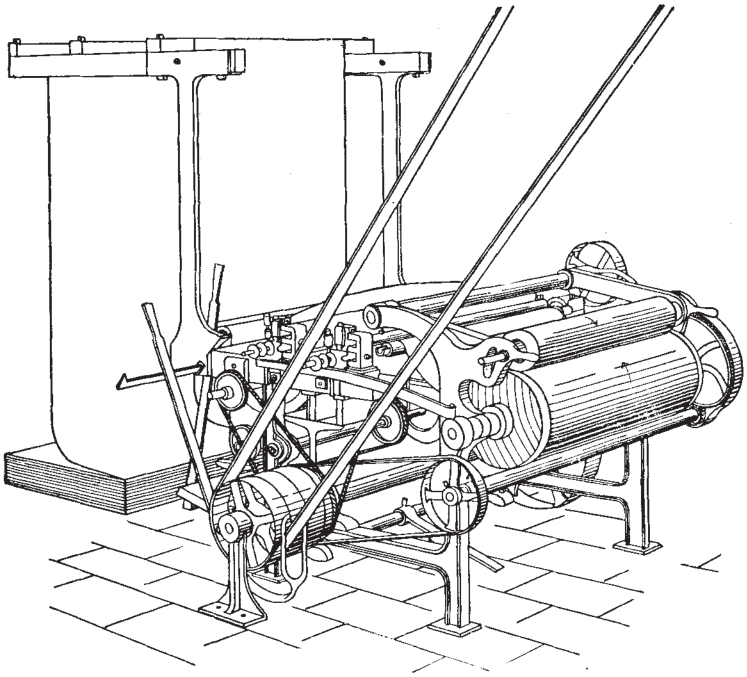


Fig. 27. Mather and Platt Shear.

99. Lime Boil. The lime boil follows the gray wash and consists in boiling, or to use the term of the works, "BOWKING" the cloth in a solution of lime water, calcium hydroxide $Ca(OH)_2$, for a number of hours in an especially constructed boiler known as a kier. (For description of kiers See No. 100.)

The quick lime used should be perfectly white, as nearly pure calcium oxide as possible, and free from iron. If stored before use, care should be taken not to expose it to the air, or it will become air-slaked or carbonated.

The lime is often slaked with water in a wooden bin or box, where the following reaction takes place:

$$CaO + H_2O = Ca(OH)_2$$

Quick Lime + Water = Calcium Hydroxide or Water Slaked Lime.

The Calcium Hydroxide thus formed is of a damp powdery nature, and when mixed with a little water makes a thick paste of a creamy consistency. This is then worked through a sieve into a special mixing apparatus, which commonly consists of an iron tank provided with a mechanical agitator. The sieve should be of such a sized mesh as to completely remove any lumps or particles of quick lime or unslaked lime, for these would tender the cloth if they came in contact with it at the high temperature of the kiers.

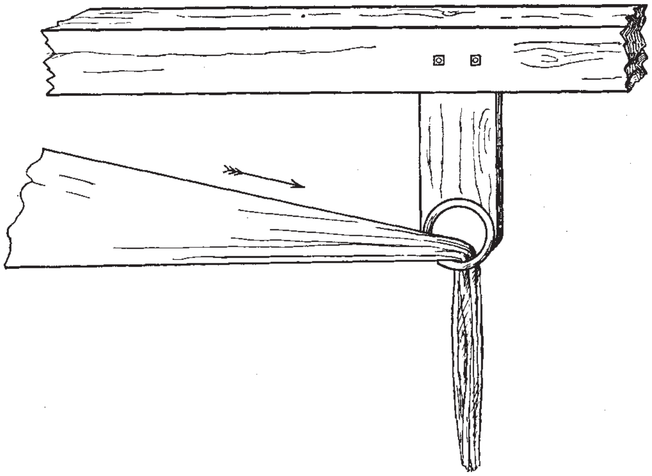


Fig. 28. Pot Eye.

Calcium hydroxide is not extremely soluble in water, and the liquor issuing from the mixing apparatus is not a clear lime water, but a so-called milk of lime having a milky white appearance due to the presence of a large amount of finely divided calcium hydroxide held in suspension.

The milk of lime is run directly into the box or pit of the liming machine, a very common form of which is represented in Figs. 31 A and 32 A. The cloth passes directly through the lime pit A. where it is saturated, and after the excess of liquor has been removed by the squeeze roll B.B., it passes directly into the kier.

The quantity of lime used varies according to the material being bleached, from 3 to as high as 10% of the weight of the material being bleached. For print cloths, however, the amount is commonly from 4 to 6%. Some bleachers think it advantageous to add a small quantity, say one pail full of 50° Twaddle caustic soda solution to the kier after it has been filled.

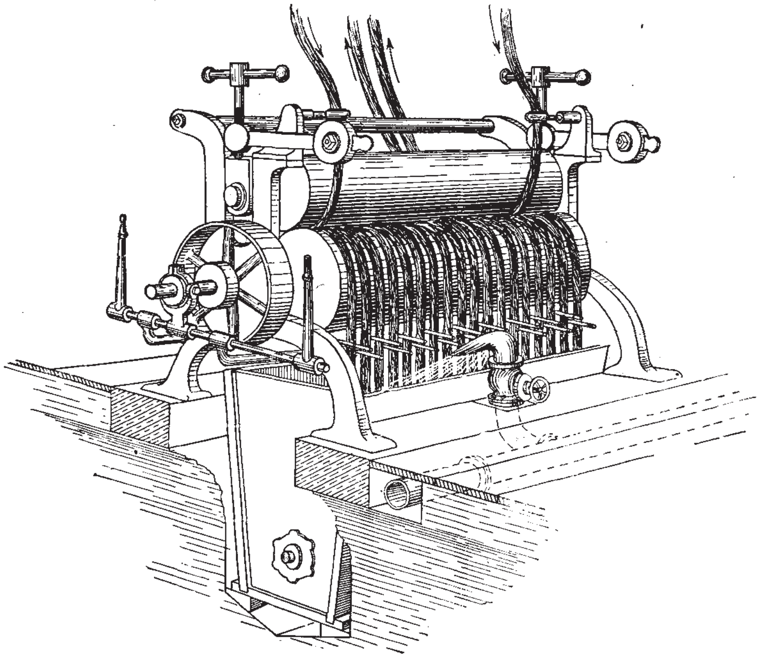


Fig. 29. Washing Machine.

KIERS.

100. To give an account and description of the numerous bleaching kiers that have been used would, even if possible, require much space and be of but little value. We will therefore speak only of the most important forms and give descriptions of some of these in use at the present time.

In general, kiers may be divided into two classes:

(1). Open or Low Pressure Kiers.
(2). Closed or Pressure Kiers.

Open Kiers. One of the oldest forms of open kiers is represented in Fig. 33. It consists of a cylindrical vessel either of iron or wood, 9 or 10 feet in diameter, provided with a false or perforated bottom AA, about 18 inches above the true bottom. It contains a large center pipe or well B B, which is open at the bottom C, and at the top D. Through this large pipe B B, runs a smaller pipe E, through which steam is passed in the direction

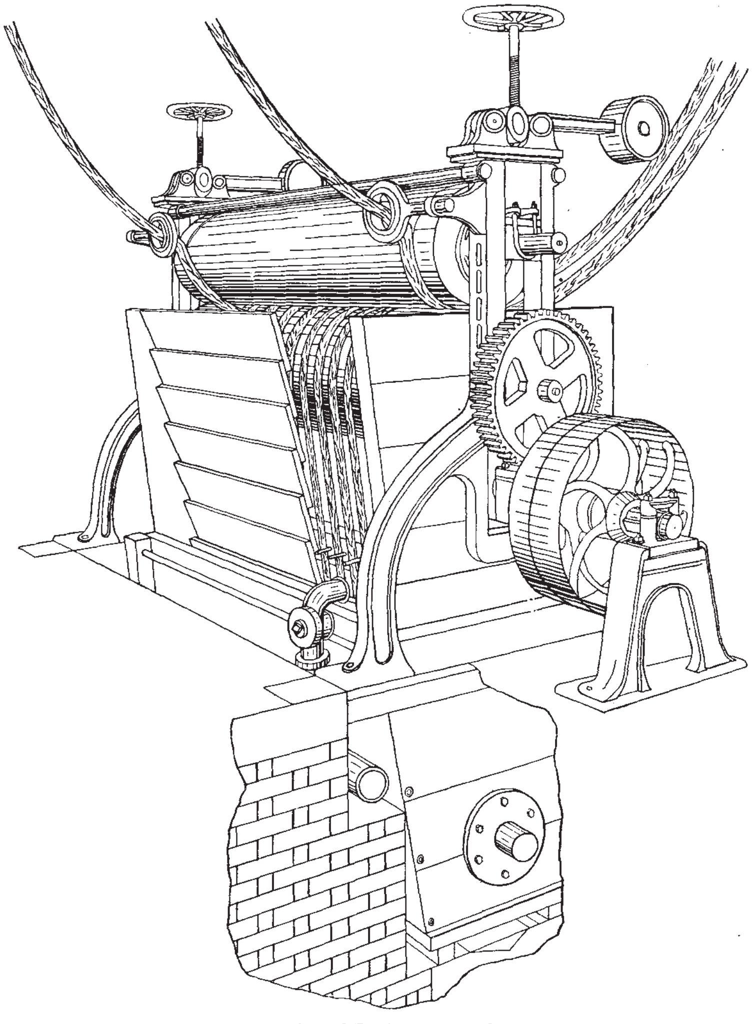


Fig. 30. Washing Machine.

indicated by the arrow head. This steam pipe heats the liquor in BB, and this together with the fact that a certain amount of steam is continually escaping at the bottom through the perforations FF, cause a general movement of the hot liquor up through B, the colder coming in at the bottom opening CC, to take its place, thus keeping up more or less of a circulation. When the rising liquor comes against the Baffle plate or bonnet P, it showers over the surface of the material which is contained in the kier, gradually leaches through it, passes through the false bottom, and is finally brought to the top again through BB.

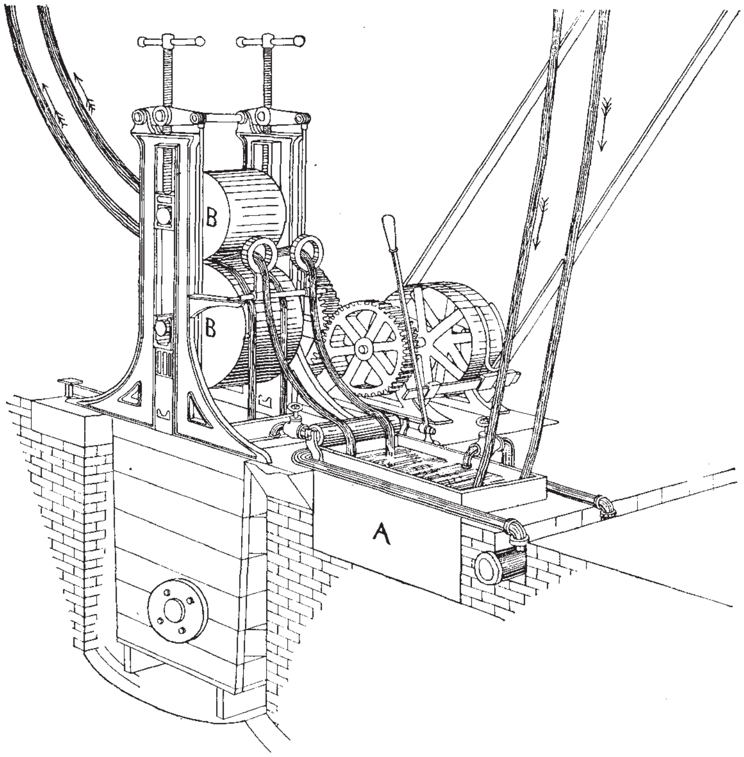


Fig. 31. Liming Machine.

The great loss of heat from this kier by radiation, and the large amount of steam necessary to keep up the circulation, led to the introduction of the so-called closed Low Pressure Kier, Figs.

34 and 35 serving as an example. In this form of kier the top may be closed tight and the boiling done under a slight pressure, say of 5 to 10 lbs., or a vent pipe is sometimes introduced in the top which allows the boiling to take place at atmospheric pressure. The circulation of the liquor in the kier is kept up in this way. Steam enters the injector B. through the pipe C, and the steam in passing up through the central pipe D, carries with it the liquor which is constantly flowing from the bottom of the kier into the injector through the pipe A. Through the valve E, the contents of the kier may be discharged after the boiling.

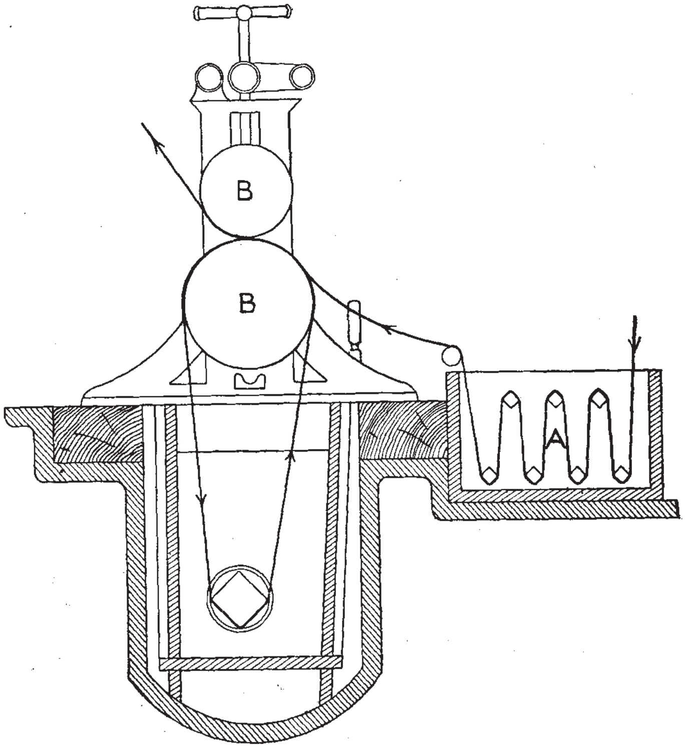
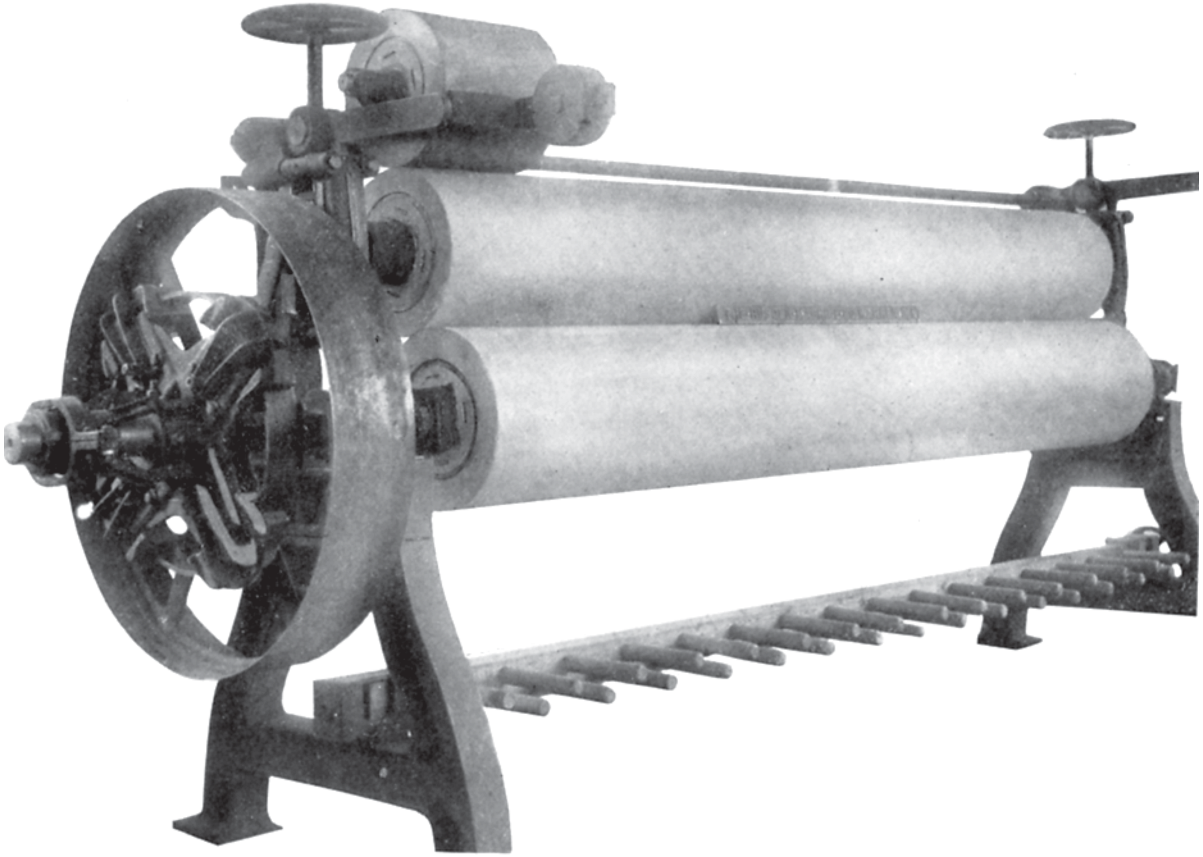


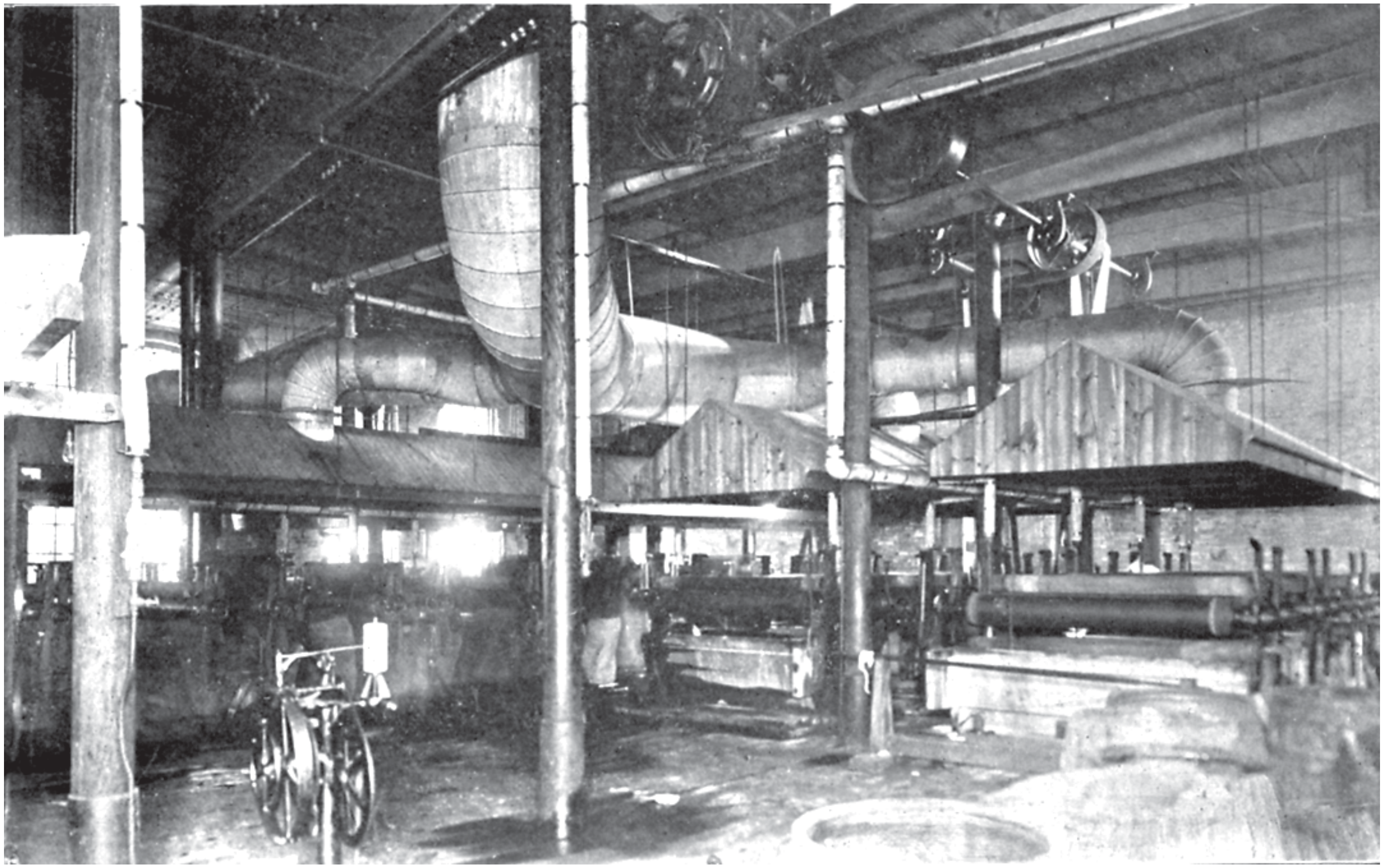
Fig. 31 A. Cross Section of Fig. 31.

The gain in economy of this kier was slight, but nevertheless many of the older bleachers hold to this form, and it is not uncommon at the present time to find bleacheries using low pressure kiers of some type or other. Open kiers have the advantage of



BLEACH HOUSE WASHING MACHINE, DRIVEN BY FRICTION PULLEY

Textile Finishing Machinery Co.



20 H. P. INDUCTION MOTOR DRIVING JIGGS

Lonsdale Bleachery

of the subject says, "It has been shown that at 120° C, the natural fats of cotton are saponified in less than two hours by the lime boil, and tallow in four hours. This is remarkable since caustic soda and rosin at the same temperature require eight hours." In addition many bleachers claim that goods given a lime boil have less tendency to become yellow on storing.

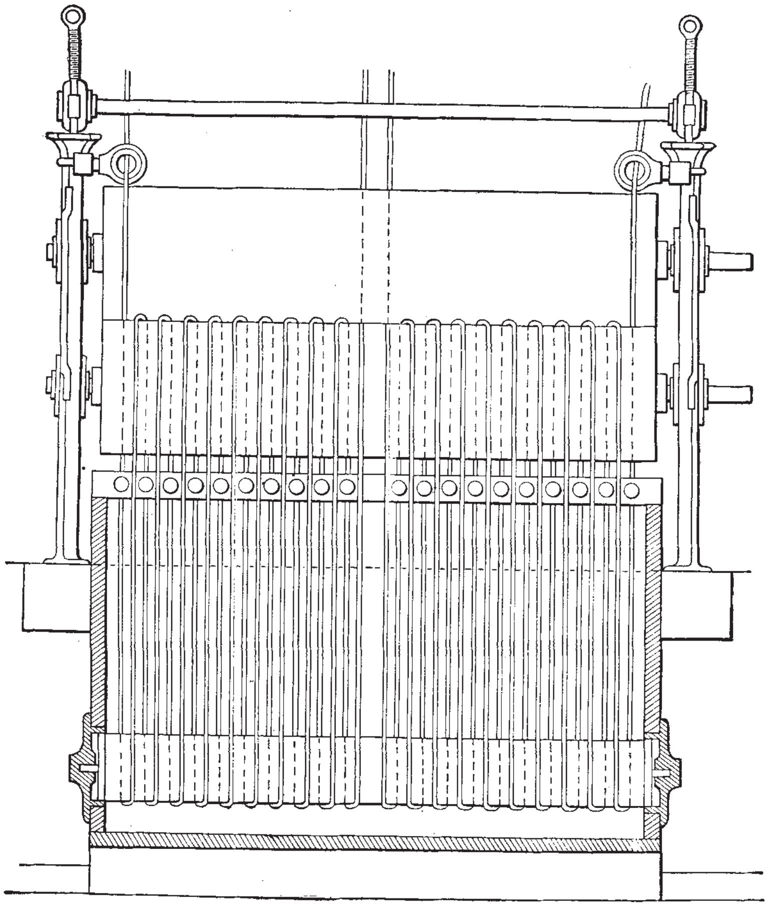


Fig. 45. Washing Machine.

The exact cause of tendering during the lime boil, particularly in high pressure kiers has been a much discussed point. Experimental investigation shows that lime at a high temperature in the presence of the oxygen of the air will convert cellulose into oxycellulose, a substance having but little structural strength. Kier tendering is undoubtedly due to the existence of these conditions in the kier, commonly brought about by an insufficient amount of liquor.

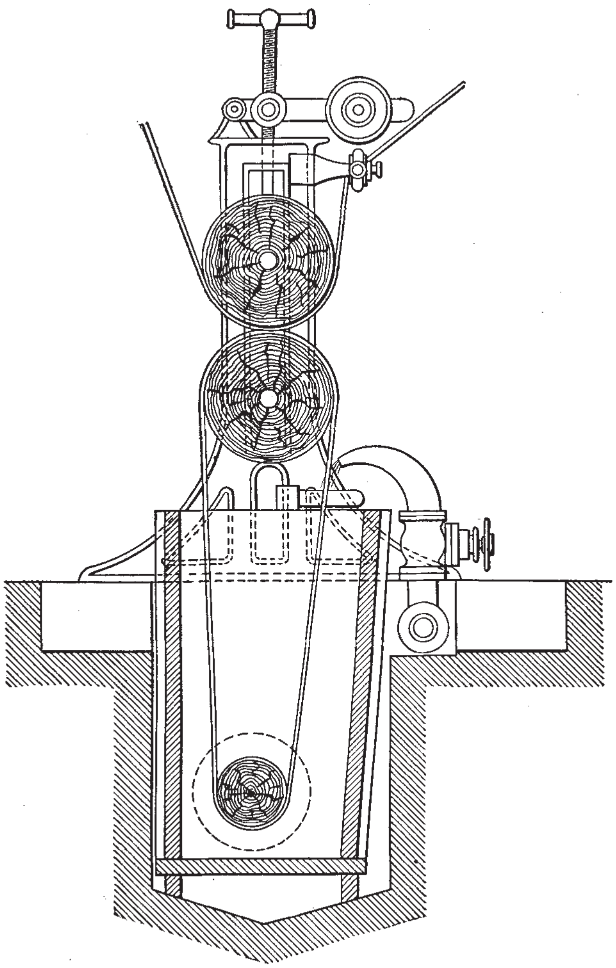


Fig. 45 A. Cross Section of Fig. 45.

102. Wash Following the Lime Boil and its Object. When the lime boil is finished the liquor is run off, and it is well to immediately give the goods a preliminary wash with cold water in the kier, particularly if found necessary to leave the material some time before running it through the washing machine. This cools off the goods before they come in contact with the air, and prevents them from drying while saturated with lime.

As soon as possible, the goods are run directly from the kier through a washing machine. See Figs. 45 and 45A. The object of this wash is to remove the excess of lime, and any soluble substances that may have been formed during the lime boil.

For further discussion of the washing of Textiles see also 112.

103. The Brown Sour and its Chemistry. The acid treatment following the lime boil is commonly known as the Brown sour, also as the grey sour, and sometimes as the lime sour. It consists in passing the cloth through a dilute acid solution, allowing it to stand for a short period dampened with this acid solution, and then washing with water.

The object is to remove all calcium (or lime) that may be present, as well as any other metals, such as iron, that may have been precipitated upon the cloth in some insoluble form during the lime boil.

The acids commonly used for souring cotton material during bleaching processes are sulphuric (oil of vitriol), and hydrochloric (muriatic) acids. For the brown sour it is not advisable to use sulphuric acid alone, since the calcium sulphate formed would be very difficultly soluble in water, but instead either hydrochloric acid, or a mixture of hydrochloric and sulphuric acids, thus forming calcium chloride which is extremely soluble in water and therefore easily removed during the wash which follows.

Experience has shown that a mixture of hydrochloric and sulphuric acids made up as follows works very well: In the mixing tank introduce 75 gallons of water then two carboys of sulphuric acid followed by two carboys of hydrochloric acid, then enough water to bring the Sp.G. to 10° Tw. This is then run into the souring machine. The water introduced by the cloth, as it enters the souring machine dilutes the acid considerable but enough water should be added along with the 10° acid to constantly keep it at a strength of about 3° Tw.

The souring machine should be of such construction that the goods pass through slow enough to insure that every portion of the material is acted upon by the acid. The same form of machines as are used for liming, see Fig. 31 and 32, are also commonly used for this purpose.

After leaving the souring machine the goods are commonly allowed to remain piled up in a bin for several hours or even over night. In the latter case it is advisable to sprinkle or wet down the cloth with water to prevent it from becoming tendered, see No. 21. Where time is an object the strength of the acid may be increased, say to 3½° Tw. but when possible it is better to lengthen the time of souring and diminish the strength of the acid to 2° or even 1½ Tw. Some bleachers recommend using acid as weak as ½° Tw. and heating it to about 90° C. for twenty minutes to one half hour.

The chemistry of the Brown sour is as follows:

There is present upon the cloth as it comes from the lime boil the insoluble calcium soaps [as for example calcium stearate $(C_{17}H_{35}COO)_2Ca$,] a certain amount of calcium carbonate $CaCO_3$ formed by the action of the carbon dioxide of the air upon the lime, and sometimes small amounts of the insoluble soaps of metals other than calcium and the oxide and carbonate of iron.

The following equations represent the reactions taking place if hydrochloric acid is present in the souring bath:

$$(C_{17}H_{35}COO)_2Ca + 2HCl = 2C_{17}H_{35}COOH + CaCl_2$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$
$$2FeCO_3 + 6HCl + O = 2FeCl_3 + 3H_2O + 2CO_2$$
$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

The chlorides formed being readily soluble in water are completely removed in the washing which follows. The fatty acids liberated (as for example Stearic Acid $C_{17}H_{35}COOH$) are all insoluble in water and consequently remain on the cloth. These however are readily removed in the lye boils.

The so-called lime stains which sometimes appear upon the bleached cloth and cause trouble in dyeing and printing are most frequently due to insufficient souring or the use of too little hydrochloric acid.

After the brown sour the cloth is passed through a washing machine and is ready for the lye boils. If any free acid remains in the cloth there is danger of the formation of iron stains when it is run into the kier. To prevent this it is advisable to run the cloth through soda ash solution then through squeeze rolls before entering the kier.

104. Lye Boils. Originally there were two and sometimes three so-called lye boils given during the madder bleach.

The first was always a short one and had for its object the thorough wetting out and softening of the cloth, and the complete neutralization of any acid that might have remained on the cloth after the brown sour. Soda ash alone was used in this.

In the second, which was the essential one of the three, the boiling lasted from 12 to 24 hours in the case of open kiers and from 6 to 12 hours in the case of pressure kiers, and there were used in addition to soda ash, rosin soap and a small amount of caustic soda.

The third was a short one, with soda ash alone, and was to insure the complete removal of any of the rosin soap that might remain on the cloth.

Of late years the tendency has been to shorten the process as much as possible, the first boil being entirely done away with when the cloth is passed through soda ash solution and squeeze rolls before entering the kier, and the second and third combined as one which we will designate as the rosin soap boil.

Rosin Soap Boil. The alkalies available for this boil are sodium carbonate (soda ash), and sodium hydroxide (caustic soda), the corresponding potassium compounds being ruled out on account of expense.

The other boiling agent used is rosin or rosin soap which may conveniently be made by boiling

100 lbs. of Rosin with
10 gallons of Caustic Soda solution 60° Tw.

and sufficient water to make a perfectly homogeneous mass.

The main object of the Rosin Soap Lye Boil is to convert all fatty acids present into their soluble sodium salts or soaps, and at the same time remove other fatty and waxy matters, and most of the resinous brown coloring matter still remaining in the cloth.

Caustic Soda attacks these substances very energetically and is particularly useful in removing any natural fatty compounds which may have escaped decomposition during the lime boil. Theoretically it is an excellent reagent for this purpose but great care must be taken in its use or tendering will result.

Soda ash accomplishes the same purpose as caustic soda but is much slower in its action. It is by far the safer and is the standard alkali for this purpose. In order to shorten the time however without running too great risk, bleachers often use a mixture of soda ash and caustic soda, a good proportion being 85 parts of the former to 15 of the latter.

The same form of kier (See 100), may be used for the lye boils as are used for the lime boils, although it is customary to have separate ones for each.

The length of the boil necessarily varies with the form of kier, the material being bleached, and the fancy of the bleacher, but for ordinary print cloth it usually lasts from 6 to 12 hours.

For 500 pieces of print cloth it is customary to use approximately the following chemicals:

150 lbs. of Soda Ash, and
Rosin soap corresponding to 13 lbs. of Rosin.

In place of the above amount of Soda Ash, a mixture of

20 lbs. of Caustic Soda, and
120 lbs. of Soda Ash

may be used.

105. Chemistry of the Lye Boils. The most important chemical reaction taking place during the Lye boil is the conversion of the free fatty acids present into their corresponding sodium salts or soaps which are soluble in water. Illustrating with stearic acid, we would have the following reactions taking place

With Soda Ash:

$$2C_{17}H_{35}COOH + Na_2CO_3 = 2C_{17}H_{35}COONa + CO_2 + H_2O$$

With Caustic Soda:

$$C_{15}H_{35}COOH + NaOH = C_{17}H_{35}COONa + H_2O$$

The Rosin Soap boil has always been a special feature of the madder bleach, for it was found that in some way, not thoroughly understood, this agent removed, far better than soda ash alone, certain impurities which if allowed to remain, would attract certain coloring matters during subsequent dyeing and printing processes and thus detract from the purity of the white grounds. The action of the rosin soap is apparently of a mechanical emulsive nature rather than chemical. Other soaps might be used for this purpose, but as yet none have been found that work as well, or are as cheap as rosin soap.

106. Wash Following the Lye Boil and its Object. The wash following the lye boil is carried out in the ordinary washing machine Fig. 30 and if the third lye boil mentioned in 104 has been omitted, should be thorough in order to completely remove any rosin soap, which might stain the cloth if allowed to remain.

If the lye boil has been properly carried out, all the fatty matter still remaining will be present in a form perfectly soluble in water, and consequently easily removed at this time, and after leaving the washing machine, were it not for a small amount of natural coloring matter, the cloth should be nearly free from impurities.

107. Chemicking or Bleaching Proper. The chemicking or bleaching proper is given at this stage of the process.

It has for its object the complete removal or decolorization of the small amount of coloring matter remaining.

This is accomplished by passing the cloth through a moderately dilute bleaching powder solution (1° to 2° Tw.) allowing it to remain exposed to the air in a pile, while still damp with the bleaching powder solution, and then after a hasty wash passing it through a dilute acid solution (white sour), and thoroughly washing.

The bleaching powder solution may be applied to the cloth by various arrangements but all consist essentially of a cistern for saturating the cloth and squeeze rolls for removing the excess. The same form of machine as is used for souring will do, only in this case it is well to replace the wooden cistern with one of cement.

The bleaching powder is best dissolved in a special apparatus, as it goes into solution with some difficulty, and undissolved lumps coming in contact with, and attaching themselves to the cloth may result in the formation of oxy cellulose. A simple form of apparatus for this purpose is represented in Fig. 46. It consists of a perforated, wrought iron, lead-lined drum, into which the bleaching powder is put. This drum is revolved in a rectangular lead-lined iron tank through which water is run. The bleaching powder solution is drawn off at a tap located far enough from the bottom to prevent the removal of sediment.

Numerous other forms of apparatus have been devised for this purpose, but need not be described here.

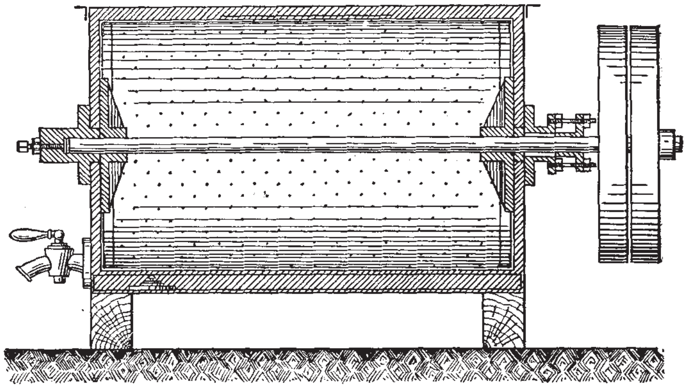


Fig. 46. Apparatus for Dissolving Bleaching Powder.

The solution of bleaching powder in the stock reservoir should stand at about 3° Tw. and the water introduced with the cloth will dilute this to about the proper strength. If not, water is introduced along with the stock solution as it passes into the chemicking machine. The cloth is passed through this solution, then through squeeze rolls and allowed to stand in a pile 1 or 2 hours. The time of this exposure varies with different bleachers. Some even allow the cloth to remain in this condition over night. This however is a dangerous practice, unless the bleaching powder solution is extremely dilute, owing to the danger of formation of oxy cellulose. For bleaching solutions of from 1° to 2° we should place the limit of exposure for the best results at 5 to 6 hours. It is also well to remember that the solution at a temperature of 75° to 85° F in the summer will act much quicker than that of from 50° to 65° F, or colder, in the winter.

108. Wash After Chemicking and its Object. Before entering the white sour the goods are given a hasty wash, to remove any excess of bleaching powder. If this were not done, the amount of chlorine liberated during the souring would be so great as to be injurious to the workmen, even if it did not drive them all out of the bleach house.

109. White Sour. The white sour is carried out in a similar manner to the brown sour (See No. 103). It consists in passing the goods through a 2° to 2½° Tw. sulphuric acid solution, then through squeeze rolls and into the final washer.

Its object is two-fold. First to decompose any bleaching powder that may remain, thus liberating the chlorine and preventing its subsequent action upon the cloth; and secondly to aid in the removal of all calcium compounds, particularly the carbonate, which is formed during the exposure with bleaching powder to the air.

A very energetic bleaching action also goes on during the white sour, owing to the rapid liberation of chlorine, and the cloth is left in a very white and bright condition.

As in the brown sour, it would, from a theoretical point of view, be better to use hydrochloric acid, but on account of the cheapness of sulphuric acid, and the fact that commercial hydrochloric acid sometimes contains enough iron to detract from the whiteness of the goods, the former is used.

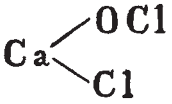
110. Bleaching Powder. Chlorine and certain of its compounds are as yet the cheapest and, considering everything, the best bleaching agents for cotton, and the compound depended upon almost entirely for the liberation of these is Bleaching Powder.

When chlorine is allowed to act upon Calcium Hydroxide (water slaked lime), reaction takes place according to the following equation:

$$2Cl_2 + 2Ca(OH)_2 = \underbrace{Ca(OCl)_2 + CaCl_2}_{\text{Bleaching Powder.}} + 2H_2O$$

and bleaching powder results.

In the above equation bleaching powder is written as a mixture of Calcium Hypochlorite, Ca $(OCl)_2$, and Calcium Chloride $CaCl_2$, in molecular proportions. This could also be written as two molecules of an oxychloride of calcium $2CaOCl_2$, which would have the following structural formula:



There has been much discussion as to which was correct, but at the present time the opinion of most chemists is that bleaching powder, in the dry form, is a definite compound of the formula $CaOCl_2$ which when dissolved in water dissociates or breaks up the same as would the mixture Ca $(OCl)_2 + CaCl_2$.

Evidence very strongly in favor of this theory, which anyone can notice, is this. Calcium chloride $CaCl_2$ is one of the most deliquescent compounds we have, while dry bleaching powder does not seem to be at all deliquescent. This latter fact would not seem possible if dry bleaching powder was made up of a little less than $\frac{1}{2}$ calcium chloride.

Commercial Bleaching Powder may practically be considered as a mixture of calcium hypochlorite and calcium chloride in a somewhat variable proportion, with some calcium hydroxide and if the sample is old, and has been exposed to the air, some calcium carbonate.

As will be understood later (See 111,) it is only the Cl of the hypochlorite that is available for bleaching purposes and the value of any bleaching powder depends upon the amount of this present.

111. Theory and Chemistry of Bleaching with Chlorine. It is now believed by all chemists, that oxygen just liberated, (that is, when in the atomic condition, or nascent state), is the most powerful bleaching agent we have.

For hundreds of years it has been known that textile fabrics laid upon the grass exposed to the sun and air became thoroughly bleached and that the same material exposed to the sun and air but away from the grass, bleached much slower. This fact is easily explained when it is known that all vegetation is constantly taking up carbon dioxide, retaining the carbon, which contributes to its growth, and giving up the oxygen. It is the oxygen given up from the grass that so actively aids in bleaching.

It is also known that many peroxides as those of hydrogen and sodium which readily liberate nascent or atomic oxygen are excellent bleaching agents.

Furthermore if a piece of perfectly dry cotton cloth is put into perfectly dry chlorine gas, there seems to be little if any bleaching action, but if the same piece of cloth be slightly moistened with water, and returned to the same chlorine it is rapidly bleached.

These and other facts lead to the belief that even when chlorine is used, the real bleaching action is due to the liberation of atomic or nascent oxygen, by the action of chlorine on water, thus:

$$2Cl + H_2O = 2HCl + O$$

Calcium Hypochlorite $Ca(OCl)_2$ already spoken of as containing the available chlorine for bleaching powder, is a very unstable compound being readily decomposed by acids, even by carbonic acid gas, with the liberation of hypochlorous acid HClO which readily decomposes liberating hydrochloric acid and nascent oxygen as follows:

$$HClO = HCl + O$$

During the bleaching process dependence is mainly placed upon the slow decomposition brought about by the action of the carbon dioxide of the air upon the bleaching powder while the cloth is exposed dampened with a solution of the latter.

The following equations represent the reactions taking place:

$$Ca(OCl)_2 + CaCl_2 + 2CO_2 + 2H_2O = 2CaCO_3 + 2HClO + 2HCl$$

$$HClO + HCl = H_2O + 2Cl$$
$$2Cl + H_2O = 2HCl + O$$
$$HClO = HCl + O$$

Hydrochloric and Sulphuric Acid liberate Hypochlorous acid and Chlorine according to the following equations:

$$Ca(OCl)_2 + 2HCl = CaCl_2 + 2HClO$$
$$2HClO + 2HCl = 2H_2O + 4Cl$$
$$Ca(OCl)_2 + H_2SO_4 = CaSO_4 + 2HClO$$
$$CaCl_2 + H_2SO_4 = Ca\ SO_4 + 2HCl$$
$$2HClO + 2HCl = 2H_2O + 4Cl$$

Or considering the formula of bleaching powder as $CaOCl_2$

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + 2Cl$$
$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + 2Cl$$

The above equations represent the principal reactions taking place during the bleaching but in general it may be said that there is a cycle of reactions going on, in which the products of one reaction react with those of another, resulting in the slow but more or less uniform liberation of nascent oxygen; this nascent oxygen destroying or decolorizing the coloring matter that is present in the cloth.

112. Final Wash and General Discussion of Washing. Too much stress cannot be laid on the importance of careful and thorough washing of the material at the different stages of the bleaching process, and particularly after it has been completed, for in many cases deterioration and tendering of the cloth might be traced to insufficient washing rather than too strong liquors.

For satisfactory results it is imperative that all acid and bleaching powder should be removed from the cloth at the proper time, and it should also be remembered that heat is many times generated by the action of one chemical upon another, which in some cases is enough to cause tendering, unless it is overcome by immediately passing the cloth into an excess of water.

The commonest forms of washing machines are illustrated by Figs. 29-30-45-45A. They consist of large cisterns through which water can be passed with varying rapidity, and some means of passing the cloth through these, so that every portion will come in with a large volume of water.

The machines are commonly constructed with two heavy squeeze rolls above the cistern which vary in diameter. The lower roll is commonly the larger, being from 20 to 24 inches in diameter, while the upper is from 12 to 18 inches. There should be enough pressure between them, to draw in the wet cloth without slipping. The nip of the rolls is sometimes increased by covering them with rope.

The speed at which the cloth is passed through the washing machine depends on the nature of the material. the construction of the machine, and the number of times the cloth passes through the squeeze rolls. For an ordinary machine with print cloth the rate is from 3 to 5 miles per hour. With certain tension machines this may be increased somewhat, but with very heavy material the speed is sometimes reduced to as low as 1 mile per hour. At any event the washing should always be thorough enough to remove the last traces of acid or the material will become tendered when dried.

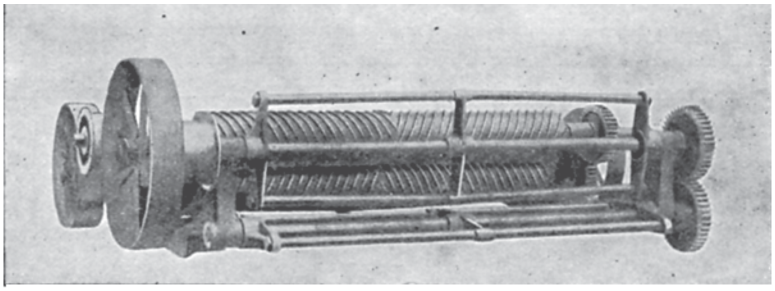


Fig. 47. Cylindrical Scutcher.

113. Finishing. After the final wash the cloth is hydro extracted or passed between the squeeze rolls and then brought again to the full width. It is sometimes opened out by hand, but a machine called a scutcher is more commonly used for this purpose. Scutchers vary in construction and working detail but all involve the principle of producing a stretching of the cloth from the center toward the edge by passing it over spirally grooved or

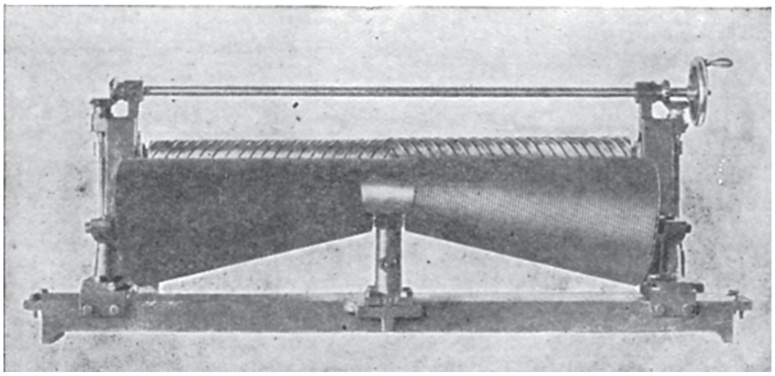


Fig. 48. Conical Scutcher.

fluted rolls or diagonally grooved surfaces. Fig. 47 represents a plain cylindrical scutcher, Fig. 48 one of conical construction, Fig. 49 a reel scutcher, while Fig. 50 represents a self regulating one recently introduced by Wm. Mycock & Co. of Manchester, Eng., which is said to be giving great satisfaction.

If the cloth is to be printed it is simply dried by passing over drying cans, see Fig. 51, but if it is to be finished white it is passed through a starch mangle and through other finishing machines as calenders, beatlers, etc. The finishing of cotton cloth being a subject by itself will not be further considered here.

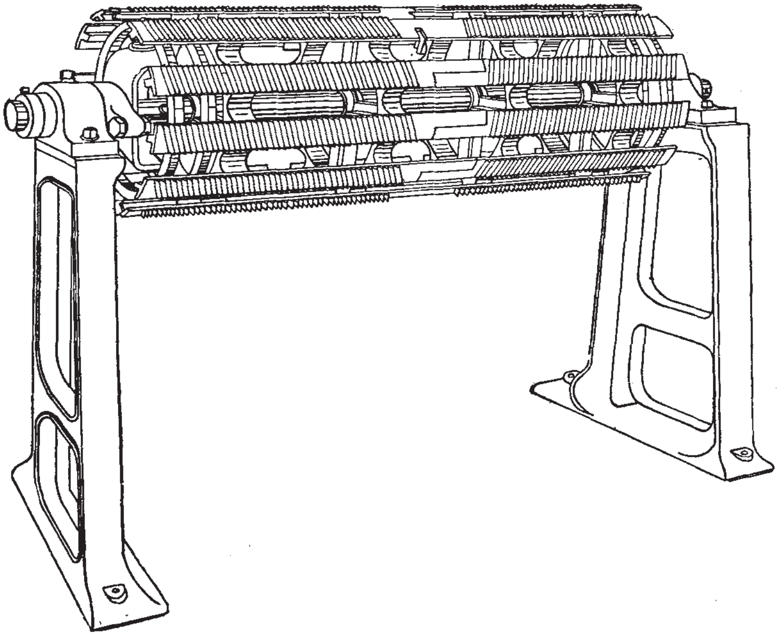


Fig. 49. Reel Scutcher.

114. Turkey Red Bleach. In the case of cloth that is to be dyed a full shade of Turkey or alizarine red, it is not necessary to give a complete madder bleach, for there is no white ground to be preserved, and many hold the opinion that previous treatment with bleaching powder detracts from the production of the most brilliant reds. This may be due to the formation of oxy-cellulose which prevents the proper fixation of the mordant. The treatment for the so-called Turkey Red bleach differs from the madder bleach in that the lime boil, brown sour, and treatment with bleaching powder are omitted. The slight yellow color left on the cloth after this bleach tends to increase the fiery character of the shade produced.

115. Market Bleach. This term is sometimes applied to the bleach-given cloth that is sold in the white. It is an indefinite term, but in general consists of a bleach similar but not as thorough as the madder bleach. Any remaining yellow tint is neutralized by blueing. The cloth is commonly starched and often slightly weighted and calendered.

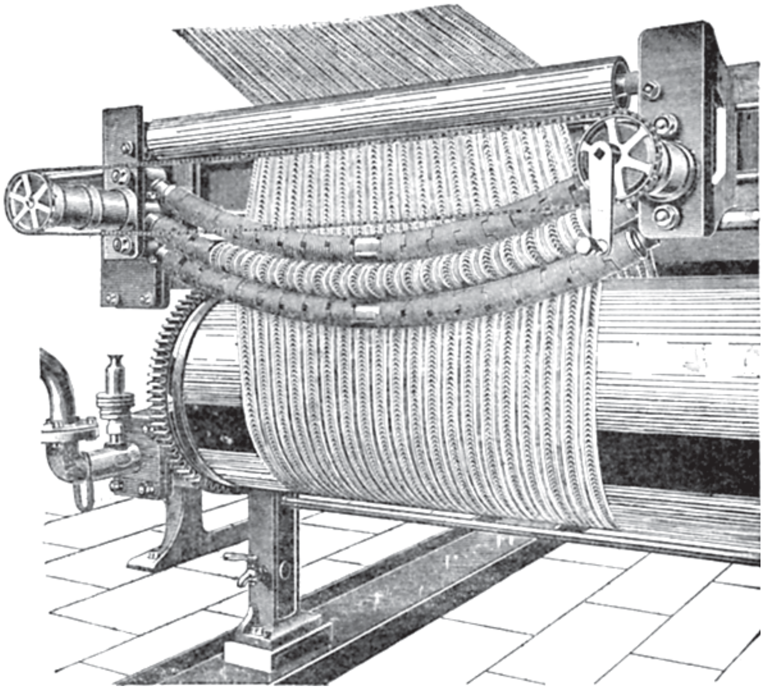


Fig. 50. Self Regulating Expander.

116. Rapid Bleach for Cloth that is to be Dyed Dark Shades. Where cotton cloth is to be dyed a solid dark shade, it is only necessary to give it sufficient preliminary treatment to remove the cotton, wax, grease and dirt. It is commonly washed, boiled several hours with soda ash, given a rapid treatment with bleaching powder and a sour. Sometimes the bleaching powder treatment is omitted entirely.

117. Bleaching of Cotton Yarn. (General Consideration.) When cotton yarn is to be dyed black or dark colors, it matters little whether it is previously bleached or not. If bleaching is omitted the yarn is commonly boiled in a slightly alkaline bath until thoroughly softened and wet out. If an alkali is used for this purpose the yarn should be washed previous to the dyeing. Bleaching is necessary when the yarn is intended for the production of delicate tints or to be finished as a pure white.

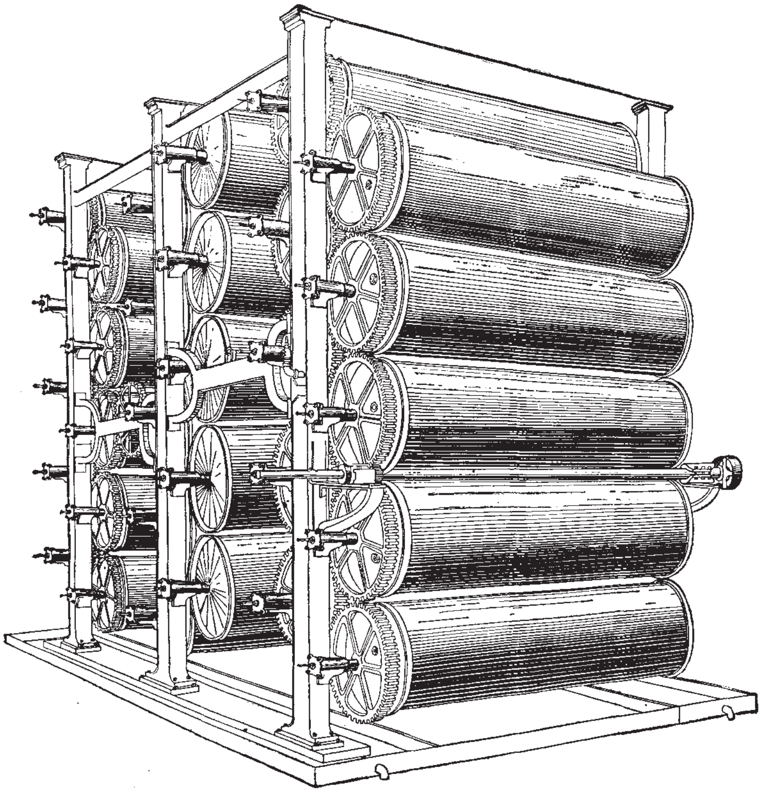


Fig. 51. Can Dryer.

In general, the process of bleaching cotton yarn consists of three essential steps.

(1.) Boiling or scouring in an alkaline solution, usually soda ash or caustic soda.

(2.) Steeping in a dilute solution of bleaching powder.

(3.) Steeping in a dilute acid solution.

This series of operations is always followed by a thorough washing. The methods of carrying out these steps vary only in detail and apparatus used.

118. Detail of Process and Machinery Used. The detail of the process varies at different works but depends upon the ideas of the bleachers, the facilities at their disposal and the purposes for which the yarn is to be subsequently used.

The following may be taken as the outline of a typical yarn bleaching process:

(1.) Boil yarn 12 hours in a low pressure kier using soda ash 4% of the weight of the goods. The addition of a small amount of soap materially aids in the removal of the natural impurities. In case a pressure kier is used the period of boiling may be shortened.

(2.) Wash thoroughly.

(3.) Chemick by allowing to remain in a $1\frac{1}{2}°$ to 2° Tw. bleaching powder solution (entirely under the surface) for 5 to 6 hours.

(4.) Wash to remove excess of bleaching powder.

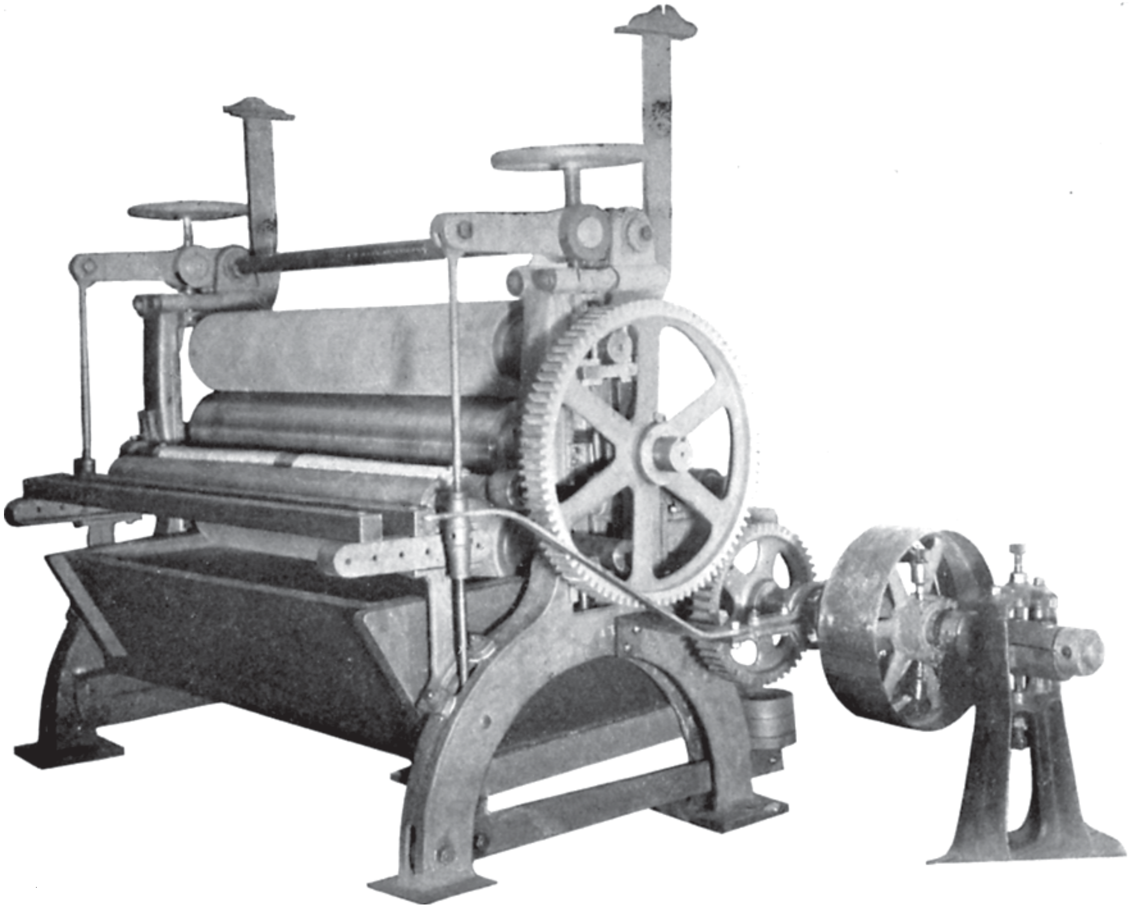
(5.) Sour 15 to 20 minutes in $\frac{3}{4}°$ to 1° Tw. sulphuric acid solution, or a hydrochloric acid solution of the same density.

(6.) Wash thoroughly, rinse in a mild soap bath, hydro extract and dry. A small amount of blueing is sometimes added to the rinsing bath.

The above will give as thorough a bleach as is necessary for most purposes.

The yarn may be bleached either in the form of skeins or in the chain form, the latter being the term commonly applied to long continuous rope-like bundles of yarn, made up of hundreds of individual yarns, all arranged parallel to each other, and in such a way that they may easily be separated and reeled after the bleaching and dyeing operation is completed.

When in the chain form yarn is easily handled, but in the skein form more difficulty is experienced. It is often the practice



THREE-ROLL PADDING MACHINE, DRIVEN BY FRICTION PULLEY, PINION, AND GEAR

Textile Finishing Machinery Co.

to tie skeins together end to end, thus making a continuous chain.

The boiling is commonly done in low pressure kiers, although some bleachers prefer pressure kiers for this purpose (for description of which see No. 100) and the boiling is continued as long as is necessary.

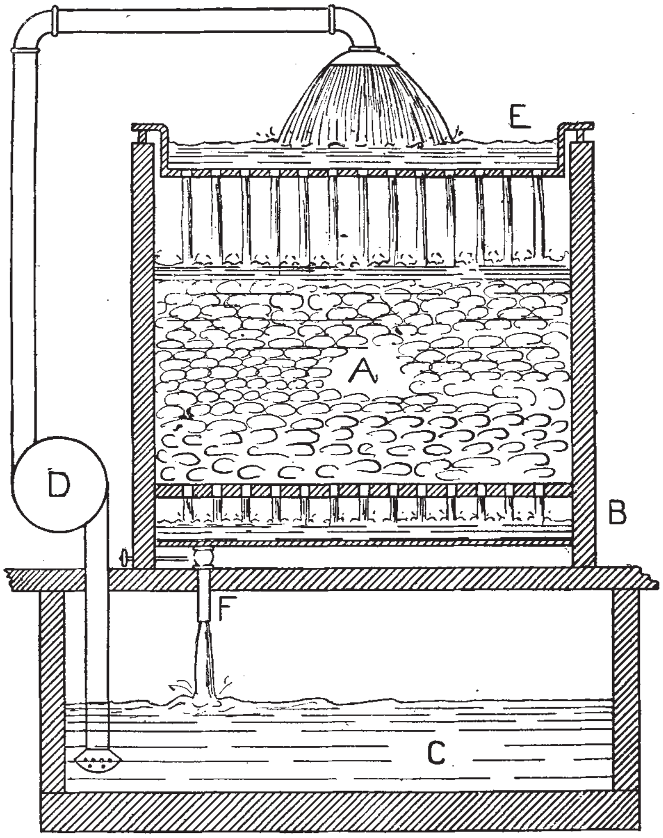
The washing, scouring, and chemicking is usually done in some form of an open cistern. Fig. 52 illustrates a simple form of cistern which may be conveniently used for washing and also for chemicking and scouring.

The yarn is carefully packed in the cistern A, which is provided with a false bottom B, a sub-cistern C, containing the water, chemick or acid solution as the case may be, and a rotary pump D, forces the liquid from C to the perforated top E where it is sprinkled even upon the top of the goods and after slowly perculating through the yarn, it returns through the out-let pipe F to the sub-cistern C from which it repeats the circulation. By placing a valve in F it is possible to hold the liquor in A any length of time.

The Mather and Platt arrangement illustrated in Fig. 53 is similar to the apparatus described in Fig. 52 but is so arranged that the lye boil, chemicking, souring and washing may all be done in one and the same cistern, without moving the material, thus saving a great deal of labor and handling. As will be seen from the cut, separate tanks are provided for the various liquors, each of which has its own pump or injector, and system of return pipes.

119. Bleaching of Raw or Loose Cotton. Raw or loose cotton is seldom bleached, since about the only finishing products containing cotton in this state are wadding and lint, and there is usually no necessity for bleaching these. Special cases, however, come up from time to time, as for instance the production of a pure white single yarn for filling in cloth that cannot be bleached, for which a varying amount of bleached cotton is required, and the dyer or bleacher should know how to meet these demands.

Cotton bleached in the loose state invariably gives a better white for the same amount of treatment than yarn. This is probably due to the fact that the yarn has taken up oil and dirt during the spinning. The great drawback in bleaching raw cotton on a large scale is the manner in which wet cotton mats and wads together. A specially constructed kier having perforated diaphrams would have to be used, and it is extremely doubtful if the better bleach obtained would be of sufficient advantage to counteract the difficulties met in the operation. Again, the bleached cotton would be liable to become very much soiled during the spinning and weaving and in many cases would have to be rebleached when finished.



No. 52. Bleach Cistern.

The processes used for bleaching yarn and cloth (already described) cannot be used for bleaching raw or loose cotton on account of the different nature of the material.

The greatest difficulty is experienced in giving the loose cotton the preliminary lye boil which is so efficient in removing the oily and fatty matter from the fiber. In works where there is a frequent demand for bleached cotton, it might be well to have specially constructed baskets or cages that will hold several hundred pounds, and have a traveling pulley over head so that these baskets when filled might be lowered for the necessary length of time into a boiling lye bath, then raised, washed thoroughly and lowered in a bath containing bleaching powder solution, then washed, and into a dilute acid bath and finally given a thorough wash.

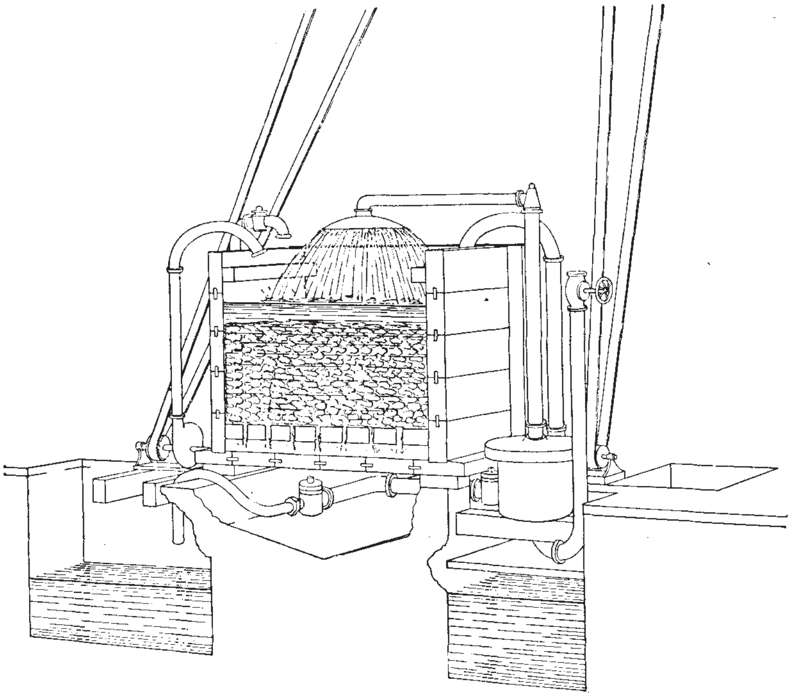


Fig. 53. Mather & Platt Improved Bleaching Cistern.

In some cases an alkali boil is given by placing the cotton securely in bags, about 100 lbs. each, and then subjecting a number of these filled bags to a lye boil in a regular kier, and then washing, chemicking, souring and washing in open tanks.

Some bleachers have used regular raw stock dyeing machines successfully for the bleaching of loose cotton.

From laboratory experiments it has been found that the use of sodium hypochlorite solution (slightly alkaline) instead of calcium hypochlorite bleaches loose cotton very satisfactorily and at the same time aids to a considerable degree in the removal of the natural impurities. In fact, by the use of this bleaching agent it is even possible to obtain a bleach satisfactory for most purposes, when the preliminary lye boil is omitted.

A sodium hypochlorite solution may be made by adding concentrated sodium carbonate solution to a bleaching powder solution until no more calcium carbonate is precipitated, adding a slight excess of the sodium carbonate.

$$Ca(OCl_2) + CaCl_2 + 2Na_2CO_3 = 2CaCO_3 + 2NaClO + 2NaCl$$

When the calcium carbonate has settled, the supernatent liquor may be drawn off, made up to 4° Tw and is ready for use.

An ordinary vat or tub may be used for the bleaching and it is better to do small quantities at a time to prevent matting. The cotton is entered directly into the bath of sodium hypochlorite, and allowed to remain completely under the surface of the liquor for three hours after it has become thoroughly wet out. Sometimes the cotton may be steeped in the bleaching liquor over night, but in this case the strength of the bath should be reduced somewhat.

In the bleaching of cotton yarn and cloth, it is customary to follow the bleaching with an acid treatment or "sour," as it is called, and this is sometimes done in the bleaching of loose cotton, but the thorough washing of cotton in this form is difficult, and as any traces of acid remaining in the fiber would be sure to tender it, sodium bisulphite solution 2° to 3° Tw. or a sulphurous acid solution had better be used to neutralize any free chlorine remaining in the material.

Yarn is often washed by hand in ordinary rectangular tubs, by hanging the skeins on sticks as in the process of dyeing and sometimes in specially constructed machines (Haubolds Yarn Washing Machine) Fig. 54 serving as a good example. It consists of a circular tank over which radiate a large number of horizontal axes each carrying a square bobbin, upon which the yarn is hung.

When the machine is in operation these axes travel completely around the tank at each revolution of the central upright axis, and at the same time revolve independently, thus keeping the yarn in constant motion as it passes through the water.

OTHER BLEACHING PROCESSES.

120. The Mather and Platt Steamer Kier Process. Since 1880 a number of chlorine bleaching processes have been proposed, which differ considerably from the old process already described. Some have been carried out on the large scale with more or less success, while others have proved to be positive failures. Of all these, none have met with greater success than that proposed by M. Horace Koechlin about 1887, and carried out in the Mather and Platt Steamer Kier. In this process the lime boil is entirely dispensed with and the lye boils with soda ash replaced by a single boil with caustic soda and rosin soap.

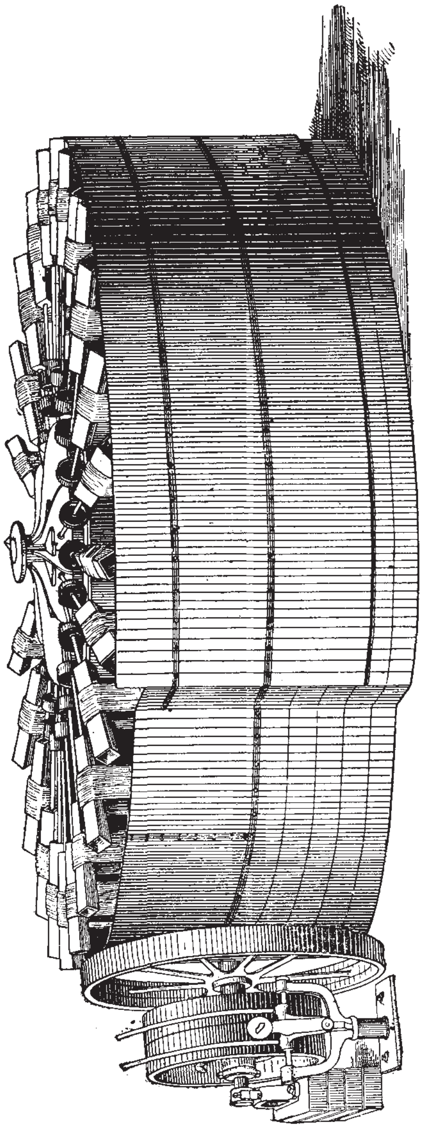


Fig. 54. Yarn Washer.

The Mather and Platt Steamer Kier, see Fig. 55 and 56, consists of a horizontal cylindrical, wrought iron boiler or kier with the ends slightly curved to give it strength. One end is stationary while the other consists of a heavy wedge shaped door D, raised and lowered by a hydraulic lift L, and which when lowered wedges itself steam tight into the frame F. In the bottom of the kier is a track T, on which the two trucks or cars CC′, can be run in and out. These cars are constructed of galvanized iron; are provided with a perforated bottom and hold the goods during the boiling process. When the goods have been evenly packed in the cars, they are run into the kier, the door is closed and all the air expelled from the kier by the admission of steam. Great care must be taken in this particular, for a bubble of air remaining in the goods may result in local tendering.

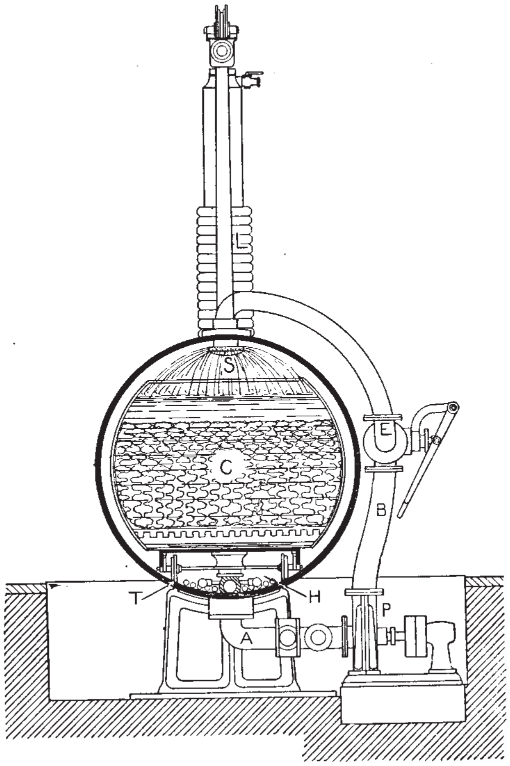


Fig. 55. Mather & Platt Steam Kier.

Sufficient caustic soda solution is now run into the kier; the steam pressure raised to the proper point, and a constant and positive circulation of the liquor kept up by the pump P, which draws the liquor from the bottom of the kier through the pipe A, forces it through the pipe B, which divides at E, and terminates in the two sprinklers S, and S′, which shower the hot caustic soda solution over the goods in the cars. The solution leaches through the goods, passes the perforated bottoms, collects in the bottom of the kier where it is heated by a coil of pipes H, and is ready to circulate again. After the boiling, the goods may be easily washed in the kier and the subsequent treatment is the same as that following the lye boils in the Madder bleach, that is, chemicking, souring, final washing and finishing.

In carrying out the process the gray cloth is wet out, sometimes given a sour with sulphuric acid, and allowed to stand in a pile several hours, then washed, saturated with the caustic soda solution and run into the kier.

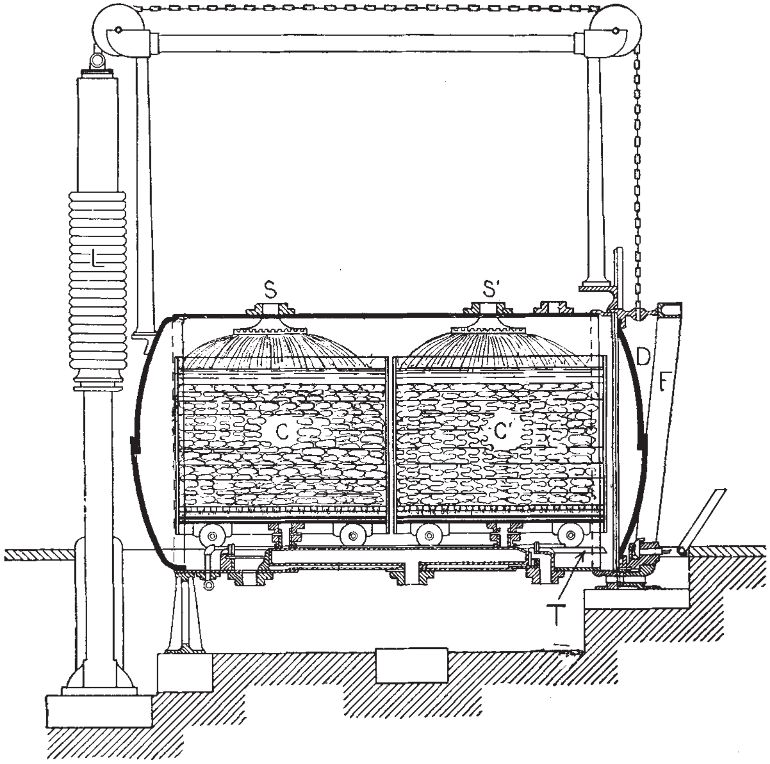


Fig. 56. Another View of Mather & Platt Steam Kier.

The following strength of liquor may be taken as a good example of that in common use.

50 lbs. Caustic Soda. (70%)
30 lbs. Rosin.
425 to 450 gal. of Water.

When first introduced the kiers were run at a pressure of from 7 to 15 pounds, but of late the tendency has been to increase the pressure, often as high as 40 pounds, and the whole bleaching process is sometimes carried out in 24 hours.

Many modifications of this process are made to suit the class of goods being bleached. Often a mixture of caustic soda and soda ash is used and it is possible (and in fact often done with back cloths) to give a lime boil in this kier.

Within a few years an improved form of this kier has been introduced which is constructed to work at a higher pressure, is of greater capacity, and provided with a method of raising the door by means of a simple mechanical worm gear instead of a hydraulic ram. A device for producing a partial vacuum in the kier before the introduction of the circulating liquor is added, and also an arrangement for forcing the liquor up through the cloth as well as down. **Fig. 57** shows the new type of kier.

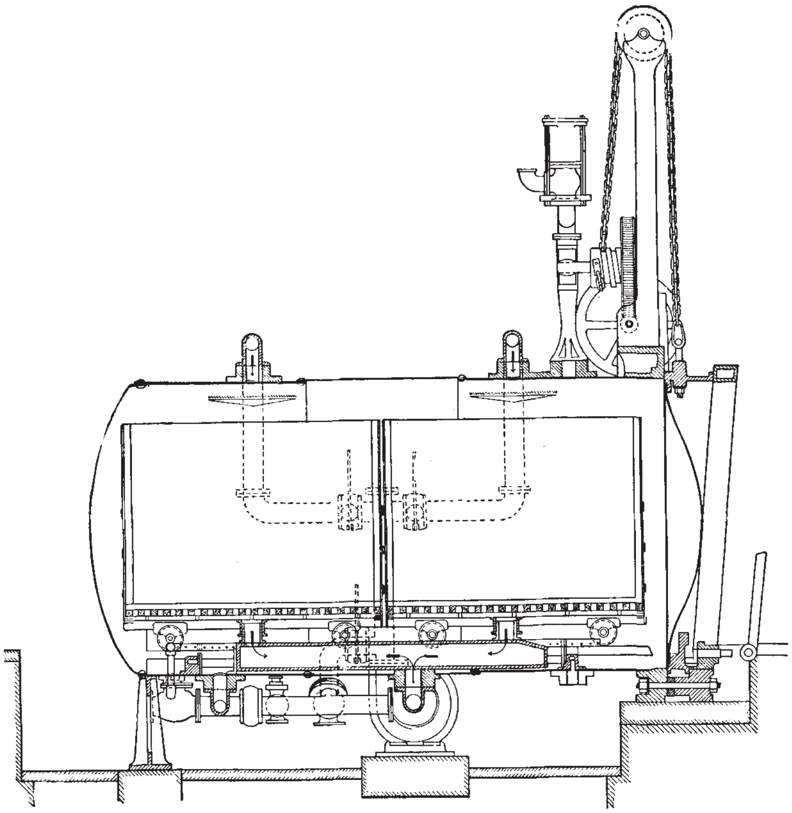


Fig. 57. Improved Form of Mather & Platt Kier.

The Mather and Platt Steamer Kier seems to be giving great success in many places and it certainly is a clever device for saving time and producing positive circulation of the bowking liquor.

121. Electrolytic Bleaching Processes. At the present time it is not uncommon to hear mention made and to see in the current Textile literature, articles in regard to the application of electricity in bleaching processes. None of these have apparently met with sufficient success to insure their adoption by more than here and there a progressive concern ready to experiment with the latest devices, and even at these places they are not depended upon entirely.

These Electrolytic Processes may be divided into two classes: First: those in which the hypochlorite solution is formed directly in the electrolytic apparatus, and second, those in which the chlorine is formed and then conducted away and used to produce a hypochlorite solution in another apparatus. Of the former the "Hermite Process" is probably as representative as any. In this a solution of magnesium chloride, or a mixture of magnesium chloride and sodium chloride is electrolyzed.

Among the best representatives of the second class are the "Le Sueur Process" and the "Castner Process." Both of these consist in the electrolysis of sodium chloride solution, with the production of free chlorine and metallic sodium, the latter uniting with water to form caustic soda.

122. Other Bleaching Processes Using Chlorine. Among the other bleaching processes using chlorine may be mentioned the Mather and Thompson continuous process. It consists in giving the cloth the necessary lime and lye boils and completing the bleaching by passing through a special bleaching chamber consisting of a dozen or more separate compartments, containing water, bleaching powder solution, and carbonic acid gas, and before leaving the apparatus, through a compartment containing dilute (1%) hydrochloric acid. It takes the cloth three to five minutes to pass through the apparatus and the special feature is use of carbon dioxide as a souring agent or liberator of chlorine.

Mention might also be made under this head of Lunge's process of using a mixture of acetic acid and bleaching powder solution. The reaction upon mixing the two is

$$2\,[Ca\,(OCl)_2 + CaCl_2] + 4CH_3\,COOH = 2CaCl_2 + 2\,(CH_3COO)_2\,Ca + 4HClO$$

followed by

$$4HClO = 4HCl + 4O$$

The hydrochloric acid liberated in the last reaction is theoretically just sufficient to liberate the acetic acid from the calcium acetate.

$$2\,(CH_3COO)_2\,Ca + 4HCl = 2CaCl_2 + 4CH_3COOH$$

Thus the amount of acetic acid used at the beginning of the operation with a small addition now and then is sufficient to carry on the reaction of liberating the chlorine for a long time. It is claimed that by using this process the white sour is unnecessary.

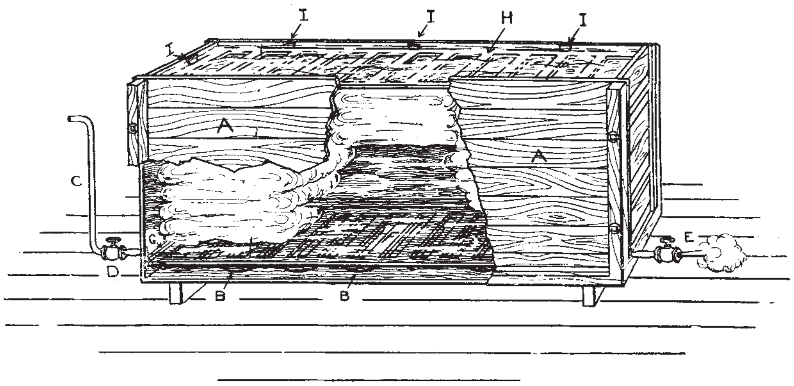


Fig. 58.

BLEACHING WITHOUT CHLORINE.

123. Bleaching with Hydrogen Peroxide and Sodium Peroxide. In No. 111 the active bleaching power of nascent oxygen was described and mention made that certain peroxides particularly those of Hydrogen and Sodium were excellent bleaching agents because of the ease with which they liberated nascent or atomic oxygen.

Hydrogen peroxide decomposes readily, even upon standing, liberating nascent oxygen and forming water according to the equation,

$$H_2O_2 = H_2O + O$$

So also sodium peroxide when added to water is readily decomposed, forming sodium hydroxide or caustic soda, hydrogen peroxide and finally nascent oxygen.

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$$
$$H_2O_2 = H_2O + O$$

The large amount of heat developed during this reaction in conjunction with the strong alkalinity of the bath, cause a rapid evolution and consequent loss of oxygen and if nothing were done to check this action, the greater part of the available oxygen would rapidly escape into the air and be entirely lost as far as any bleaching action were concerned.

In the case of textile materials of animal origin for which hydrogen peroxide is also well adapted, the strong alkalinity would have a serious deteriorating action.

This objectionable action of the caustic soda may be counteracted, and a gradual and uniform evolution of oxygen brought about by first adding to the bath just enough acid, usually sulphuric, to neutralize the caustic soda that will be formed during the addition of the sodium peroxide.

The best results are obtained when the total amount of acid necessary for the neutralization is added to the bath first followed by the sodium peroxide in small quantities with constant stirring. The reaction taking place is represented as follows:

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

The sodium sulphate (Na_2SO_4) formed remains in the bath but in no way interferes with the process and is wholly without action upon the material, if a thorough washing follows the bleaching.

The Roessler & Hasslacher Chemical Company of New York have been foremost in the introduction of sodium peroxide as a bleaching agent, and they recommend the following process for bleaching vegetable fibers, which is based upon both experiment and practice and which has been applied successfully in many cases. A convenient form of apparatus is represented in Fig. 58.

The wooden vat A, is provided with a lead heating pipe B, coiled along the bottom and connected with the iron steam supply pipe C, by means of a valve and wiped joint D. The steam exhausts at the valve E, after passing through the heating coil B.

Over the coil B, is a false bottom F, held down by wooden cleats G, which are fastened with wooden pins. The material is held under the surface of the bleaching solution by the wooden frame H, fixed in place by the wooden wedges I. No metal except lead should come in contact with the bath. A safety valve may be attached at E, to avoid the possibility of bursting the pipe in case the outlet valve is not opened when the steam is turned on.

When using wooden vessels for the first time, they should be boiled out with soda, rinsed with hot water and regular peroxide bleaching solution allowed to stand in them for some hours or over night. This will prevent the color coming out of the wood and staining the cloth.

After whatever preliminary treatment as is deemed necessary, the goods are washed and entered into a bleaching bath made as follows: To every 100 gallons of water add

$5\frac{1}{3}$ lbs. Sulphuric (66° Be.)
and then 4 lbs. Sodium Peroxide, little by little,

and with constant stirring until the bath gives a slight blue color to litmus paper. If the paper does not turn blue after all the sodium peroxide has been added, add ammonia (only a little needed) until it does. Should the bath become too alkaline add a very little acid.

Enter the material, heat to 120° F, from one to two hours depending upon the nature of the goods. Lift, drain allowing liquor to return to vat, and then rinse thoroughly. Succeeding batches are entered at once, allowing more time to each, but without strengthening or restoring the bath, which is finally exhausted by leaving the last batch to bleach over night.

Great care must be taken to prevent any iron from coming in contact with the bleaching liquor.

Until within a few years the expense of bleaching by the use of peroxides has been so great as to rule them out for only very special cases, but of late, improvements in the process of making sodium peroxide has reduced the cost materially. For many purposes sodium peroxide is now found to be a valuable and not too expensive bleaching agent. Its value in the bleaching of union goods cannot be overestimated.

The third class, however, is of minor importance in the Textile Industry.

5. Members of Each Class. Of *vegetable fibres*, cotton is by far the most important, then follows linen, hemp, jute, China Grass, or ramie, and a few others of less importance, such as Manilla hemp, Sunn hemp, New Zealand flax and the fibre obtained from various palms.

The other vegetable substances with which the dyer may have to deal are straw for hats, vegetable ivory used for buttons, wood fibre, and paper pulp which may consist of almost any vegetable fibre or mixture of vegetable fibres.

The only *animal fibres* of great importance are wool, and a few varieties of hair, and silk. To this class also belong such substances as leather, feathers, horn and bone, all of which are sometimes colored.

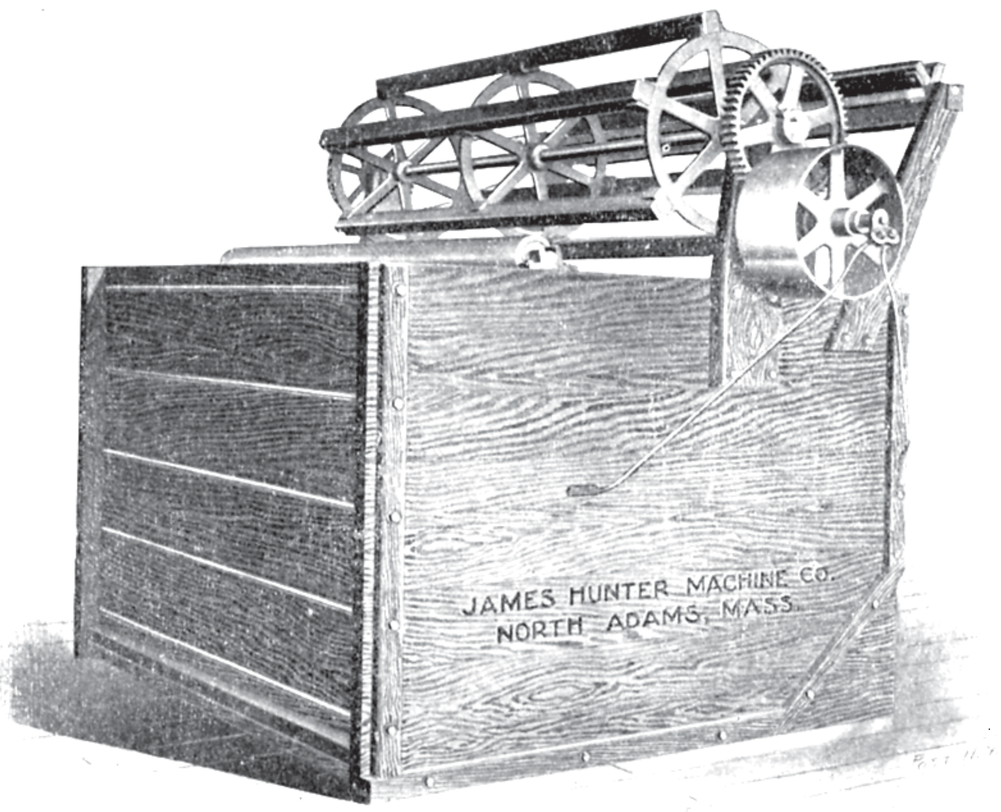
Under the head of *mineral fibres* are included such substances as glass wool, slag wool, asbestos, etc. These are used in certain chemical operations, and in covering steam-pipes, boilers, steam-jacketed kettles and stills, on account of being non-conductors of heat, but for practical purposes they are never colored, and need not be further considered.

Under the head of *artificial fibres* are included all fibres produced artificially from chemical products. The only one of importance, however, is artificial silk, and this will be considered later. (See Art. 24.)

COTTON.

6. Cotton is the downy, fibrous material that covers the seeds of several species of plants known botanically as *Gossypium*. The fibre and seeds are enclosed in a three to five valved capsule or cotton boll, which when ripe bursts open. The cotton is then picked and separated from the seeds by a process known as ginning, the products being cotton, ready to be baled, and cotton seed.

7. Cotton Seed Industry. Formerly, cotton seeds had no commercial value, but in recent years they have become a source of great income, owing to the large amount of oil which can be pressed from them, and also for the various animal feeding



REEL DYEING MACHINE

The James Hunter Machine Co.

TEXTILE CHEMISTRY AND DYEING.

PART III.

EDUCATIONAL REQUIREMENTS OF THE TEXTILE COLORIST.

124. To become an efficient dyer one should have a knowledge of the material to be colored, its chemical and physical properties, its structure, and its action with the various reagents with which it may come in contact during the coloring process. Furthermore, it is essential that the dyer be well acquainted with the properties of different dyestuffs, and that he know, as far as possible, their composition, but more particularly their action toward the different fibers under various conditions.

The former consideration we have taken up with considerable detail; and, having brought the material to where it is ready to be colored, we shall take up the latter consideration.

PRINCIPLES OF TEXTILE COLORING.

125. Textile Coloring may be defined as the process, or combination of processes, used to fix a color or colors permanently and uniformly upon textile material, and includes both dyeing and textile printing.

Dyeing is sometimes given almost as broad an interpretation as textile coloring; but, to be specific, it should include only those processes in which *the entire body* of the material that is being colored is immersed in the coloring bath for a greater or less period of the time required for the coloring.

Textile Printing is a process by which the colors are confined, by use of a printing machine, to certain *portions* of the material, thus producing a definite colored design. The color paste is applied by means of copper rollers, one for each color; and often prints containing ten or more different colors are produced. In some cases mordants are printed upon the material, and the colors developed later by a dyeing process. Many different effects may be produced by combined dyeing and printing.

The coloring of such materials as paper, leather, straw, feathers, bone, wood, and ivory — which, strictly speaking, are not textile materials — is more commonly designated as **Staining** than as dyeing.

CLASSIFICATION OF DYESTUFFS.

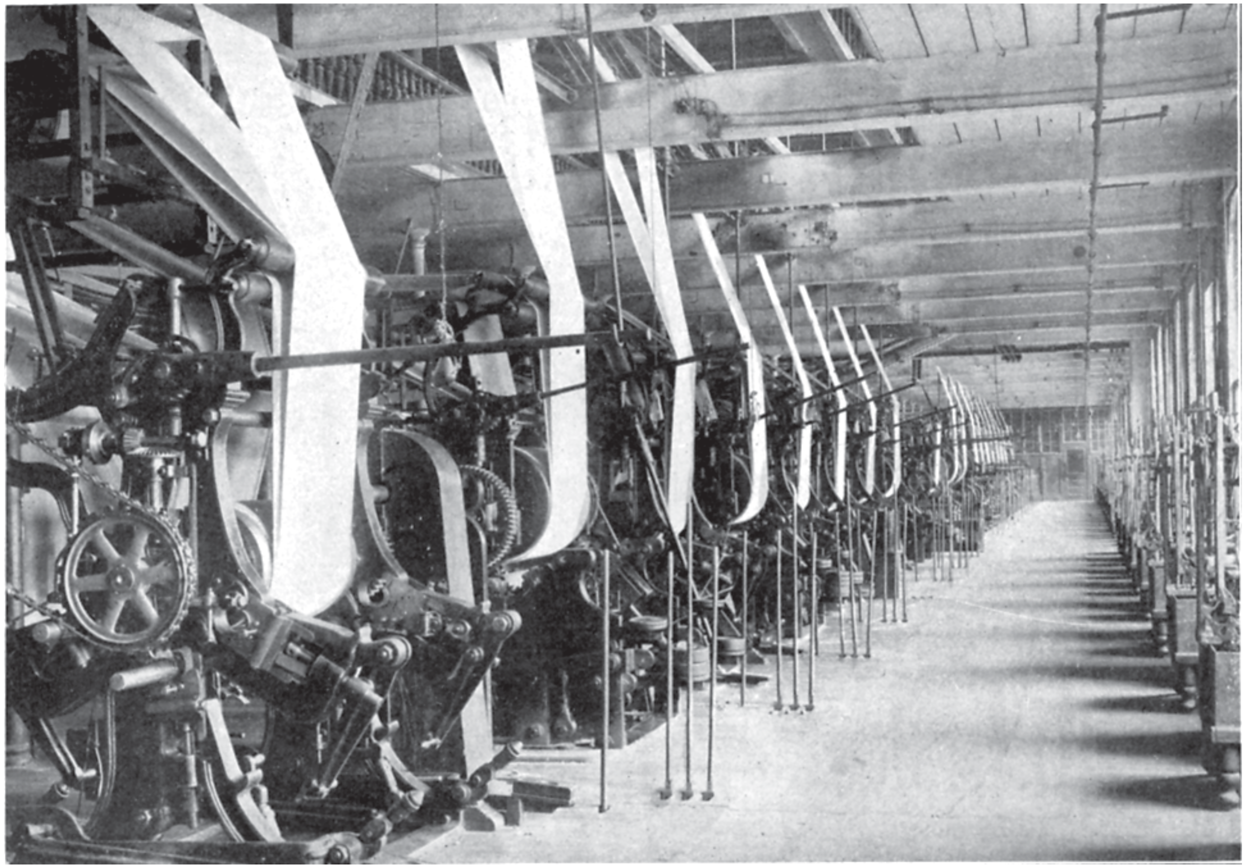
126. The first classification of dyestuffs was made about one hundred years ago by Bancroft, one of the earliest color chemists. He divided the dyestuffs then existing into two classes, **Substantive** and **Adjective.**

As **substantive dyestuffs** he designated those capable of producing a full shade upon textile material without the necessary assistance of any other combining substance; and as **adjective dyestuffs** those requiring an intermediate combining substance (called a **mordant**) to fix satisfactorily and fully develop the color.

This classification has been used ever since, but of late there has been a constant tendency to replace the term "substantive dye" with that of **direct color,** and "adjective dye" with the term **mordant color.**

As examples of substantive or direct colors, we might mention turmeric, indigo, and the direct cotton colors; and as examples of adjective or mordant colors, alizarine and related dyestuffs, logwood, and fustic.

The above classification is not entirely satisfactory, there being many dyestuffs that are substantive toward one fiber and adjective toward another. The basic colors, for instance, are substantive toward wool fiber but adjective toward cotton; while the acid colors are substantive toward wool but have no direct affinity for cotton. Again, there are the insoluble azo colors, like the common Para and Naphthylamine reds, that cannot in the truest sense be considered as belonging to either class.



SECTION OF PRINTING ROOM, SHOWING 19 MACHINES IN OPERATION

American Printing Co.

Another common method is to classify dyestuffs according to their source into

(1) Natural Dyestuffs:
  (*a*) Vegetable.
  (*b*) Animal.
(2) Mineral Dyestuffs.
(3) Artificial Organic Dyestuffs.

Though the various divisions of this classification, particularly the artificial, are quite sweeping in the number and character of the dyestuffs they include, they have the advantage of conciseness, and one class does not overlap another.

The natural dyestuffs include such coloring matters as logwood, indigo, fustic, cutch and cochineal.

The mineral colors include prussian blue, chrome yellow, iron buff, and a large number of inorganic pigments.

The artificial organic dyestuffs are the most important, and this class may be divided into twenty or more important sub-classes. It includes all of the so-called coal-tar dyes, such as magenta, benzo-purpurin, acid violet, tartrazine, alizarine, etc.

It is this latter classification that we shall follow.

THEORIES OF TEXTILE COLORING.

127. There are three theories in regard to the nature of textile coloring processes, which are definite enough to be named. They are as follows:

1. The Mechanical Theory.
2. The Chemical Theory.
3. The Solution Theory.

The **mechanical theory** assumes that the various coloring matters are fixed to the fiber by purely mechanical means.

The **chemical theory** assumes that there is a direct chemical combination between the dyestuff and the fiber.

The **solution theory,** the most modern of the three, was proposed by the German color chemist, Dr. Otto Witt. It was originally proposed as an explanation of the dyeing of direct cotton colors, but applies to all substantive dyestuffs. This theory assumes that a cotton fiber dyed with a direct cotton color — or in fact any fiber dyed with a purely substantive color — is a solid solution of the dyestuff.

The true nature of the dyeing process is, as yet, a conjecture in most cases. In some instances there is strong evidence of chemical union between dyestuffs and fiber; while in others — as, for instance, the fixation of pigments in calico printing — mechanical principles are evident. In the case of color lakes like turkey red, no one doubts that the color is developed by the chemical union of alizarine with aluminium and, perhaps, a little calcium; but this color lake is probably held in the pores and attached to the fibers mechanically rather than by chemical combination. In the case of the direct colors, the solution theory is a reasonable explanation; but the fact that an alteration in the chemical composition of a fiber often noticeably influences its affinity for dyestuffs, is strong evidence in favor of the chemical theory. The establishment of the true theory of dyeing is therefore an open question; and with these facts in mind, together with many others that will be learned through study and practice, each student will gradually establish a theory of his own.

DEFINITIONS.

128. Mordants. A mordant may be defined as a substance capable of uniting with certain dyestuffs to form insoluble colored compounds (usually color lakes) which, under certain conditions, will become attached to or united with textile material.

Color Lakes. A color lake is an insoluble colored compound produced by the chemical union of an organic compound with an inorganic substance (usually an oxide or a hydroxide of a metal).

Example. The organic substance alizarine unites with the hydroxide of aluminium and calcium to form a valuable color lake known as Turkey red.

Pigments. A pigment is any insoluble compound, usually colored, in a very finely divided or powdered state. Most pigments are of inorganic origin, as lead chromate ($PbCrO_4$), cinnabar (HgS), and chromium sesquioxide (Cr_2O_3); but the term also includes the color lakes and such substances as para red, indigo blue, lamp black, and sepia, which are of organic origin.

Mordanting Process. This is the operation by which various mordants are precipitated or fixed upon textile material, in order that they may unite with coloring matters to form color lakes.

Mordanting Principle. As often applied, the term "mordant" indicates the metallic salt used to produce the mordant; but in the strictest sense, the mordant is that compound which, in direct combination with the dyestuff, forms the color lake. In order to avoid confusion, we shall designate the compound used to produce the mordant as the **Mordanting Principle.**

Example. In one of the most important wool mordanting processes, potassium bichromate ($K_2Cr_2O_7$) is used in the mordanting bath; but the actual mordant precipitated upon the fiber is an acid oxide of chromium (CrO_3).

The potassium bichromate is, therefore, the mordanting principle.

Fixing Agents. The term "fixing agent" is frequently used in an indefinite sense, and, as commonly applied, leads to confusion rather than enlightenment. The misunderstanding arises through the difficulty experienced in making a precise division between a true mordant and a fixing agent. By strict adherence to the following classification, which recognizes six distinct classes of substances, the writer believes that little if any misunderstanding can arise.

(1) Metallic Mordants.
(2) Acid Mordants.
(3) Chemical Fixing Agents.
(4) Mechanical Fixing Agents.
(5) Developing Agents.
(6) Mordanting Assistants.

(1) **Metallic Mordants.** This term is used to include only substances (usually metallic oxides or hydroxides) which, in chemical union with certain dyestuffs known as "Mordant Colors," will produce color lakes.

(2) **Acid Mordants.** This term includes tannic acid and the various substances rich in this acid (such as sumac, gall nuts, and various bark extracts), various fatty acids (such as oleic and stearic acids), and Turkey red oil — all of which are of an acid character. These compounds, when used in conjunction with the basic dyestuffs, cause, by chemical union or otherwise, a relatively fast deposition of coloring matter upon cotton, a fiber for which they alone have but little affinity. The acid mordants are of minor importance as compared with the metallic mordants.

(3) **Chemical Fixing Agents.** This term is used to include only the following classes of compounds:

(I) Those which are instrumental in the fixation of a mordant upon textile material by uniting chemically with the mordant and holding it there in an insoluble condition until such time as the proper dyestuff shall be ready to react with it.

Examples. (*a*) The various antimony compounds used to fix tannic acid upon cotton fiber as an insoluble antimony tannate, previous to dyeing with basic colors; (*b*) The tannin compounds (as sumac) used to fix iron upon cotton and silk in the form of an insoluble tannate of iron, when the iron is to be used as a mordant for logwood.

(II) Those which cause the precipitation of the actual mordant upon the fiber when the material already saturated with the mordanting principle is passed through a solution of the fixing agent.

Example. If cotton material saturated with a solution of nitrate of iron (mordanting principle) is passed through a solution of sodium carbonate (fixing agent), the latter reacts with the former, precipitating iron as a basic carbonate or hydrate and thus fixing an iron mordant upon the fiber.

In a number of cases, compounds precipitated in this way have a decided color, and material may be allowed to remain in this condition without dyeing. In the example cited, for instance, a brownish-yellow shade known as "iron buff" is produced.

(4) **Mechanical Fixing Agents.** This term is used to include any substances (such as albumen and certain gums) capable of holding pigments permanently upon textile material by mechanical means.

Example. In calico printing, a pigment like chrome yellow may be made into paste with albumen solution, and printed upon cotton material. Upon steaming, the albumen coagulates, becomes insoluble in all ordinary reagents, and the color is permanently held upon the fiber.

(5) **Developing Agents.** This term includes any organic substances capable of uniting with other substances (sometimes a dyestuff already upon the fiber) to produce an insoluble colored organic compound or pigment, not a color lake.

Examples. (*a*) Cloth prepared with Beta naphthol, when passed through a bath of diazotized para nitro-aniline, will become dyed a beautiful red, by the formation of an insoluble red pigment throughout the material. In this case the diazotized para nitro-aniline is the developing agent.

In case the substance already upon the fiber is a dyestuff, the operation is commonly called the **coupling process**, and is to render the original shade faster. Usually the original shade is retained, but in some cases it is modified or changed completely.

(*b*) If cotton material dyed with Primuline, a direct cotton yellow, is diazotized and passed through a solution of Beta naphthol, the Primuline will become coupled with the latter, and a bright red will be produced.

(6) **Mordanting Assistants.** Under this head should be included such substances as tartar (potassium acid tartrate) and lactic, oxalic, and sulphuric acids, which are often used in metallic mordanting baths. They assist in the uniform deposition of the mordant upon the fiber, but are not themselves taken up by the fiber and in no way enter into the final color lake.

APPLICATION OF MORDANTS — General.

129. The periods of the coloring process at which the mordant may be applied are as follows:

(1) *Previous to its union with the color stuff.* This is by far the commonest and most important time of application. In this case the mordant is applied to the material in one bath, and the color stuff applied later in a separate bath.

(2) *In conjunction with the color stuff.* This is very common in textile printing processes. Processes have also been devised in which both mordant and color stuff are used in the same bath; but they are few in number and for the most part unsatisfactory, there being too great a tendency for the color lake to form and precipitate in the bath rather than upon the fiber.

(3) *The color stuff applied first and the mordant subsequently.* This process is sometimes called **stuffing** or **saddening,** but more frequently, **after treating.** When a chromium compound is used, which is often the case, the process is known as **after-chroming.**

In general it may be said that the mordanting process consists in treating the fiber in some way with a soluble compound of a metal (mordanting principle) which is decomposed in the case of animal fibers, by the presence of the fiber itself or through dissociation by solution in the mordanting bath, the oxide or hydroxide of the metal becoming fixed upon the fiber. In the case of vegetable fibers, which differ greatly from those of animal origin in character, the mordant becomes attached to the fiber more through chemical precipitation and fixation.

The Mordanting process is of great importance, as the mordant plays almost as necessary a part in the application of the so-called mordant colors as does the dyestuff itself, and among this class are included some of the most valuable of color stuffs.

Of all the metals, only a few are valuable as mordants. These are: Chromium, aluminium, iron, copper and tin. On account of its general applicability, chromium is most frequently used. Iron and copper seem to produce the fastest color lakes, while aluminium and tin form the brightest.

Combinations of two mordants are frequently used, particularly in textile printing, thus producing a great variety of shades. Such compounds as the oxides of calcium, magnesium, and zinc, though of little value alone, often increase the fastness of the color lakes of other mordants. They are sometimes spoken of as being **supplementary mordants.**

130. Mordanting of Wool. The chemistry of the mordanting of wool is not only complicated but more or less theoretical. For the present, therefore, we shall let the following points suffice:

Wool apparently has more or less natural attraction for certain compounds both basic and acid in character. When in dilute solution, the highly dissociated condition of the mordanting principle, aided by this natural affinity of wool, brings about a deposition of various metallic compounds (usually oxides or hydroxides) upon the fiber, which depend in their composition chiefly upon the mordanting principle used, but to a certain degree also upon the other conditions of the mordanting bath. This process takes place most completely and uniformly in a boiling bath, and in the presence of some other soluble compound which we have already described as a "mordanting assistant."

Chromium Mordants on Wool. The present methods of applying mordant colors to wool, especially for the production of dark shades, depend almost entirely upon the use of chromium mordants. *Potassium bichromate* ($K_2Cr_2O_7$) is the most important chromium mordanting principle.

When wool is boiled in a plain dilute solution of potassium bichromate, decomposition appears to take place as follows:

$$K_2Cr_2O_7 = K_2CrO_4 + CrO_3$$

Potassium Bichromate = Potassium Chromate + Chromic Anhydride,

the chromic anhydride in some way combining with the wool, and the potassium chromate remaining in solution.

It is the *basic oxide of chromium* (Cr_2O_3), however, which seems to be the most valuable as a mordant, except, perhaps, in the case of the application of some logwood extracts. In dyeing with alizarines as well as other mordant dyestuffs, if much CrO_3 is present, it is reduced to Cr_2O_3 at the expense of the dyestuffs, which is, of course, an expensive method and which furthermore detracts from the brilliancy and general tone of the finished color by the formation of a greater or less amount of some muddy-appearing oxidation product of the dyestuff.

The mordanting of wool in a plain potassium bichromate bath is, therefore, not practicable in the majority of cases.

In order to reduce as much of the CrO_3 to Cr_2O_3 as is necessary, and to bring the deposition about slowly and uniformly throughout the wool, a mordanting assistant is added to the mordanting bath. The substances most frequently used for this purpose are:

Tartar (*Bitartrate of Potassium*, $KHC_4H_4O_6$),
Lactic Acid ($C_2H_4OH.CO\,OH$),
Oxalic Acid $(CO\,OH)_2$.

The following may be taken as representative wool-mordanting processes in which potassium bichromate is used as the mordanting principle:

METHOD A. *Potassium bichromate alone.*

2 per cent — $K_2Cr_2O_7$. For light shades.
3 per cent — $K_2Cr_2O_7$. For medium shades.
4 per cent — $K_2Cr_2O_7$. For dark shades.
Necessary amount of water.

Boil material in this bath one and one-half hours.

NOTE. The percentages given above, as well as those which may follow, refer to the amount of material being mordanted or dyed, unless otherwise specified.

METHOD B. *Potassium bichromate and Sulphuric acid.*

$$\left.\begin{array}{l}\text{3 per cent — } K_2Cr_2O_7 \\ \text{1 per cent — } H_2SO_4\end{array}\right\}\ \text{For light shades.}$$

and

$$\left.\begin{array}{l}\text{4 per cent — } K_2Cr_2O_7 \\ 1\tfrac{1}{2}\text{ per cent — } H_2SO_4\end{array}\right\}\ \text{For heavy shades.}$$

Necessary amount of water.

Enter at 140° to 150° F. Bring to a boil, and boil for one and one-half hours.

METHOD C. *Potassium bichromate and Tartar.*

3 per cent — Potassium bichromate.
$2\frac{1}{2}$ per cent — Potassium bitartrate.
Necessary amount of water.

These are the ordinary proportions. For very dark shades the quantities may be advantageously increased to 4 per cent $K_2Cr_2O_7$ and 3 per cent Tartar; and for light shades the quantities may be reduced to 1 per cent $K_2Cr_2O_7$ and 1 per cent Tartar.

Enter at 130° to 140°F; bring slowly to a boil; and mordant at a boil for one and one-half hours, working the material well, particularly during the first part of the operation.

METHOD D. *Potassium bichromate and Lactic acid.*

FOR LIGHT SHADES.	FOR ORDINARY SHADES.	FOR VERY DARK SHADES.
1 per cent	3 per cent	4 per cent — $K_2Cr_2O_7$
1 per cent	2 per cent	3 per cent — Lactic acid.

Necessary amount of water. Process same as Method C.

METHOD E. *Bichromate of potash and Oxalic acid.*

FOR LIGHT SHADES.	FOR ORDINARY SHADES.	FOR VERY DARK SHADES.
1 per cent	3 per cent	4 per cent $K_2Cr_2O_7$
½ per cent	1½ per cent	2 per cent — $H_2C_2O_4$

Necessary amount of water. Process same as method C.

Of the above mordanting processes, A and B cannot be used to advantage, except in cases where an oxidizing mordant is desired.

Method C is the favorite, particularly for light shades where results rather than cheapness are desired. It gives a clean bath, and the finished colors are very clear. For dark shades, crude tartar (argols) is sometimes used to reduce cost.

Method D also gives excellent results, particularly for dark colors, and is comparatively cheap.

Method E gives excellent results in certain cases.

With all these methods, it is best to start the mordanting at a comparatively low temperature — say 130° to 140°F — and to bring slowly to a boil. The various ingredients of the bath should be dissolved separately, for when introduced in the concentrated form they will react with each other, precipitating the mordant in the dye bath rather than on the fiber. If the material is introduced at a boiling temperature, or is heated too rapidly, it is likely to be precipitated on the fiber too rapidly, producing lack of penetration and causing unevenness of coloring. The material should be well worked, particularly at the beginning of the operation; and the amount of mordanting liquor should be from 30 to 50 times the weight of the material that is being mordanted.

After the mordanting, the material should be well washed to remove any excess of mordant not well fixed upon the fiber; otherwise a superficial color lake will be formed during the dyeing. Finally, the material should be well hydro-extracted and, if possible, dyed without drying.

Sodium Bichromate ($Na_2Cr_2O_7$) acts the same as potassium bichromate in nearly every case, and on account of its cheapness is used instead of the latter. It does not crystallize as well, nor keep as well when stored, as the potassium compound. For wool-dyeing, preference is commonly given to the potassium salt.

Chrome alum [$K_2Cr_2(SO_4)_4.24H_2O$] and *Chromium sulphate* [$Cr_2(SO_4)_3$] are now seldom used as wool-mordanting principles. They are, however, valuable in the preparation of other chromium mordanting principles. *Chromium fluoride* (CrF_3)* has been introduced recently as a mordanting principle, and is meeting with much favor, particularly in cases where the strong oxidizing action characteristic of the potassium bichromate is undesirable. It deposits the mordant readily and uniformly as Cr_2O_3; and some spinners say that it does not affect the feel and spinning qualities of the wool as much as some other mordanting principles. Chromium fluoride is also used for after-chroming, and with alizarine in wool-printing.

The following method of mordanting wool with Chromium fluoride gives very good results:

3 to 4 per cent — Chromium Fluoride.
1 to 2 per cent — Oxalic Acid.
Necessary amount of water.

Enter at 140° F; bring to a boil; and mordant at a boil one and one-half hours.

Chromium Acetates are used to a limited extent with wool, particularly in printing, but chiefly in the printing and dyeing of cotton, and will be considered under the latter head.

Aluminium Mordants on Wool. Aluminium mordants on wool are not used now as much as formerly. About their only standard uses at the present time are for the production of alizarine reds, pinks, and oranges, cochineal reds, logwood blues, with the yellow natural dyestuffs, and with mixtures of the preceding colors.

---

*Note.—Chromium fluoride should be stored in wooden containers, as it readily attacks glass and metals. When used in dyeing apparatus made of copper, a small sheet of zinc hung in the bath will prevent corrosion.

The presence of iron will detract from the brightness of the shades produced upon an aluminium mordant, especially with alizarine colors.

Alum and Aluminium Sulphate [$Al_2(SO_4)_3$] are the only aluminium mordanting principles commonly used with wool. Aluminium fluoride [AlF_3] gives good results, but is not used in practice.

The alums are a series of compounds having the general formula·

$$R'_2R'''_2(SO_4)_4.24H_2O,$$

in which R' is a metal having a valence of 1, and R''' is a metal having a valence of 3. These salts crystallize well and easily, and for this reason are usually very pure. Owing to their reliability, they are largely used in mordanting and in the preparation of other aluminium compounds.

The commonest aluminium alums are the potassium alum [$K_2Al_2(SO_4)_4.24H_2O$] and the ammonium alum [$(NH_4)_2Al_2(SO_4)_4.24H_2O$].

It is only the $Al_2(SO_4)_3$ contained in the alum that is of value in the mordanting process, the potassium sulphate not entering into the reaction at all.

In the past, alum was used in preference to the straight Al_2SO_4; but during recent years improvements in the process of manufacture have brought out an aluminium sulphate, which, in most cases, is quite free from iron, and which, being of lower cost, has largely superseded alum. It crystallizes as follows:

$$Al_2(SO_4)_3.18H_2O.$$

There is a marked tendency for aluminium salts when in solution, especially at high temperatures, to change gradually from normal to basic salts with the liberation of free acid. This change takes place to a greater extent when wool fiber is present in the solution: an insoluble compound of aluminium is deposited upon the fiber, and, upon boiling, the wool becomes mordanted with $Al(OH)_3$ or Al_2O_3. This process goes on with such ease that unless some acid or acid salt is added to retard the process, the mordant will be deposited unevenly. Oxalic acid and tartar are most frequently used for this purpose. They form salts of aluminium which, possessing greater stability than the aluminium sulphate, dissociate more slowly , in this way causing a more even deposition of the mordant, which, after washing and drying, appears to be the oxide of aluminium (Al_2O_3).

PROCESS:

	FOR LIGHT SHADES.		FOR DARK SHADES.
	5 per cent	to	10 per cent — Alum
or,	3½ per cent	"	7 per cent — Aluminium Sulphate
	1½ per cent	"	3 per cent — Tartar
or,	1 per cent	"	2 per cent — Oxalic Acid.

Necessary amount of water.

Enter the material (wool) at 85° F; bring to a boil; and mordant at a boil one and one-half hours.

Some dyers prefer to increase the amount of tartar and diminish or entirely do away with the oxalic acid.

Iron Mordants on Wool. Iron mordants can be used only for the production of blacks and very dark shades of violet and brown. Of recent years, chromium has largely replaced iron in wool mordanting; and at the present time the latter is but little used in wool-dyeing except for the production of logwood blacks, and as a saddening or after-treating agent.

Ferrous sulphate ($FeSO_4.7H_2O$), commonly called "copperas," is the most important iron mordanting principle used with wool. It is chiefly used either alone or with copper sulphate, in the production of logwood blacks. It can be applied *previous to dyeing*, by boiling the wool in a bath made up with ferrous sulphate, oxalic acid, and tartar; *at the same time as the dyestuff*, in a bath made up with $FeSO_4$, oxalic acid and logwood; or *after the dyeing*, as a saddening or after-treating agent. For further discussion see "Logwood on Wool."

Tin Mordants on Wool. Tin mordants are sometimes used for the production of bright cochineal reds and bright yellows, with the yellow natural dyestuffs. When used alone, tin mordants are of minor importance in the coloring of wool. Their value lies chiefly in the fact that when used in conjunction with other mordants the brilliancy of the resulting color lake is greatly increased. For this reason tin mordants are often used with those of aluminium for the production of bright reds, *Stannous chloride* ($SnCl_2$) is the tin compound most frequently used as a mordanting principle for wool. Wool boiled in a solution of stannous chloride in the presence of oxalic acid or potassium bitartrate, becomes mordanted with the oxide of tin. With tin mordants the dyestuff is often applied in the same bath.

Stannic Chloride ($SnCl_4$) is sometimes used in wool printing.

Copper Mordants on Wool. Like the compounds of tin, those of copper are rarely used alone in wool mordanting. Tin increases the brilliancy of color lakes into which it is introduced, but diminishes their fastness. Copper, on the other hand, when introduced into color lakes, diminishes their brilliancy but increases their fastness.

Copper sulphate ($CuSO_4.5H_2O$) is the chief copper mordanting principle for wool, and the only one that need be considered. Its principal use is in conjunction with iron and chromium compounds in the production of logwood blacks (which see). It is also used as a saddening or after-treating agent.

Application of Dyestuffs to Mordanted Wool. This will be discussed in detail under the head of Mordant Colors, but a few words at this point may not be out of place.

In general, the previously mordanted wool is introduced into a plain bath of the dyestuff, at, or a little above, ordinary temperatures; is brought slowly to a boil; and is dyed at a boil for one and one-half hours. In case the water used is hard, it should be corrected by the addition of a small amount of acetic acid.

Application of Mordant and Dyestuff in same Bath. This can be done successfully in only a few cases, and these will be referred to under their various heads. It is a very irrational method, and, ordinarily, nothing but failure can be expected.

After-Mordanting. Mention must be made of this third process, as it has recently developed into one of the most important mordanting methods for wool. It has always been used to some extent with logwood and the natural dyestuffs, and is known as the "stuffing" or "saddening" process; but during recent years a number of acid dyestuffs have been introduced which, with metallic mordants — particularly those of chromium — form color lakes that are practically of the same color as the dyestuff but are faster.

The process is simple, and usually consists in boiling the previously dyed material in a bath containing 1 to 3 per cent of potassium bichromate for one and one-half hours. A gradual dissociation of the $K_2Cr_2O_7$ takes place; and the chromium, as an oxide, unites with the acid dyestuff to form a color lake in the body of the fiber, shades being produced which are often much faster than those of the original dyestuffs. This method does not apply to all of the acid dyestuffs, but only to a certain group which we shall designate as the **mordant acid dyestuffs.** The process is often spoken of as "after-treating" or "after-chroming."

131. Mordanting of Silk. Silk possesses even a greater affinity than wool for certain compounds, and among these are the oxides and hydroxides of the metals commonly used as mordants.

The absorbing character of silk, unlike that of wool, seems to be greater at moderately low temperatures, and from slightly basic rather than acid solution.

Cold and comparatively concentrated solutions of basic salts of chromium, aluminium, and iron, are best suited for silk mordanting. The silk is steeped in these solutions for a number of hours. Very little dissociation takes place in the concentrated bath, and the silk takes up the basic salt chiefly as such; but when the material is subsequently washed in a large volume of water, preferably running water, the dilution causes more dissociation, and the hydroxide of the metal is deposited in the fiber. Upon the final drying of the material, the hydroxides in most cases lose their water and become oxides.

The acid ions of the salt used are necessarily liberated during this process; but they are neutralized by passing the silk through an alkaline after-bath (usually of silicate or bicarbonate of soda), which completely fixes the mordant upon the fiber.

132. Mordanting of Cotton. The mordanting of cotton is rendered more complex and difficult of application than either that of wool or silk, since vegetable fibers have little if any natural attraction for metallic oxides or hydroxides, and of themselves seem to exert no decomposing or dissociating influence over mordanting principles.

So numerous and varied are the methods of applying mordants to cotton, that even a brief description of all the processes and compounds that have been used and are being used at the present time, would make a volume by itself. We shall, therefore, confine ourselves to the methods of applying mordants, which are now largely depended on in the application of mordant colors to cotton. These may be enumerated under four heads:

1. The combined padding, ageing, and dunging processes.
2. The combined printing, ageing, and dunging processes.
3. Direct chemical precipitation upon the fiber.
4. Steam Printing.

Considered briefly, the principles of these are as follows:

FIRST METHOD.—*Padding, Ageing, and Dunging.* Certain metallic salts decompose at comparatively low temperatures when heated in a moist atmosphere. The acetates of aluminium and iron are the best examples of such compounds. These are readily soluble in water; and cotton material can easily be saturated with their solution, by the process called **padding.** Upon the cloth being dried, and heated for some time in a moist atmosphere, these salts decompose, forming basic acetates and, finally, hydroxides, with the liberation of free acetic acid, which, being volatile, is driven off by the high temperature and by the circulation of the air. The mordant is still further fixed upon the cloth, and any remaining acid neutralized, by the **dunging process.**

Padding consists in saturating the cloth by passing it, full width, through a bath of any given liquor; then working the liquor evenly and thoroughly into the cloth, and finally removing the excess by squeeze rolls.

After leaving the padding machine, the material is passed over drying cans or through a drying chamber and is ready for the "ageing."

The **ageing** process was formerly carried out by heating the cloth for 48 hours, more or less, in a large, well-ventilated room heated with steam pipes and in which the atmosphere was kept moist by the admission of free steam. This method is used to some extent at the present time; but in modern practice, steam ageing machines have largely replaced the older methods.

The steam ager consists of a long chamber containing two series of rolls, one at the bottom and one at the top, over which the cloth can be passed up and down, thus requiring several minutes for its passage through the machine. During this time the cloth is acted upon by steam at atmospheric pressure, a condition which brings about a rapid ageing, or decomposition of the mordanting principle. The cloth is then allowed to stand loosely piled, or hung, in a warm moist room for some time, when the process is completed.

Assuming that aluminium acetate is being used, then the complete ageing is represented by the following equation:

$$(CH_3CO.O)_3Al + 3H_2O = Al(OH)_3 + 3CH_3CO.OH.$$

Intermediate reactions undoubtedly take place with the formation of various basic acetates; but when the process is efficient, most of the aluminium is finally deposited upon and in the fiber as the hydroxide.

The **Dunging** or **Fixing** consists in passing the cloth continuously through a bath containing some substance or substances capable of neutralizing any acid that has not been driven off during the ageing, and of completing the fixation of the mordant. Cow dung was formerly used almost exclusively for this purpose; hence the name "dunging." This substance contains a mixture of the phosphates, carbonates, silicates, and other salts of ammonium, potassium, sodium, and calcium, with certain fibrous and adhesive organic substances; and, when mixed with a small amount of precipitated chalk, makes a very effective neutralizing and fixing agent.

For convenience, modern methods have largely replaced the dung bath with baths of various substances and mixtures, such as sodium phosphate, ammonium carbonate, silicate of soda, and sodium arsenite; but it is held by many that the older method, although slower in action, gave better and more reliable results. The old name for the process has been commonly retained.

SECOND METHOD.— *Printing, Ageing and Dunging.* This process is similar to the first except that the mordanting principle (say acetate of aluminium) is made into a printing paste with various thickeners and is printed upon the cloth. Often a small amount of some inert color is added for the purpose of aiding the printer in his work. The material is then aged and dunged as above.

THIRD METHOD. This consists in padding the cloth with some mordanting principle, and then passing it through a bath containing some precipitant, or *vice versa,* that substance being used first which has the greatest affinity for the cotton, and which is the least likely to be flushed off upon passing into the second bath.

Examples. (*a*) Cotton cloth padded with sumac extract is passed through a bath of nitrate of iron or one of black liquor, the result being the precipitation of an insoluble tannate of iron upon the cloth.

(*b*) Cotton cloth padded with Turkey red oil is passed through a bath of basic aluminium sulphate, the result being the precipitation of an insoluble aluminium soap upon the cloth, which is useful as a mordant in Turkey red dyeing.

FOURTH METHOD.—*Steam Printing.* This consists in printing the dyestuff, together with the mordanting principle and the necessary thickener, upon the cloth; then drying and steaming. During the steaming process the color lake is developed directly upon and in the pores of the fiber. With the alizarines, it is quite essential that the cloth be given a preliminary preparation with Turkey red oil.

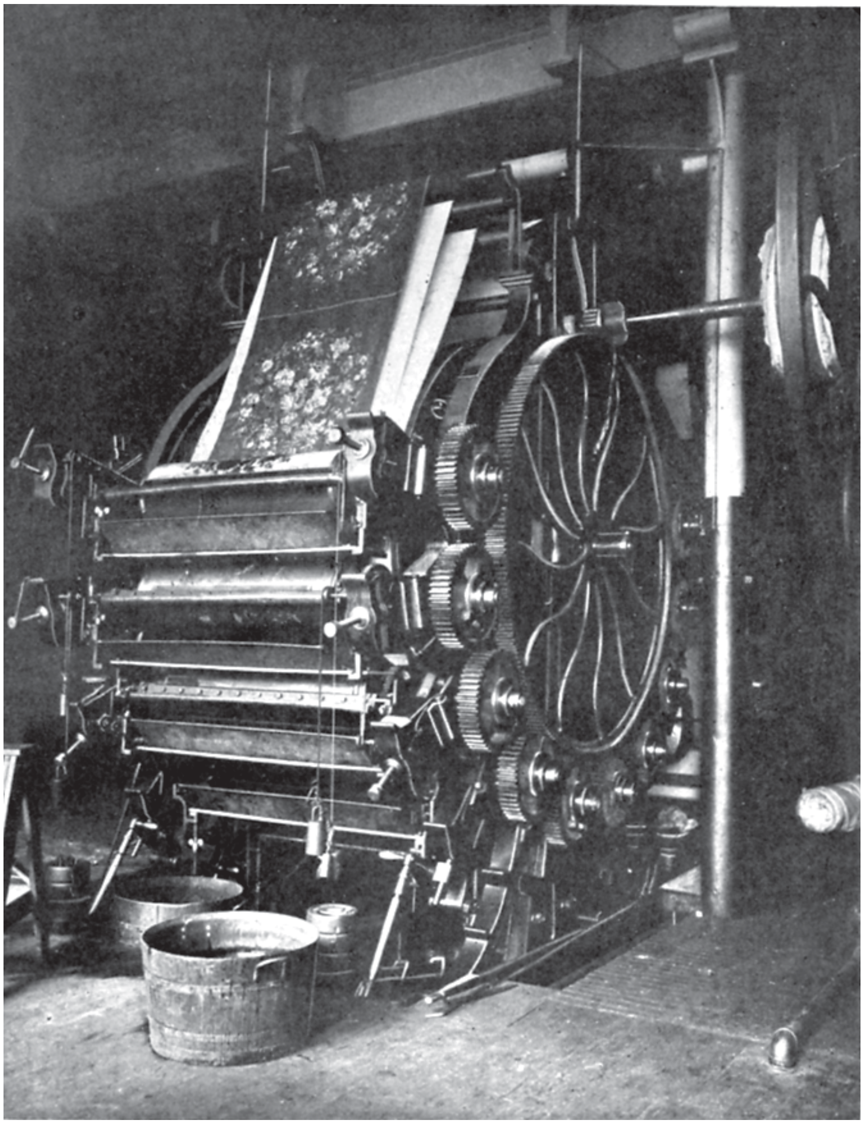
Aluminium Mordants on Cotton. The most important aluminium mordanting principles for cotton are aluminium acetate, aluminium sulphacetate, alum, aluminium sulphate, and the basic sulphates, sodium aluminate, and aluminium sulphocyanate. The nitrate, chloride, and chlorate are used to some extent in calico printing. As already explained, the aluminium mordanting principle should be free from iron.

Aluminium acetate $[(CH_3CO.\ O)_3Al]$ may be prepared by dissolving $Al(OH)_3$ in acetic acid, but more commonly by the double decomposition of aluminium sulphate with lead or calcium acetates, as follows:

$$Al_2(SO_4)_3 + 3(CH_3CO.\ O)_2Pb = 2(CH_3CO.\ O)_3Al + 3PbSO_4$$
$$Al_2(SO_4)_3 + 3(CH_3CO.\ O)_2Ca = 2(CH_3CO.\ O)_3Al + 3CaSO_4$$

By using less of the lead or calcium acetates, aluminium sulphacetate is formed as follows:

$$Al_2(SO_4)_3 + (CH_3CO.O)_2Pb = 2CH_3CO.O.Al.SO_4 + PbSO_4$$



PRINTING MACHINE INSTALLED AT PACIFIC MILLS

Solutions of the aluminium acetates are known as **red liquor** since they are largely used as a mordanting principle in the production of Turkey reds.

Alum and Aluminium sulphates are seldom used as mordanting principles in the normal form; but the basic sulphates are frequently used, particularly in processes 1 and 3.

Normal *Aluminium sulphate* [$Al_2(SO_4)_3$] will not decompose even when boiled in dilute solution, but the basic aluminium sulphates decompose or dissociate readily. The basic sulphates, for this reason, are well suited for the ageing process.

Sodium Aluminate ($NaAlO_2$) comes in commerce usually in the lump or powdered form, and is soluble in water. For the production of "Turkey reds" on cotton the use of sodium aluminate as a mordanting principle has been found to reduce the susceptibility of the shade to the influence of iron and heat.

Aluminium sulphocyanate [$Al(CNS)_3$] is used in the production of alizarine reds by steam printing, as it acts upon the steel doctor blades less than the other aluminium mordanting principles. The introduction of iron from this source is thus avoided, and the brilliancy of the prints correspondingly increased.

Iron Mordants on Cotton. The only important iron mordanting principles for cotton are ferrous sulphate, ferrous acetate, and ferric sulphate.

Ferrous sulphate [copperas, $FeSO_4.7H_2O$] is most commonly applied by the cloth being first padded with some tannin material, and then passed through a ferrous sulphate bath which acts as a precipitant, depositing an insoluble tannate of iron upon the material.

Ferrous acetate [$(CH_3CO.O)_2Fe$] is the most important iron mordanting principle used with cotton. The crude ferrous acetate made by dissolving scrap iron in crude acetic acid or pyroligneous acid, is known as *pyrolignite of iron*. The chief use of the pyrolignite of iron is for the production of blacks, and for this reason it is called **black liquor**. It is also used with alizarine, producing purplish blacks when used alone and chocolate colors when in conjunction with aluminium mordants.

Ferric sulphate [$Fe_2(SO_4)_3$], known in commerce as "Nitrate of Iron," is often used in cotton mordanting. The normal salt is sometimes used, but more frequently the basic sulphate. The material is first padded with the ferric sulphate, and then passed through a bath of soda ash, lime water, or suspended chalk; or it is first impregnated with tannin, and then passed through the ferric sulphate.

Chrome Mordants on Cotton. The rapid increase in the use of chromium mordants has not been confined wholly to wool, for in recent years these mordants have received much favor in the printing, and to a less degree in the dyeing, of cotton with mordant colors. The chief chrome mordanting principles used with cotton are the chromium acetates and chromium bisulphite. Potassium bichromate is rarely used with cotton as a mordanting principle, but largely as an oxidizing agent in dyeing cotton with aniline black, cutch, and sulphur colors. Chrome alum is largely used in the preparation of chromium acetates and other chromium compounds used in cotton dyeing.

Chromium acetates are used in several forms but principally as the normal and basic salts. Normal chromium acetate has the formula $(CH_3CO.O)_3Cr + H_2O$.

The basic chromium acetates $(CH_3CO.O)_2Cr\,OH$ and $(CH_3CO.O)Cr\,(OH)_2$, and intermediate acetates, are formed by adding sodium carbonate, caustic soda, or ammonia to a solution of the normal acetate. These acetates are commonly sold in solutions of about 32° Tw. The normal is green, and the basic violet in color.

Chromium bisulphite $[Cr(HSO_3)_3]$ is best prepared by the action of sodium bisulphite with a chromium salt. The resulting solution is of a yellowish-green color.

It is necessary simply to pad the cloth with a hot solution of the chromium bisulphite, and then allow it to dry.

Tin Mordants on Cotton. Tin mordants are not so frequently used independently as in conjunction with aluminium and chromium mordants for brightening agents. The chief tin mordanting principles for cotton are stannic chloride and sodium stannate.

Stannic chloride or *Tin tetrachloride* $(SnCl_4)$ is used largely with the natural dyestuffs, being fixed upon the fiber by first treating with tannin and then working in a stannic chloride bath.

Sodium stannate (Na_2SnO_3) is used for the natural dyestuffs, and is found to work well with the eosins and certain azo colors. The material is impregnated with a solution of sodium stannate, and then passed through very dilute sulphuric acid or a solution of normal or basic aluminium sulphate.

Copper Mordants on Cotton. As a mordant, copper is not very important in cotton dyeing, and *Copper sulphate* is the only mordanting principle used. Its chief use is in the dyeing of cutch and logwood blacks, where it acts both as a mordanting principle and an oxidizing agent.

Acid Mordants on Cotton. The acid mordants of importance in cotton dyeing are tannic acid and related substances, and several of the fatty acids.

Tannic acid and *sumac extract* are both extensively used in the dyeing and printing of cotton with basic colors.

Turkey red oil (also known as soluble oil, sulphated oil, and olein) is also used for the above purposes.

THE NATURAL ORGANIC DYESTUFFS.

133. General Consideration. Although for the most part superseded by the more modern artificial coloring matters, the natural dyestuffs hold an important place in history; and some of them, indeed, still have no equals in regard to certain characteristic properties that they may possess.

134. Subdivision. For convenience we shall subdivide the natural organic dyestuffs as follows:

1. Indigo, and related compounds.
2. Logwood.
3. Natural dyestuffs producing shades of a red character.
4. Natural dyestuffs producing shades of a yellow to brown character.

INDIGO.

135. General Consideration and Sources of Indigo. For thousands of years, indigo has been the favorite blue dyestuff for both cotton and wool. It is said that textile material dyed with indigo has been found accompanying Egyptian mummies known to be at least 5,000 years old.

Indigo blue or *Indigotin* occurs in many plants, chiefly those of the genus *Indigofera*, the *Indigofera tinctoria* yielding the largest quantity. Among the other indigo producing plants, *Isatis* *tinctoria*, or *Woad* is the most important. This is still cultivated and used in the so-called "woad vat." The *Indigofera* thrive only in tropical climates; and the supply comes chiefly from the Bengal, Oude, and Madras Districts of India, and from Manila, Java, Japan, China, Central America, Brazil, and Africa.

Artificial indigo, a product of recent years, usually comes as a deep-blue paste, consisting approximately of 20 per cent indigotin and 80 per cent water.

136. Cultivation and Preparation of Natural Indigo. Indigo cultivation is one of the chief industries in certain districts of India. The plant is of a herbaceous character, growing three or four feet high, with a stem about $\frac{1}{4}$ inch in diameter.

Indigo blue does not exist as such in the plant, but is developed when the stems and leaves are steeped in water and allowed to ferment. A clear yellow liquid results, which contains the indigo as the soluble indigo white. Upon agitation and stirring, the oxygen of the air converts the indigo white into the insoluble indigo blue. This is allowed to settle, is pressed into cakes, and, when dry, is ready for the market.

137. Chemistry of Indigo Coloring. Unlike the majority of dyestuffs, indigo is insoluble in all the reagents that the dyer can employ practically; but nature has fortunately given it a property that renders its application comparatively simple. Upon reduction in an alkaline bath, it is readily converted into indigo white, as follows:

$$\underset{\text{Indigo Blue.}}{C_{16}H_{10}N_2O_2} + 2H = \underset{\text{Indigo White.}}{C_{16}H_{12}N_2O_2}$$

Upon even the mildest oxidation indigo white passes back to indigo blue, as follows:

$$\underset{\text{Indigo White.}}{C_{16}H_{12}N_2O_2} + O = \underset{\text{Indigo Blue.}}{C_{16}H_{10}N_2O_2} + H_2O$$

Indigo white is readily soluble in water, especially in alkaline solution; and both animal and vegetable fibers absorb this solution with ease. Upon exposure of the saturated fiber to the air, the indigo white is oxidized almost immediately to the insoluble indigo blue, which is rapidly precipitated upon and in the pores of the fiber to as great a depth as the penetration of the indigo-white solution. The alkaline bath of indigo white is commonly called an **indigo vat**; and the process of coloring is usually spoken of as **vat dyeing.**

138. Application of Indigo.— Vat Dyeing. There are at the present time three forms of indigo vats largely depended upon for indigo dyeing:

1. Fermentation Vats.
2. Zinc Lime Vats.
3. Hyposulphite or Hydrosulphite Vats.

The principle above mentioned (See Art. 137) is involved in them all, and they differ only in the method used to reduce the insoluble indigo blue to the soluble indigo white. In every case the vat must be alkaline, and this condition is usually maintained by means of lime or caustic soda. If the vat becomes in the least degree acid, the indigo white cannot be held in solution.

139. Indigo Grinding. In vat dyeing, the indigo must be in an extremely finely divided condition, otherwise the reduction is slow and incomplete. In the case of artificial indigo, which comes in the form of paste, the particles are sufficiently minute; but with natural indigo, a prolonged grind, often lasting two weeks, is necessary. The grinding is done in water, and is accomplished by allowing iron cannon balls or cylinders to roll over the indigo in iron drums.

140. Fermentation Vats. Previous to the 18th century, all indigo dyeing was done by means of fermentation vats. These are still largely depended upon in wool dyeing, but have been superseded in many places by hyposulphite vats. They are not used for cotton dyeing.

Of all the types of fermentation vat that have been used only the **Woad Vat** and the **Soda Vat** or **German Vat** are of sufficient importance to be mentioned.

The **woad vat** is the most important, and the one chiefly used at the present time. The following are the common ingredients. Different dyers have different ideas as to the quantity of each ingredient required; but the accompanying amounts may be considered approximately correct:

Woad (well broken)	200 to 400 lbs.
Bran	20 to 30 lbs.
Madder	5 to 30 lbs.
Lime	20 to 25 lbs.
Indigo (thoroughly ground)	10 to 20 lbs.
Contents	1,500 gallons.

Syrup and molasses are often added in place of bran, owing to the tendency of the latter to choke the vat. A portion of the lime may also be replaced with an equivalent of soda ash.

The vat having been made up as above, it is covered and allowed to stand over night. The cover is then removed and the contents examined. If fermentation has begun, there will be a slow but constant escape of bubbles of gas (CO_2) at the surface; the bath will have a yellowish-green cast; and, upon gentle stirring, a coppery-blue scum will appear, and a sour but not disagreeable odor will arise. In most cases, decided fermentation sets in after thirty-six hours. It is well not to add all of the lime until the fermentation is well started; but on the other hand, the addition must not be delayed too long or decomposition will set in and the indigo be destroyed.

The process is controlled chiefly by the addition of lime and fermentation media. If the fermentation is too rapid, it may be reduced by adding lime; and if too slow, it may be increased by addition of bran, syrup or molasses. The result of too active fermentation is the wasting of indigo, and the final destruction or "blackening" of the vat, as it is called.

Experience alone can teach the requisite amount of lime to be added, and the time to add it. The vat should be ready for use on the third day.

The dyeing process is best carried out at a temperature of 120° to 130° F (50° to 55° C). The scum must be removed from the top before the material is entered. Sometimes a large iron hoop covered with netting is lowered into the vat to keep the material away from the sediment at the bottom.

Piece goods are sewed into an endless band, well wet out, and are worked beneath the surface of the liquor by the process called **hawking**. This was formerly done by hand, but a **hawking machine** is now used, which consists of a pair of rubber-covered squeeze rolls located just below the surface of the vat and capable of keeping the cloth in constant motion. This process is continued until the cloth is thoroughly permeated with indigo-white solution (15 minutes to 2 hours), whereupon the cloth is passed between squeeze rolls and the color developed by immediate exposure to the air.

The use of too strong baths must be avoided or the goods will not be fast to rubbing. Two or even three dips in weaker baths will give the same depth of shade, and much faster and more even colors.

A thorough washing should follow the last dip of the dyeing.

Loose wool is commonly dyed in a circular vat, being introduced in nets. It is worked about by the process called **poling,** constant care being taken to keep it below the surface of the liquor. When the wool has become sufficiently permeated, the whole net is raised and allowed to drain; the excess of liquor is squeezed out; and the wool is then thrown in a loose pile on the floor and constantly worked over with a fork until it has become oxidized and the color developed. This takes at least fifteen minutes. The wool is then given another dip, or, if the color is deep enough, it is rinsed in a dilute acid bath, and then thoroughly washed.

The vat is fed at the close of each day's work by adding the necessary amounts of indigo and bran or syrup, lime being used to control fermentation. A fermentation vat cannot be used to advantage for more than six months.

The Soda Vat or **German Vat.** This is another form of fermentation vat, which, as its name indicates, is largely used in Germany. The *Badische Anilin* and *Soda Fabrik* recommend the following ingredients and quantities of each:

Syrup	8 lbs.
Bran	20 lbs.
Solvay Soda	14 lbs.
Lime	3 lbs.
Madder	6 lbs.
Indigo (20 per cent)	12 lbs.

Contents 600 to 800 gallons.
It is reinforced with indigo, bran, syrup, lime, and soda.

The shades of blue are not as deep as, but are brighter than, those produced in the woad vat. This soda or German vat is useful in the production of light blues. Its application is the same as in the case of the woad vat.

141. Inorganic Reduction Vats. We shall now consider the three important vats of this class, first studying the chemistry and setting of each, and then their application as a whole.

The ferrous sulphate vat, also known as the **vitriol vat** or **copperas vat,** the oldest of the three, was first used during the 18th century, but has been almost entirely replaced by the zinc-lime vat and the hyposulphite vat. The ferrous sulphate vat is set as follows for 500 gallons of liquor:

Indigo (well ground)	15 to 20 lbs.
Lime	30 to 40 lbs.
Ferrous Sulphate	30 to 50 lbs.

The customary practice is to first add the indigo and ferrous sulphate to vat, and then the lime gradually, as a milk of lime. This, however, is varied by some dyers. The vat is then well stirred, and is ready for use in 24 hours. From time to time it may be strengthened by addition of proper quantities of indigo, lime, and ferrous sulphate; but this form of vat does not remain in good condition more than three or four weeks, when it has to be thrown away.

The chemistry of the reaction in the ferrous sulphate bath is as follows:

The ferrous sulphate reacting with calcium hydroxide (water-slaked lime), gives ferrous hydroxide and calcium sulphate:

$$FeSO_4 + Ca(OH)_2 = CaSO_4 + Fe(OH)_2.$$

Ferrous hydroxide, in the presence of water, passes into Ferric hydroxide, liberating nascent hydrogen:

$$Fe(OH)_2 + H_2O = Fe(OH)_3 + H.$$

The nascent hydrogen reduces the indigo blue to indigo white:

$$C_{16}H_{10}N_2O_2 + 2H = C_{16}H_{12}N_2O_2.$$

The zinc lime vat, also called **composition vat,** was introduced about the middle of the 19th century, and has ever since been used extensively for cotton dyeing. The zinc lime vat is set as follows:

Water	500 gals.
Indigo	15 to 20 lbs.
Zinc Powder (Composition)	8 to 10 lbs.
Lime	20 to 25 lbs.

The well-ground indigo and zinc powder are added to the vat first and are well stirred; and then the lime, which has previously been slaked and made into a milk of lime, is slowly added. The vat is allowed to settle, and is then ready for use. Some dyers add the indigo and lime first, but the order of addition of ingredients makes but little difference. By adding the proper amount of indigo, lime, and zinc from time to time, the vat can be used for three or four months.

The chemistry of the reaction in the zinc-lime vat is as follows:

Zinc powder in the presence of an alkali will reduce water as follows:

$$Zn + 2H_2O = Zn(OH)_2 + 2H;$$
$$\text{or, } Zn + Ca(OH)_2 = ZnCaO_2 + 2H.$$

The above equations represent the general reaction taking place, but the detail of the reaction is undoubtedly more complicated.

The hyposulphite vat or **hydrosulphite vat** is the most modern of the indigo vats. It is applicable in both cotton and wool dyeing, and its use is constantly increasing. In this vat the reduction is brought about by the action of a hyposulphite solution. This hyposulphite solution is sometimes sold in air-tight casks; but it keeps only a short time, and accordingly it is preferable for each dye house to manufacture its own hyposulphite. This chemical is ordinarily made by the action of zinc dust with sodium bisulphite at a low temperature. The process is as follows:

With 10 gallons of bisulphite of soda solution 72° Tw. mix 10 to 12 lbs. of zinc dust made into a paste, and slowly stir. Rise in temperature is prevented by the addition of ice, or the mixing may be done in a water-cooled iron vessel. In either case, enough cold water should be finally added to bring total volume to 19 gallons.

This mixture is well stirred for ½ hour, then allowed to stand for 1 hour, and finally there is slowly added, with gentle stirring, 10 lbs. of quicklime, which has been made into a milk of lime with 6 gallons of water and cooled. The stirring should continue ¼ hour after the lime has been added; and the whole mixture, which is now 25 gals., should be allowed to stand for two or three hours. The zinc settles out, and the hyposulphite solution remains above as a clear liquid. This is drawn off or filtered into air-tight casks or carboys, and must be kept from the action of the air until used. An addition of ¾ lb. to 1 lb. of caustic soda dissolved in a little water, will improve its keeping qualities.

The reduced indigo solution is prepared as follows:

75 lbs. Indigo Blue Artificial (20 per cent paste), or its equivalent in Natural Indigo.
10 gals. Boiling Water.
13 lbs. Caustic Soda made up to 8 or 9 gals. with water.

Heat mixture to 113°F or 45°C. Stir well, and allow to stand ½ hour; then add 25 gallons of the hyposulphite solution as previously prepared, stir well, and keep at 113°F or 45°C until the indigo has been completely reduced and has gone into solution. The addition of a little hyposulphite solution (1 to 2 gallons) from time to time will aid in the solution of the indigo. When the reduction is completed, a little of the solution carefully drawn with a pipette and allowed to run on to a filter paper, will develop a decided blue in less than 30 seconds.

The vat is set as follows:

For 500 gallons capacity, add 400 gallons of water heated to 20°C or 68° F, and 1 gallon of hyposulphite solution, and allow to stand over night.

In the morning the necessary amount of reduced indigo is added, by means of a funnel with a stem long enough to reach to the bottom of the vat. For a full-strength vat add 25 gallons of the reduced indigo prepared as above; stir gently; and allow to stand quietly for an hour, when the vat is ready for use.

The reduced indigo should be kept on hand and added to bath as is necessary.

This vat is applicable to both cotton and wool material. In the case of cotton it is commonly used cold; but for very heavy material, such as duck or canvas, better penetration is secured if the vat is heated to 120°F.

Our knowledge in regard to the chemistry of the hyposulphite vat is somewhat uncertain, but it is known that powdered zinc reacting with sodium bisulphite ($NaHSO_3$) gives rise to the acid sodium salt of hyposulphurous acid. To this the formula $NaHSO_2$ is most commonly assigned. It reacts with indigo as follows:

$$C_{16}H_{10}N_2O_2 + NaHSO_2 + H_2O = C_{16}H_{12}N_2O_2 + NaHSO_3.$$

The application of the hyposulphite vat to wool is similar in manipulation to that of the fermentation vat already described; and the dyeing is carried on at a raised temperature, usually about 120° F.

142. Application of Indigo to Cotton. The principle of the application of indigo to cotton is practically the same with all vats. Deep rectangular vats are commonly used, which contain two sets of horizontal rolls, one located at the top just below the surface of the liquor, and the other set several feet below, but far enough from the bottom to avoid disturbing the sediment.

The general form of apparatus will be understood from Fig. 59. The cloth enters at A, and rollers over which it passes are so arranged that it does not again come in contact with the air until it leaves the vat at B. It immediately passes between squeeze rolls, and then travels through the air several minutes, by passage about a second set of rolls, usually located above the vat to economize room. It is while passing through the air that the indigo white becomes oxidized, and the color developed. If a deeper shade is desired the cloth may be run through a second or even a third vat, or may be piled up and run through the first vat a second time.

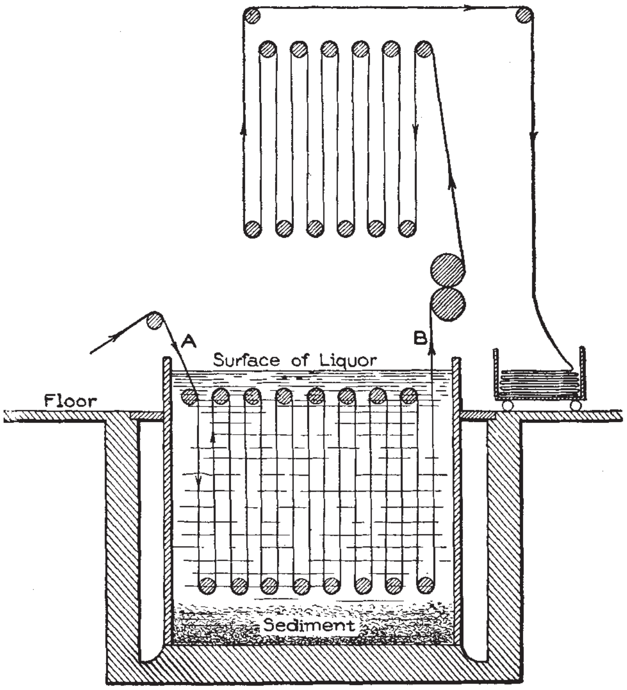


Fig. 59.

143. Indigo Extracts. These are prepared by the action of concentrated sulphuric acid upon indigo blue, the reaction giving rise to the sulphonic acid derivatives of indigotin, which are soluble in water and which have the property of easily dyeing wool from an acid solution. They have been and are still used in wool dyeing, giving brighter shades of blue than can be produced in the indigo vat; but whereas vat indigo blue is one of the fastest colors known, the extract blue is fugitive to both light and alkalies.

LOGWOOD.

144. Source of Logwood. Logwood is the product of a large tree of rapid growth known botanically as the *Hœmatoxylon Campechianum.* It is a native of Central America and the adjacent islands, Jamaica being the chief center of the industry at present. Raw logwood, as its name indicates, comes in the form of rough logs. These are ground, or rasped, into small chips, and may be used in this form or as water extracts.

145. Chemistry of Logwood Coloring. By carefully extracting freshly cut logwood, there can be obtained a yellowish-white crystalline compound having the formula $C_{16}H_{14}O_6$, and known as *hœmatoxylin.*

When exposed to the air, hæmatoxylin, especially in the presence of an alkali, rapidly oxidizes to a reddish-brown substance called *hœmatein*, which has the formula $C_{16}H_{12}O_6$. This is the active coloring matter of logwood. Upon further oxidation, hæmatein passes into a brown, resinous body which is of no value for coloring purposes.

Hæmatein has the property of uniting with various metals to form salt-like compounds that possess decided colors. For instance, when we add sodium hydroxide ($NaOH$) to a solution of hæmatein, we get the sodium compound of hæmatein, which possesses a deep reddish-violet color, but which, being very soluble in water, cannot be satisfactorily attached to textile material. With such metals as chromium, iron, aluminium, and copper, however, hæmatein forms insoluble colored compounds, or color lakes, which, by using certain of the soluble compounds of these metals as mordanting principles, can be fixed upon the fiber by various methods. Logwood is an adjective color in every sense of the word. It is also polygenetic, but the range of shades is limited between blue and black, and black and gray.

146. Logwood Ageing. Ordinarily a sample of logwood is most efficient when all of the hæmatoxylin has been oxidized or developed to hæmatein, but with none of the latter over-oxidized to the brown, resinous product. This ideal condition can never be exactly attained, and even the best samples of logwood will contain both hæmatoxylin and hæmatein. With this in view, logwood is commonly subjected to an ageing or curing process. This condition may also be brought about, to a certain extent, in the dye bath, by the addition of a small amount of some oxidizing agent or by the use of an oxidizing mordant.

Logwood chips are commonly aged as follows:

> After having been made into a large pile several feet in depth, the chips are well moistened with water, and then worked over with wooden shovels, every portion of the pile being thus brought in contact with the air. This is continued for a period of from three to four days to two weeks, depending largely upon atmospheric conditions. After some experience, one can tell, from the appearance of the chips, when the right stage of oxidation is reached. The chips are then stored in such a way that they will be exposed as little as possible to the oxidizing influence of the air.

147. Logwood Liquor. Logwood liquor is a decoction of logwood made by extracting aged logwood chips with water. It usually stands at about 15° Tw., and is freshly made as needed, as it does not keep well. Sometimes the extraction is done in the dye bath, previous to the dyeing, by entering the logwood chips in bags, and boiling several hours, but more frequently by extracting the chips in a separate boiler at a temperature of from 60° to 80°F.

148. Logwood Extracts. These are the commonest commercial forms of logwood at the present time. They are made by two methods:

(1) Extracting the logwood at boiling temperature with pure water.
(2) Extracting under steam pressure of 20 to 30 lbs. per square inch.

In either case the resulting logwood liquor, which has a specific gravity of 15° Tw., is concentrated in vacuum pans until it reaches a gravity of about 50° Tw., when it is known as the "liquid" extract; or it may be evaporated to dryness, giving the "solid" extract.

149. Application of Logwood to Wool. Logwood is extensively used for the production of cheap blacks on wool. There are three general methods of application:

(1) CHROME BLACKS: If logwood is well aged, either of the mordanting methods C and D (see Article 130) will give excellent results. If the logwood is unaged, method B is the best. With a straight chromium mordant, blue shades are produced. To overcome this, a small amount of some yellow dyestuff, as fustic or alizarine yellow, and a very little of a mordant red, are added to

the dye bath along with the logwood, the result being a dead black.

For 100 lbs. of wool mordanted by methods B, C, D, or E, prepare the dye bath with

40 lbs. Logwood Chips, or equivalent in Extract.
4 lbs. Fustic.
½ lb. Alizarine.

Enter at 100° F; bring slowly to a boil; and dye at a boil for 1½ hours. For cheap blacks the alizarines may be omitted.

In order to produce a dead black instead of a blue, copper sulphate ($CuSO_4$) is often used as a mordanting principle in connection with potassium bichromate, sulphuric acid being used as a mordanting assistant.

(2) IRON BLACKS. These are the oldest forms of logwood blacks. Ferrous sulphate and copper sulphate are the mordanting principles used. The following may be taken as a representative dyeing process:

For 100 lbs. of wool:
Mordant in a bath containing
8 to 12 lbs. Ferrous sulphate (copperas).
3 to 4 lbs. Copper sulphate.
6 to 8 lbs. Tartar.

Enter at 140°F; bring slowly to a boil; and mordant at a boiling temperature for one hour. Then dye in a bath made up with

50 to 80 lbs. logwood Chips, or equivalent in Extract.
3 to 5 lbs. Fustic.

Enter at 100°F, and dye at a boil 1½ hours.

Iron blacks are produced also by the stuffing or saddening method (see Article 129-3). This is accomplished by first boiling the wool for one and one-half hours, in a bath made up with plain logwood (say, the equivalent of 50 to 80 lbs. of logwood chips) and fustic (say, 4 to 6 lbs. per 100 lbs. of wool). The material is then raised, and 5 to 7 lbs. of ferrous sulphate and 2 to 3 lbs. of copper sulphate added, and boiling continued ¾ to 1 hour.

(3) ONE-DIP BLACK. This is accomplished by using the logwood and mordanting principle in the same bath, and adding enough of some acid (usually oxalic) to prevent the precipitation of the color lake. The following gives good results:

For 100 lbs. of wool:

50 lbs. of Logwood Chips, or equivalent in Extract.
4 to 6 lbs. of Ferrous sulphate.
1 to 2 lbs. of Copper sulphate.
2 to 2½ lbs. of Oxalic acid.

The bath is first boiled for a few minutes, then cooled a little; the material added, and boiling continued from 1 hour to 1½ hours.

150. Application of Logwood upon Cotton. The use of logwood in cotton dyeing has greatly declined during recent years, particularly for printing and piece dyeing, owing to the introduction of aniline black, and the direct cotton and sulphur blacks. Logwood is still largely used, however, in dyeing cotton warps, and to a less extent in dyeing loose cotton. It is applied chiefly upon an iron tannin mordant, and the following will serve as a representative process:

(1st) Saturate the material with sumac solution at 150°F — if cloth, in a jig dyer; if warp, in a chain dyer; and if skeins, by hand — using 10 to 20 lbs. sumac extract (depending upon quality) per 100 lbs. cotton. Work well in this sumac solution; then allow to steep 12 hours, or over night, in the slowly cooling bath; and then wring or squeeze well, but do not wash.

(2d) Work in an iron bath of either the pyrolignite or the so-called nitrate of iron, which should stand at 5° Tw.

(3d) Work in a weak bath of milk of lime $Ca(OH)_2$, and after rinsing, the material is ready for the dyeing process.

(4th) DYEING. For every 100 lbs. of material, the dye bath is made up with

10 lbs. Logwood Extract.
1 lb. Fustic Extract.

Enter cold; bring slowly to boil; and dye at a boil until the black is fully developed, not less than 1 hour. To render the color faster, 1 to 2 lbs. of copper sulphate may be added to the dye bath, when the dyeing is about two-thirds completed. A final soaping gives the black a brighter appearance, and softens the "feel" of the material.

One-dip blacks are often used on loose cotton. The process consists in boiling the cotton in a bath made up as follows:

Necessary amount of Logwood.
6 lbs. Copper acetate,
4 lbs. Copper sulphate,
or
4 lbs. Soda ash.

Enter cold; bring slowly to boil; and dye at a boil for 1 hour. Lift the cotton, and expose to the air several hours. If not dark enough, repeat the process.

151. Application of Logwood upon Silk. Logwood is extensively used for the production of black upon silk. Iron mordants are almost exclusively used for this purpose, and tin mordants less often. The other metallic mordants are here of little or no value.

The process usually consists in treating the silk alternately with some tannin material and the nitrate of iron, until the silk is thoroughly filled with a tannate of iron. It is then dyed in a logwood bath. In this way the weight of the silk greatly increases, sometimes 3 or 4 times its original weight.

RED NATURAL DYESTUFFS.

152. Soluble Redwoods. These include Brazil wood, peach wood, sapan wood, and Lima wood. They all contain the same coloring principle *brazilin*, which is soluble and easily extracted by water. Upon oxidation brazilin passes into *brazilein*, which is the active coloring matter. These dyewoods are adjective, and also polygenetic, producing the following colors:

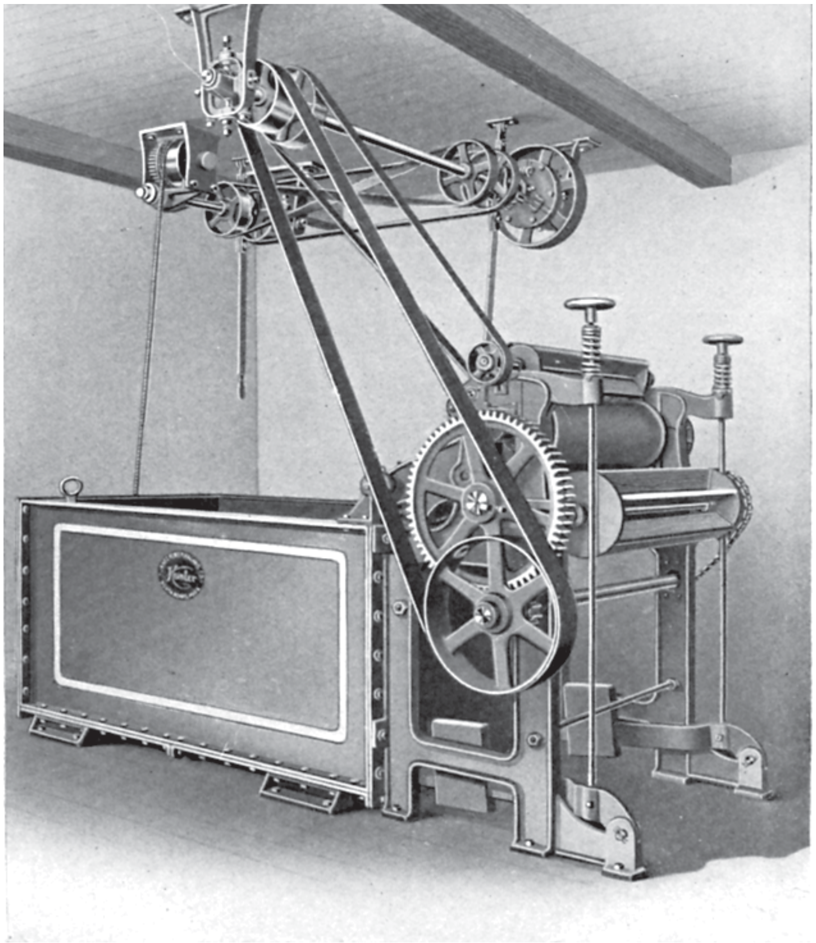
With Aluminium mordant	Red.
With Chromium mordant	Violet to Claret Red.
With Iron mordant	Violet to Purple.
With Tin mordant	Crimson Red.

They may be applied to mordanted cotton or wool by boiling in a plain bath of the extracted color. (For methods of mordanting see Articles 130 and 132.)

153. Insoluble Redwoods. These include bar wood, saunders wood, and cam wood. They are much harder and closer-grained than the soluble redwoods, and their coloring principle, known as *santalin*, is practically insoluble in water. For this reason, extracts cannot be prepared, and the chips have to be added directly to the dye bath. They are adjective, and also polygenetic, producing the following colors:

With Aluminium mordant	Red to Brownish Red.
With Chromium mordant	Purplish to Reddish Brown.
With Iron mordant	Violet to Purplish Brown.
With Tin mordant	Red to Brown Shades.

They may be applied to mordanted wool and cotton, by boiling the material for a long time in a dye bath containing the ground



INDIGO DYEING MACHINE

James Hunter Machine Co

or chipped wood. They are more valuable for the production of compound shades, with logwood, madder, fustic, and other natural dyestuffs, than as self colors.

None of the redwoods can be considered fast to light; but the colors produced with the insoluble dyewoods stand milling very well. The redwoods are very seldom used at the present time, artificial dyestuffs having been introduced, which give faster shades at lower cost.

154. Madder. This is prepared from the root of a plant known botanically as *Rubia tinctorium*, which is native to Asia Minor. It was known to the ancients, and was always used by the old school of dyers for the production of fast reds upon both wool and cotton. It is adjective and polygenetic, giving shades as follows:

With Aluminium mordants	Bright Reds and Pinks (Turkey Red).
With Chromium mordants	Wine Color, Claret Reds.
With Iron mordants	Violet Black.
With Tin mordants	Reddish Orange.

Alizarine ($C_{14}H_8O_4$) is the principal constituent and active coloring agent of madder, *Purpurin* ($C_{14}H_8O_5$) occurring in smaller quantities.

In 1868, Grabe and Liebermann discovered the process of manufacturing alizarine. The artificial product, being cheaper and more even and reliable in quality, has replaced madder entirely in dyeing and printing, except in Oriental countries where it is native. It is still used to some extent in the setting of fermentation indigo vats. Alizarine is used largely in steam calico printing, for the production of Turkey reds on cotton with an aluminium mordant, and in wool dyeing.

155. Cochineal. This red coloring matter is obtained from the dried body of an insect which is native to Mexico and Central America. The insect lives upon certain kinds of cactus plants. The coloring principle of cochineal is *Carminic acid* ($C_{17}H_{18}O_{10}$), which is soluble in water, and which has the property of forming bright color lakes with metals as follows:

With Tin mordants	Scarlet.
With Aluminium mordants	Crimson.
With Chromium mordants	Purple.
With Iron mordants	Purple.

The principal uses of cochineal have been for the production of scarlets and crimsons on wool, aluminium and tin mordants being the most important for these purposes. The mordant may be applied previous to the dyeing, or at the same time. The latter method is the commoner in practice, and the following process gives excellent results:

For 100 lbs. wool:
10 to 20 lbs. Cochineal.
4 lbs. Oxalic acid.
2 lbs. Tartar.

Add last 6 lbs. *Stannous chloride.* Boil bath 5 or 10 minutes, then cool to 160° F. Enter wool, bring slowly to a boil, and dye at a boil for ¾ hour. To increase the fiery character of the scarlet, a little yellow dyestuff should be added.

The acid scarlets (artificial colors) have now superseded cochineal to a great extent.

156. Kermes and Lac Dye. These are two more red coloring matters of similar origin to cochineal, but of less importance.

157. Orchil and Cudbear. Two coloring matters derived from certain rock mosses, which give bluish-red colors on wool and silk.

YELLOW NATURAL DYESTUFFS.

158. Under this head are commonly included a number of vegetable coloring matters that give shades varying between yellow and brown. The following are the most important: Fustic, Quercitron Bark, Persian Berries, Turmeric, Weld, and Cutch. These have for the most part been replaced by the artificial dyestuffs.

159. Fustic or **Cuba wood** is sold either as ground wood, or in the extract form. It is a mordant color, and is still used in wool dyeing, chiefly in combination with logwood; and for the production of compound shades, with indigo and the alizarine colors.

160. Quercitron Bark comes from a species of oak, growing in the middle and southern states. It is sold either as the ground bark or in the form of extract. It is a mordant color, and gives brighter shades than fustic. It is used to some extent in wool, cotton and silk dyeing, both as a self-color and in the production of compound shades.

161. Weld is an herbaceous plant grown in Europe. It dyes wool and silk a bright yellow color, but is seldom used at the present time.

162. Persian Berries. A name applied to the berries of the buckthorn. Usually sold as an extract. Its principal use at the present time is in steam calico printing.

163. Turmeric is the ground root of a plant that grows in Asia. It possesses the characteristic of being a substantive or direct dye for cotton, wool, and silk. It gives bright shades of yellow, but they are fugitive to light and washing. Its chief use at the present time is as an adulterant for mustard.

164. Cutch or **Gambia** is the extract of the nuts and tender portions of various forms of acacia trees growing chiefly in India. It is largely used for the production of browns on cotton. The process is as follows:

For 100 lbs. of cotton:
Boil the material for one hour in a bath made up with
10 lbs. Cutch.
1 lb. Copper sulphate.

Allow it to remain in the cooling dye bath for several hours. Develop color by working ½ hour in a hot bath at 180° F. containing
2 to 3 lbs. Potassium bichromate.

The shade may be varied by diminishing or increasing the amount of cutch used, and the copper sulphate in the same proportion.

Cutch is very largely used for the production of fast tan shades upon cotton warps and hosiery. It may be applied to wool by the same process as for cotton, but is little used for this purpose. It is used in silk dyeing, where it acts as a tannin material, assisting in holding the iron upon the fiber.

FARBWERKE VORM. MEISTER LUCIUS & BRÜNING, HOECHST a. M.

TEXTILE CHEMISTRY AND DYEING.

PART IV.

ARTIFICIAL DYESTUFFS.

165. Dyers of the olden times depended almost entirely upon the so-called natural dyestuffs, of which the number of useful ones was limited. In those days the young dyer was seriously handicapped in his search for information, for the dealers in these natural dyestuffs knew little, if anything, about their application, and as there were no publications on the subject, the young man's only source of information was from older dyers.

A decided change took place between the years 1856–1860, when it was discovered that coloring matters, which surpassed any of the natural dyestuffs in brilliancy, could be manufactured from the products of the distillation of coal tar. Many of these so-called coal-tar colors were discovered and put upon the market, and, as the manufacturers knew more about their application than the dyers, it was to the advantage of the former to circulate this information. As a result, the dyestuff manufacturers published sample cards and books containing dyed samples and the necessary information for the successful application of their colors. At the present time enormous sums are spent every year by them in the investigation and publication of the best methods of applying the colors they place upon the market.

In more recent years numerous books have been published on the various branches of textile coloring; this, with the establishment of textile schools, makes it possible for bright young men to become expert dyers, without assistance from friendly dyers.

166. Classification of Artificial Dyestuffs. For the practical dyer there is but one satisfactory method of classifying the artificial coloring matters, *i.e.*, according to their action upon the different fibers; in other words, according to their application. Therefore, in our study of them we shall consider the following classification:

(1) Basic colors.
(2) The Eosins and related Dyestuffs, known as the Phthalic Anhydride Colors.
(3) Acid Colors.
(4) Direct Cotton Colors.
(5) Sulphur Colors.
(6) Mordant Colors.
(7) Mordant Acid Colors.
(8) Insoluble Azo or Ingrain Colors.
(9) Reduction Vat Colors.
(10) Aniline Black.

BASIC COLORS.

167. The basic colors were the earliest of the so-called artificial dyestuffs or coal-tar coloring matters. They belong to that class of compounds known as the *substituted ammonias* or *amines*, *i.e.*, they are derived from ammonia (NH_3) by the replacement of one or more hydrogen atoms of one or more molecules of ammonia with various other elements, or groups of elements. These substituted ammonias, like ammonia, are basic in character, and, like all bases, have the power of neutralizing acids. It is for these reasons that this class of dyestuffs is designated as the *basic colors*. It is only when the color bases, *i.e.*, the substituted ammonia compounds, from which the coloring matters are derived, are neutralized with acids that their coloring power is fully developed.

A study of the *properties and composition of wool* indicates that it is of a weakly acid character, and its acid properties seem to be sufficient to cause it to unite with these color bases and develop their characteristic colors. For this reason wool may be dyed directly with the basic colors.

With cotton it is different, for this fiber apparently has no acid character and cannot combine directly with these color bases. Therefore, the basic dyestuffs have no direct affinity for cotton, and cannot be applied to this fiber except by the aid of some assisting acid substance. Tannic acid is most frequently used for this purpose, and acts as an acid mordant. (See No. 132.)

168. Application of Basic Colors to Wool. Although the basic colors have a direct affinity for wool, they are not extensively used in wool-dyeing, because there are, in most cases, acid colors (see No. 180), which will not only give the same color but possess greater fastness.

The following process is well adapted to the dyeing of wool with the basic colors.

For 100 pounds of wool material prepare the dye bath with:
1 to 2 lbs. Color.
½ lb. Acetic Acid (to counteract hardness of water).
10 lbs. Glauber's Salt.

Enter the material at 180° F. and dye at a boiling temperature for forty-five minutes to one hour, then wash and dry.

169. Application of Basic Colors to Silk. The basic colors dye silk directly and are extensively used with this fiber when bright, rather than fast colors are desired.

The process most frequently used is as follows:

Prepare the dye bath with:
10 gallons "Boiled Off Liquor".*
30 gallons Water.
Sufficient Sulphuric, Acetic, or Tartaric Acid to render the bath slightly acid.

Enter silk at 100° to 110° F., work for a few minutes at this temperature, then raise the silk from the bath and add the necessary amount of dyestuff (previously dissolved in water). Re-enter the silk, turn several times, raise the temperature of the bath to 140° F. and finally bring to a boil. It is best to raise the silk from the bath each time the temperature is raised. With colors that go on evenly at lower temperatures it is advisable not to bring the bath to the boiling point.

With some basic dyestuffs a neutral or slightly alkaline bath of boiled off liquor is preferable.

170. Application of the Basic Colors to Cotton. It is in the dyeing and printing of cotton material that the basic colors find the widest application. The cotton, whether it be in the form of piece goods, yarn, or loose cotton, must first be impregnated with tannic acid in some form, and the tannic acid then fixed upon the material as an insoluble metallic tannate (usually of antimony).

---

*NOTE.—Preliminary to dyeing, silk is subjected to the so-called "boiling-off" or degumming process. This consists in boiling the silk in a solution of potash soap, sometimes made slightly alkaline with a little soda ash or borax, for one-half hour more or less. As a result the sericin is dissolved and the fibroin or true silk fiber remains. The solution of sericin is known as "boiled off liquor" and is extensively used in silk-dyeing.

When thus mordanted the cotton is ready for dyeing, which is carried out in a bath containing the basic color.

Process for 100 lbs. of cotton yarn.

Prepare the tannin bath with

125 to 150 gallons Water.
$2\frac{1}{2}$ to 5 lbs. Tannic Acid;
or
5 to 10 lbs. Light Shumac Extract.

Raise the temperature of the bath to 180° F., enter yarn, work it at this temperature for one-half hour, then allow it to stand in the slowly cooling bath (entirely covered with the liquor) for two hours when light colors are to be produced, and over night for heavy colors. The yarn is then wrung and hydro-extracted without washing, then worked for one-half hour in a cold bath containing 1 to 2 lbs. tartar emetic or equivalent of some other antimony compound, and finally washed thoroughly.

The above treatment fixes an insoluble tannate upon the fiber.

The yarn is then dyed in a bath made up as follows:

175 to 200 gallons Water.
1 to 3 lbs. Acetic Acid (to correct hardness of water).
2 lbs. Basic Color. For full shade.

Begin the dyeing cold and bring the temperature to from 120° to 130° F. before the dying is completed. With a few colors, *e.g.*, Methylene Blue the temperature may be raised as high as 160° F., but a higher temperature than this is seldom beneficial. The addition of one or two pounds of alum to the dye bath, before the introduction of the dyestuff, is advisable with colors which have been found to dye unevenly, and in every case the dyestuff should be added to the bath in several portions rather than all at one time.

In the *dyeing of cotton piece goods*, the principles of the process are identical with those of yarn dyeing. A series of three Jig Dyeing Machines* is best adapted for this purpose, the first for the tannin bath, the second for the antimony compound, and the third for the dyestuff. Padding machines are sometimes used for the first two operations.

171. Characteristic Properties of the Basic Colors. The basic colors are characterized by their great brilliancy and high tinctorial or coloring power; 2 per cent of a basic color commonly producing as great a depth of shade as 3 to 5 per cent of an acid color or a direct cotton color. Their solubility in water is not as great as that of the direct cotton and acid colors, and a few of them, known as spirit soluble colors, are so insoluble in water that alcohol has to be used as a solvent. Their fastness to light is by

---

*A jig dyeing machine is illustrated in Fig. 69. It consists of a dye vat and two rolls, so arranged that several hundred yards of cloth may be passed full width from one roll through the liquor in the vat, and wound upon the other roll. The cloth is thus passed back and forth until thoroughly permeated with the liquor contained in the vat.

no means satisfactory, but their fastness to washing and soaping is excellent (except the reds), and for this reason they are extensively used in calico printing and in the dyeing of cotton yarn for ginghams.

172. Important Basic Colors. The following is a list of some of the more important basic colors:

REDS.
- Acridine Red.
- Magenta.
- Rhoduline Red.
- Rosaniline.
- Rhodamine (see phthalic anhydride colors).
- Saffranine.

BLUES.
- Basle Blue.
- Diazine Blue.
- Diphene Blue.
- Indamine Blue.
- Indazine Blue.
- Iondoin Blue.
- Indophenin Blue.
- Metamine Blue.
- Metaphenylene Blue.
- Methylene Blue.
- New Blue.
- Night Blue.
- Nile Blue.
- Victoria Blue.

GREENS.
- Benzal Green.
- Capri Green.
- China Green.
- Emerald Green.
- Ethyl Green.
- Malachite Green.
- Methyl Green.
- Methylene Green.
- New Green.
- Solid Green.
- Victoria Green.

ORANGES AND YELLOWS
- Acridine Orange.
- Auramine.
- Azophosphine.
- Chrysoidine.
- Flavindulin.
- New Phosphine.
- Phosphine.
- Tannin Orange.
- Thioflavine T.

VIOLETS.
- Cresyl Fast Violet.
- Crystal Violet.
- Hoffmans Violet.
- Methyl Violet.
- Tannin Heliotrope.

BROWNS.
- Aniline Brown.
- Bismark Brown.
- Diazine Brown.
- Leather Brown.
- Manchester Brown.
- Tannin Brown.

BLACKS AND GRAYS
- Diazine Black.
- Methylene Black.
- New Gray.
- Nigramine.
- Nigrosine.

173. The Janus Colors. The *janus colors*, although often classed as basic colors, constitute a group by themselves. Their molecular structure is such that they contain simultaneously the characteristic groups of both the acid and basic colors. They possess the peculiar property of *dyeing both cotton* and *wool* directly in an acid bath. Like basic dyestuffs they may also be applied to tannin mordanted cotton. They are useful in the dyeing of cotton and wool union goods.

THE PHTHALIC ANHYDRIDE COLORS.

174. This group includes a few dyestuffs such as the eosins and rhodamines, which produce very brilliant red dyeings, and are largely used for the production of bright pinks. They resemble the basic colors in certain respects, and the acid colors in others, but differ sufficiently from both to be placed in a class by themselves. The colors of this group, certain rhodamines excepted, are all related to phthalic anhydride, and it is from this fact that they derive their name. They are *used chiefly in wool and silk dyeing*, and to a limited extent in cotton dyeing. The rhodamines resemble the basic colors both in composition and properties, and are frequently used in calico printing.

175. Application to Wool. With the exception of the rhodamines, the colors of the phthalic anhydride group are best applied to wool in a bath containing tartar (potassium bitartrate), alum, and acetic or sulphuric acids.

The dye bath is made up as follows:

Necessary amount of color.
*2 per cent Potassium Bitartrate (Tartar).
2 per cent Alum.
1 to 2 per cent Acetic Acid.

Enter material at 40° C, raise the temperature gradually to 100° C, and dye at a boil for one-half hour.

With the rhodamines the following gives better results:

Necessary amount of color.
15 to 20 per cent Glauber's Salts.
1 to 5 per cent Sodium Bisulphate.

The rhodamines are often used in shading other colors.

176. Application to Silk. The colors of this group are often used for silk dyeing on account of their great brilliancy. The method of application is the same as that already given for basic colors. (See No. 169.) They may also be applied in a bath acidified with acetic acid, without any addition of boiled off liquor or soap. In most cases the color is taken up by the silk at a temperature of 120° to 140° F., and the bath need not be raised above that temperature.

177. Application to Cotton. Cotton may be dyed directly with the colors of this group in a concentrated bath of common salt, with or without the addition of 1 per cent alum, but the dyeings are so fugitive to washing and light that they are applied in

---

*NOTE.—In all recipes, percentages refer to weight of goods being dyed, unless otherwise stated. Thus 2 per cent of potassium bitartrate means two pounds of this compound to every 100 lbs. of material being dyed.

this way only when the material is not to be subjected to washing or much light. If the cotton is previously mordanted with Turkey-red oil or aluminium the dyeings are faster.

The following process is commonly used:

First work the material in a bath made up as follows:
1 part Turkey-red Oil.
2 parts Water.

Wring or squeeze thoroughly and repeat the operation several times, then dry at a moderate heat or steam under 5 lbs. pressure for 20 to 30 minutes. If extremely level and deep shades are desired, this operation must be repeated two, or even three times. The material is then dyed in a short, cold bath containing the necessary amount of dyestuff.

When *aluminium* is used as the mordanting metal the process is as follows:

The material is worked in a bath containing
1 part Turkey-red Oil;
8 parts Water;

then squeezed and dried as above, and finally worked for one-half hour in a bath of

Aluminium Acetate 8° Tw.

The material is allowed to steep in this solution 1 hour longer, then wrung and thoroughly dried. The mordant is further fixed by working one-half hour, at a temperature of 115° to 120° F., in a bath containing for every 5 lbs. of material

7½ gallons Water;
1 lb. Whiting;

then rinsed, hydro-extracted, and dried. For the best results this process should be repeated several times.

Rhodamine being of the same character as a basic color may be applied upon a tannin antimony mordant. (See 170.)

178. Characteristic Properties of the Phthalic Anhydride Colors. The phthalic andydride colors are characterized by their *remarkable brilliancy*, and in low percentages they produce the brightest and most delicate of pinks. Their fastness to light is poor and their fastness to washing not much better. Rhodamine is the fastest.

179. Important Phthalic Anhydride Colors. The following is a list of the most important phthalic anhydride colors:

The Eosins.
The Rhodamines.
The Erythrosines.
The Phloxines.
The Rose Bengale.

ACID COLORS.

180. General Consideration. The acid colors are so called for two reasons: first, because they are, without exception, acid in character, and second, because they dye wool so readily in an acid bath.

The acid colors are of great importance in wool dyeing, and it may safely be said that seventy-five per cent of all wool dyeing at the present time is accomplished with this class of coloring matters. The acid colors are also of great importance in silk dyeing, but are of practically no importance in cotton dyeing.

Acid dyestuffs may be subdivided into three classes according to their composition.

(1.) Those that are *nitro compounds*, *i.e.*, those containing the nitro group which has the composition ($-NO_2$) and a valence of one. The nitro compounds are prepared by the action of nitric acid upon certain organic compounds. There are but few members of this class and they all produce yellow to orange colors. *Picric acid* and *naphthol yellow* are the best examples.

(2.) The *sulphonated basic colors*, *i.e.*, those which are prepared by the action of sulphuric acid upon various basic colors. During this action the characteristic properties of the basic dyestuffs are lost, but they are at the same time converted into acid dyestuffs producing similar colors, and although their coloring power is reduced, their fastness is usually correspondingly increased.

(3.) Those that are *azo compounds*, *i.e.*, those containing one or more azo groups, which have the following chemical structure ($-N=N-$). The dyestuffs of this class are by far the most numerous and valuable of the acid colors.

181. Application of Acid Colors to Wool. The acid dyestuffs, almost without exception, go on wool readily in an acid bath and the dyeing process is comparatively simple.

The dye bath is usually prepared as follows:

Necessary amount of Dyestuff (usually 1 to 5 per cent);
10 to 15 per cent of Sodium Bisulphate;
or
10 to 15 per cent of Sodium Sulphate (Glauber's Salt);
3 to 5 per cent of Sulphuric Acid.

The material is entered into the dye bath at a temperature of 140° to 180° F., brought to a boil and dyed at a boil for forty-five minutes to one hour, at the end of which time the dyestuff is, as a rule, entirely taken up by the wool; or, to use the common expression of the dyer, "*The dye bath is completely exhausted of color.*"

Most of the acid dyestuffs go on the fiber evenly, or dye level, when applied by the above method, but with such colors as do not readily dye level, it is advisable to commence the dyeing with 2 to 5 per cent acetic acid, instead of sulphuric acid, and add 2 to 3 per cent sulphuric acid towards the end of the dyeing to complete the exhaustion of the color from the dye bath.

182. Application of Acid Colors to Silk. In the application of acid dyestuffs to silk it is customary to use a bath of "boiled-off liquor" to which sulphuric acid has been added.

The dye-bath for 10 lbs. of silk is prepared as follows:

2 to 4 gallons of "Boiled-off Liquor".
10 to 12 " " Water.
Necessary amount of Dyestuff.
Sufficient sulphuric acid to render the dye bath decidedly acid.

Begin the dyeing at 100° to 125° F. and eventually raise the temperature to 200° F., but no higher.

The acid dyestuffs may also be applied to silk without the use of boiled-off liquor. In this case the dye bath is made acid with acetic acid, and the sulphuric acid is not added until the temperature has been raised to 200° F.

183. Application of Acid Colors to Cotton. The acid dyestuffs are seldom used for cotton dyeing, as there is no direct affinity between cotton and the colors of this class, and furthermore no satisfactory process has ever been devised for applying them to cotton. A few of the acid scarlets are occasionally used for the coloring of cotton material where good fastness to light is desirable, but where the material will never be subjected to washing, as for instance with cloth that is to be used for book covers and for decorative purposes.

The dyeing process is carried on in a very concentrated or "*short*" bath containing:

Necessary amount of Dyestuff (usually 5 to 10 per cent).
5 to 10 per cent of Alum.
25 to 50 per cent Common Salt or Glauber's Salt.

The temperature of the dye bath is raised to 120° F., the material entered and worked ten to fifteen minutes at this temperature, and then