ELEMENTS

OF

THE ART OF DYEING.

Printed by Walker & Greig,
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ELEMENTS

OF THE

ART OF DYEING;

WITH A DESCRIPTION

OF THE

ART OF BLEACHING BY OXYMURIATIC ACID.

Second Edition.

Claude
Louis

By C. L. and A. B. BERTHOLLET.

TRANSLATED FROM THE FRENCH,

WITH NOTES AND ENGRAVINGS, ILLUSTRATIVE AND SUPPLEMENTARY,

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GLASGOW.

IN TWO VOLUMES.

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B, Receiver.

M, M, M, M, M, Plates which close exactly the space between the upper shallow tub, and the sides of the receiver. Only the side looking to the furnace is left open.

Q, Pipe into which the syphon for running the acid into the immersion tub is introduced.

O, O, Cross pieces which support the shallow tubs, and are fixed into the extremities N, N, N, N, of four uprights.

K, Circular groove cut out in the plate, which closes the space between the second shallow tub, and the side of the receiver, for the passage of the conductor tubes, one of which is traced in the figure.

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D, Plan of a furnace, of the boiler E, serving for a sand bath, and of the matrass F, which communicates by the tube G with the intermediate bottle H, enclosed in its double box I: in the furnace, round the sand bath, and opposite each angle, channels have been cut, which serve as chimnies and registers. A section of the second furnace D is made at the height of the fire-place, that the grate *d* may be perceived, and the plate of iron *d'*, which separate the fire-place from the ash-pit.

Fig. 2. Vertical section of the receiver, and of the immersion tub, according to the lines A B and C D.

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P, P, P, Tubes which allow the gas to pass from one shallow tub to its superior, when it contains a stratum of it, equal to the length of these tubes. The tube of the upper shallow tub is made long enough, as is shewn, to disperse the gas, which being undissolved in the water, would be diffused in the air, and annoy the workmen.

K, Conductor tube, which proceeds from the intermediate bottle, and terminates under the lower shallow tub.

Q, Pipe which communicates down to the bottom of the apparatus, in order that the syphon R may conduct the most concentrated acid (aqueous chlorine) into the immersion tub.

S, Tube of safety.

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Fig. 9. I, box, with two square cells, serving to contain the intermediate bottles, drawn on a double scale. Y, small box, which encloses the bottle held in one of the cells, by the corners X, X, X, X.

Fig. 10. Elevation of the same box, furnished with its two bottles.

Plan and elevation of the small boxes, Y.

Plate II. Fig. 1, 2, 3, 4. Apparatus for the running off leys. The same letters serve for the same objects in these different figures.

Fig. 1. Vertical section of the apparatus.

A, tub.

B, boiler, the bottom of which is concave, and provided with a stopcock T. On the pipe to which this stopcock is attached, a socket is soldered, into which the glass tube, V, enters, that communicates by another kneed socket with one of the wooden pipes F, which afford passage to the steam. This tube serves to shew what height the liquor rises to in the boiler. The bottom of this is sustained on the edges of the interior masonry of the furnace, except in the part corresponding to the aperture S, through which the smoke passes off. Its edges are turned back on the masonry for receiving the tub, they are then raised round it, in order that the vapour and the liquid may not find an outlet between the tub and the boiler.

H, Grating of deal, the ribs of which rest at their ends on the edges of the masonry of the furnace, and which are supported by two bars, I I, connected with the grating by four copper straps, which bear upon the corners.

D, Body of the pump. It has at its lower part an inverted cup, pierced with small holes, to prevent in the aspiration (sucking), the introduction of bodies, which might hinder the valves from shutting, or might scratch the body of the pump. It is prolonged by a thin copper pipe, C, which, at the upper part of the tub, carries a copper heel, on which the cylinder of copper, K, rests. This cylinder stands on four casters. It carries four sockets, to each of which an arm, X, X, is adjusted, of a length equal to the diameter of the tub, and pierced with holes, like the bulb of a watering pot. In order that the ley raised by the pump may be diffused, the pipe of the pump is perforated in like manner with small holes in the whole portion which corresponds to the copper cylinder; and in order that the ley may not run off by the bottom of this cylinder, it presses exactly at this part on the pipe of the pump. The arms X are fitted on like the bayonet to the muzzle of a musket; they are taken off, for the introduction and removal of the cloths.

The cylinder is terminated by a ratchet wheel L, the number of whose teeth should be a prime number, in order that having no exact divisor, the arms may not be periodically brought back to the same positions. The ratchet L is set in motion by a rod *a*, hooked to one of the pieces of wood that form the frame-work, on which the balance-beam *d* of the pump rests, and fixed very freely by a pin to a horizontal rod *b*. This rod is fixed in like manner, by its other extremity, to one of the branches of a bell movement M, whose other branch communicates, by the rod *c*, with the balance-beam. Hence, on turning the handle *e*, every movement of the balance-beam is communicated to the rods, and onwards to the ratchet, which, for each stroke of the piston, percurs the space of one tooth.

The body of the pump D and the pipe C, are joined by two straps and screws. Under these straps passes an iron collar, traversed by six bolts, whose screwed ends are fixed with nuts to a copper platform placed on the grating. By this means the pump rests on the grating, and bears no weight on the bottom of the boiler. The pipe C is also held fast at its upper end by an iron strap, adapted to, and fixed on the cross bar *f*.

G represents the copper funnel, by which are introduced the solution of potash, and the waters necessary for the lixivium. It terminates in one of the tubes F, to prevent the solution of potash spouting out on the adjoining pieces.

P indicates the form of the fire-place, the grate being at R, and the ash-pit at Q. The smoke issues by the aperture S, of which only half the altitude is seen here; it circulates by the flue U round the boiler, entering then into the tube of the chimney, which rises vertically.

Fig. 2. Horizontal section of the tub taken above the platform of copper *l*, on which are fixed by nuts the six bolts which support the body of the pump.

m, Furnace door.

The dotted lines *n n*, indicate the separation, formed by fire bricks, in the flue which runs round the boiler, and which determines the entrance of the smoke into this passage, as well as its issue into the vertical pipe *p*.

Fig. 3. Vertical projection of the apparatus taken in another direction.

h, Register, with which the chimney *p* ought to be furnished.

q, Rim of the boiler turned up on the outside of the tub.

Fig. 4. Horizontal projection of the apparatus, according to the line T″ G‴.

Fig. 2. V, Horizontal projection of the body of the

pump, in which the details of the adjustment of the piston are represented.

D, Vertical section of the body of the pump; R, clack valve. S, piston; T, cup attached by a strap to the lower extremity of the body of the pump.

Fig. 4. Horizontal projection, and vertical section of the cylinder K, which bears the sockets to which the arms X X are adjusted.

C, copper pipe to which is soldered the heel *x*. *y*, *y*, brass casters which rest on the heel *x*, and which support the cylinder K.

u, u, u, sockets having an opening for receiving the knob soldered to the extremity of the arms. L, ratchet wheel fixed to the upper part of the cylinder K. It contains in the figure 17 teeth.

These two figures have been made on a double scale, in order that the details might be better understood.

The apparatus for the oxygenated muriatic acid, and for the running off of leys, are on the same scales.

N. B.—To avoid embarrassing the figures, a small plank is not represented here, which, when the apparatus is constructed on as large dimensions as the present, should be placed at about two metres (yards) from the ground, for throwing the goods upon, and from which a child can hand them to the workman, who arranges them in the tub.

Fig. 5. Vessels for the testing of potashes.

1. Small measure; it is filled by plunging the bulb into the liquid, and stopping the tube with the finger whenever it is full. It may then be carried without fear of losing what it contains. To make it flow, the finger has only to be lifted.

2. Tube containing up to the mark 50 times the small measure.

3. Goblet or jar in which the mixture of the test acid is made and the solution of potash.

4. Tube employed for stirring, and making the traces on stained paper.

For the trial of the oxygenated muriatic acid, the small measure is filled with the solution of indigo, which is poured into a glass jar of the same form as the above, or into a glass tumbler; then the number of measures is introduced that are required for discharging its colour.

Fig. 6. Ordinary distribution (arrangement) of the mode of running off leys.

1. Tub on whose bottom a wooden grating is placed, or some simple pieces of wood, which prevent the cloths, when heaped, from choking up the aperture of the pipe 3, by which the ley falls back into the boiler.

2. Boiler, here represented cut vertically through its diameter, in order to see its form. Those usually employed are different, and do not possess the advantage which the present one does, of directing the liquid, which spouts up, when the ebullition is brisk, towards the middle of the boiler. It has been, moreover, represented as mounted on a furnace different from those which the bleachers usually construct. Its construction is nearly the same as that of the furnace of

Fig. 1. The form of this boiler and of its furnace is adopted in a great many dyehouses. When their dimensions are good, there is much economy of fuel, and convenience of manipulation. Those of the figure have been copied from well constructed furnaces. If pit coal be burned, the height of the fire-place should be diminished a little, and if turf, a little increased.

Instead of sinking the furnace into the ground, its bottom may, however, be put nearly on a level with that of the tub, and the ley made to fall back from the tub into the boiler by a kneed pipe, which, reaching to near the bottom of the tub, and opening above the boiler, does the office of a syphon, and reconveys to it the leys which had gone through the whole thickness of the goods.

EXPLANATION

OF THE

PLATES FURNISHED BY THE TRANSLATOR.

Plates I. and II. represent the padding machine, for applying mordants to cotton cloth, or, generally speaking, for passing cloth through any chemical solution. It consists of a frame in which are placed two rollers, either of wood with an axis of iron, or of cast-iron covered with copper. The upper roller is pressed, by means of levers, against the under one, which revolves horizontally in a box, containing the mordant that is to be put on the cloth.

The bevelled wheel and shaft that convey the power to the padding machine, are represented in Plate II. as inclined; a circumstance not essential, but accidentally required in the particular machine from which this drawing was taken.

Plates III. and IV. represent the wash or dash wheel. The pieces of cloth are put into the quadrantal compartments of the wheel, into which a stream of pure water flows through a circular slit in its posterior surface. By the rotation of the wheel, the cloth is dashed backwards and forwards between the quadrantal partitions. Twenty-five revolutions per minute is the proper speed of a wash wheel six feet in diameter. Some persons suppose them to perform better with twenty-six or twenty-seven revolutions. But any considerable deviation from this velocity either impairs the utility of the machine, or destroys its functions altogether. In these and the other plates, the parts are so distinctly delineated by the artist, as to supersede the necessity of letters of reference and minute explanations.

Plate V. A bucking boiler, exhibiting the fire-place, the iron boiler, surmounted by the wooden crib, with its grated bottom and central iron pipe. Whenever the water or alkaline ley boils briskly, its vapour, confined by the goods in the crib, presses on the surface of the liquid, and forces this to issue in a sudden stream from the top of the pipe, whence it is spread over the surface of the goods, and gradually percolates down through them. The liquid in its descent becomes slightly cooled; but after a little while, accumulating and becoming hot again in the boiler, a new eruption of boiling liquid takes place. A more complex, though, I believe, not more effective form of bucking apparatus, is described in the Edinburgh Encyclopedia—Article *Bleaching*.

Plates VI. and VII. Cylinder printing machine.

A. The engraved copper roller.

B. The mandril on which the roller is fixed.

C. The back roller covered with soft materials. It presses the piece of cloth to be printed against the copper roller.

D. Situation for a second copper roller, when two colours are to be applied at once. In this case, the back roller is pressed against it by means of the screws E.

F. The colour-box.

G. Steel doctor for scraping off the colour from those parts of the roller which are not engraved.

H. Wheel which gives a horizontal motion to the doctor.

I. A long piece of thick woollen cloth, sewed end to end, which passes under the back roller, along with the piece of cloth to be printed.

K. Beam on which the pieces of cloth are rolled before being printed.

TO

M. CLEMENT,

PROFESSOR OF PRACTICAL CHEMISTRY

IN THE

CONSERVATORY OF ARTS, PARIS,

IN TESTIMONY OF THE ESTEEM ENTERTAINED FOR HIS
SCIENCE AND FRIENDSHIP,

BY THE

TRANSLATOR.

TRANSLATOR'S PREFACE.

Among the academicians of France, who figured in the antiphlogistic revolution of chemistry, M. Berthollet, if not entitled to the first place, yields precedence to Lavoisier alone. His early discovery of the composition of ammonia, was of capital importance. It threw light on many obscure chemical phenomena, and furnished an excellent mirror of gaseous research.

But undoubtedly M. Berthollet's peculiar merit consisted in applying scientific results to the common business of life. Scheele's happy genius, while examining an ore of manganese, revealed to the world that singularly energetic element, chlorine, called by him dephlogisticated marine acid. Its power of destroying colour was noticed by the Swedish chemist, merely as it affected the cork of his phial. This cursory remark suggested to Berthollet's active mind a new art, that of bleaching without exposure to sunshine and air. This art, which has been of incalculable benefit to the manufactures of linen and cotton, was expounded by him with much sagacity and address, in a treatise, which forms a part of the present publication. Though important improvements in the mode of preparing and applying this blanching power have been made, and particularly by British manufacturers, since Berthollet's time, it must be admitted, that his principles, as far as practice is concerned, have recently received little further elucidation. The theoretical modifications, occasioned by Sir H. Davy's admirable researches on chlorine, with an account of the actual processes adopted by our bleachers, have been briefly stated in the notes of the translator.

M. Berthollet's success in the bleaching department naturally led the government of France to select him as a fit successor to M. Macquer, in superintending the dyeing establishments of that kingdom. This honourable appointment, previously held by very eminent chemists, turned Berthollet's attention to the art of dyeing, the operations of which he seems to have studied with great assiduity. His elements of this art must undoubtedly be regarded as constituting the first truly philosophical treatise on the subject; nor has any work appeared since, which can bear a comparison with it for precision of detail, and perspicuity of explication. The various essays on dyeing, and dye-stuffs, which have within these few years been multiplied in our Encyclopedias, &c. are, in a great measure, extracts from Berthollet.

It is more than probable, indeed, that these elements will henceforth be accounted his principal performance; for notwithstanding the air of profound speculation which pervades his Chemical Statics, and the valuable remarks scattered through that elaborate work, the hypothesis of indefinite combination which forms its basis, has greatly lessened its estimation among chemists, since the theory of definite and multiple combination has been satisfactorily established. Berzelius, in his essay on chemical proportions, has endeavoured, with some ingenuity, to reconcile Berthollet's statical doctrines to the atomic theory, but apparently with little success.

The first edition of the Elements of Dyeing was very ably translated into English by Dr Hamilton; and had not the French philosopher published a second edition containing important modifications and additions, the labour of the present translator would have been altogether superfluous. It is hoped that the copious notes now appended, will be found a useful supplement to the original work. They contain details of the most remarkable chemical researches connected with dyeing and dye-stuffs which have recently appeared in scientific journals, as also extracts from the valuable work of Vitalis,* on the Adrianople madder red, and on calico printing, along with some observations not hitherto laid before the public.

The Plates furnished by the translator, represent some of the most useful machines at present employed in our best dyeing establishments.

At the end, tables will be found for converting the French hydrometric degrees into the numbers denoting specific gravity, and the French weights and measures into those of this country.

The following obituary notice of Berthollet was published by M. J. J. Virey, in the *Journal de Pharmacie* for December 1822. It may probably prove acceptable to some readers:—

" M. Claude-Louis Berthollet, Member of the Royal Academy of Sciences of the Institute, and of several other academies, Count and Peer of France, &c., was born in 1749 at Talloire in Savoy. He received the degree of Doctor in Medicine, became attached to the house of Orleans, and entered the Academy of Sciences in 1780. In 1794 he received the appointment of Professor of Chemistry in the Normal school, and subsequently in the Polytechnic school. He was nominated a member of the Institute at its formation. *His probity caused him to be appointed to collect the objects of art conquered in our triumphs in Italy.* He soon afterwards joined the memorable expedition to Egypt, and returned

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* Cours Elementaire de Teinture. Paris, 1823.

in 1799 with the extraordinary man who raised him to the rank of senator along with his colleague, Monge, who appreciated the value of his genius. Nominated to the Chamber of Peers by his Majesty, in 1814, he continued a member of it till his death, which happened on the 6th November 1822, at the age of 73 years and a few months.

" His splendid career was marked by important discoveries, although his hands were deficient in address, his style and elocution in perspicuity.* A friend of the great and unfortunate founder of pneumatic chemistry, Lavoisier, he co-operated with him, with Guyton de Morveau, Fourcroy, &c. in reforming the nomenclature of this science. His analysis of ammonia,—his discoveries on fulminating silver,—the manufacture of the detonating powder of chlorate of potash,—the bleaching of goods by chlorine,—his researches on prussic acid, in which hydrogen acts the (acidifying) part of oxygen,—his valuable labours on dyeing, which first illustrated the principles of this art,—his profound observations on sulphuretted hydrogen, whose acidifying properties he pointed out,—above all, his capital work *Chemical Statics*, of which he had conceived the basis amidst the burning sands of Egypt, and while braving the murderous steel of the Arabs—the foundation of the Chemical Society of Arcueil, in that celebrated retirement of his old age, where he delighted to assemble round him young men eager to collect the fruits of his experience, in order to perpetuate his labours and his renown—such are the titles of Berthollet to immortality, if this award can be at all promised to men.

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* This want of clearness in the author's mode of expression has been experienced by his translator on several occasions, and may possibly have caused some mistakes.

" If we penetrate into the privacy of his life, we shall see him, under a modest exterior, and a robust frame, concealing a sensible heart; we shall contemplate this soul, too exalted not to be simple in its greatness, possessed of that intrepid firmness which yielded neither to the accidents of fortune, to dangers, nor to power. Never would his candour make a compromise with error or falsehood, or prefer wealth to self-esteem. Even in the bosom of those political tempests which held nothing sacred, he retained his imperturbable strength of mind. Such lofty virtues were venerated by all parties, zealous to contribute to the illustration of a glory become in some measure European.

" His tomb has received the sincere tears of his friends, Laplace, Chaptal, of his pupils erewhile, but now his honourable competitors, Gay Lussac, Thenard, and many other associates of labours, always subservient to the love of his country and of science."

Glasgow, July 2. 1824.

DIRECTIONS TO BINDER.

The Plates copied from the original work are to be placed at the end of the First Volume. The Plates furnished by the Translator at the end of the Second.

ADVERTISEMENT.

The chief object of the author of these Elements, was to apply the theories, which had recently diffused so vivid a light on chemistry, to the phenomena presented by the art of dyeing, and to its ordinary processes, of which he gave the description.

The arts can make but a limited progress, when they are directed merely by a blind practice. Thus, they have remained for several centuries in nearly the same state in China and in India. But if artisans be guided by the knowledge of those properties which have been investigated by physics, and its complement, chemistry, there are no boundaries to the perfection which they may reach. How many advantages has that nation, so powerful by its industry, derived from Watt, Wedgewood, Henry, and some other philosophers!

In this respect a happy revolution has been effected among ourselves. Our manufactories are no longer intrusted to ignorant workmen. In the greater part of them are to be found very enlightened individuals, well informed philosophers, to whom indeed we must have recourse, if we wish to excite the progress of the useful arts, and remove the obstacles which stand in their way.

By such considerations the author of this Work has been actuated. He has been less occupied with the collection of recipes, than in explaining the properties on which those effects depend which we wish to produce. He has endeavoured, however, to introduce great precision into the description of the processes, selecting those which deserve most confidence.

Some persons imagine, that physical theories are merely systems, to which we wish to accommodate nature, without regard to the practice of the workshops. Yet these theories are themselves only the result of analytical experiments. To observation they always appeal; and, in seeking to direct it, they fix attention on the very facts, whose relations cannot as yet be established with those already classed. They indicate, moreover, their application, which they also try to circumscribe within just limits.

The theory of the art of dyeing is connected on one side with the most delicate speculations of natural philosophy; on the other, with the practice of many different arts. It is not to be regarded as a portion of knowledge, which can be carried to perfection by itself. Its improvements must follow the advancement of the physical sciences, and of several other arts.

The author of these Elements, whose sole pretensions in this second edition were to render his work less defective, and to introduce recent discoveries, has associated with himself a fellow-labourer,* who, directing from his youth peculiar attention to this object, may eventually conduct it to greater perfection.

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* This fond parental anticipation does not seem to have been realized. M. Berthollet, junior, died a considerable time before his father.

HISTORICAL SUMMARY

OF

THE ART OF DYEING.

The desire of attracting public admiration may be observed even in the least civilized state of society. Among the means of distinction which are eagerly laid hold of, the glare of colours is one of the most obvious. Savages assume an imposing aspect, by staining their skins, or wearing feathers, stones, and shells, with gaudy colours. The Gaulish women gave themselves, on festivals, an olive-brown complexion, by means of woad; and those of high rank were no doubt jealous of this distinction.

The art of dyeing, therefore, has unquestionably a very ancient origin; for when nature afforded colouring substances of easy application, there might arise among people but slightly civilized, methods of dyeing which have been sought after by polished nations. Thus the Gauls prepared some dyes which were not disdained by the Romans. But for its enlargement and perfection, the art required to follow the progress of manufactures and luxury.

The Egyptians, according to Pliny,* had discovered a mode of dyeing analogous to that of our printed calicoes. Cloths, impregnated probably with different mordants, were plunged in a bath, in which they assumed different colours. He alludes to the employment of these mordants in the following passage: *Candida vela postquam attrivere, illinuntur non coloribus, sed colorem sorbentibus medicamentis.* It may, however, be presumed, that manufactures possessed little activity among a people where the authority of the priesthood prohibited by law every change in even the most indifferent customs.

It is to Greece that our attention turns, when we wish to ascertain the progress which the human mind had made in antiquity. Here, however, we find a vast difference between the fine arts,† and the useful arts, or the arts of luxury; a difference of which the cause is obvious. Public opinion set these arts at an immense distance from each other: glory was associated with the former, but the latter were confounded with servile labours.

This distinction was, in some measure, well founded. The painter, the statuary, the architect, stamped their genius on their productions. Their arts did not each require a long series of efforts for

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* Hist. Natur. lib. xxxv. cap. 2.

† Poetical arts would be here a juster expression; for statuary is surely an art of luxury.—T.

its advancement; nor did it enrich itself slowly by the casualties and experiments of ages. Imagination could suddenly overleap the boundaries of time; and the masterpieces which appeared in rapid succession among the Greeks, were destined to become the admiration of posterity.

Yet this people, so ingenious, so sensitive, and so fertile in great men, suffered themselves to be seduced in the distribution of their esteem by tastes often frivolous. He who won a victory in wrestling, pugilism, or the race, obtained crowns, and enjoyed the greatest honours; but the useful arts were degraded even in the eyes of their philosophers.

Here we perceive one of the most striking characters which distinguish the ancients from the moderns. The Greek philosophers, occupied especially in speculations which might ensure to them the homage of a people so prone to enthusiasm, regarded the useful arts as unworthy of their attention. This contempt was inherited by the Romans. Pliny, in speaking of dyeing, avowedly neglects to describe operations which do not belong to a liberal art. *Nec tingendi rationem omisissemus, si unquam ea liberalium artium fuisset.*

Ever since philosophy has taken observation for a guide, and, abandoning the illusions of systems, has adhered to the study of the phenomena of nature, and of the real properties to which they owe their origin, it has followed the chain of the numerous wonders which it has analyzed, in subserviency to the welfare of society. It has recognized in manufacturing industry, as well as in commerce, the source of the prosperity of the nation, the germ of a great population, the principal support of agriculture. But it was the Academy of Sciences of Paris which first sought to spread the light of science over all the arts, which first formed the project of publishing their description, and which, in the midst of prohibitory ordinances, arrived at this truth, That national industry was to be augmented and enlightened by a free communication of the processes which it employed ; and that the sacrifices which it might make by this publicity, are well recompensed by the advantages thence derived. This project was extended to all the objects of our studies, by the Encyclopedia, the mightiest monument which philosophy and reason have ever raised.

The art of dyeing must have felt feebly, we perceive, the influence of learning among the Greeks. Yet the activity of genius has something sympathetic, and industry multiplies her trials when solicited by luxury. Let us observe, then, to what point refinement had raised it in the prosperous days of Greece ; let us consult the picture of it traced by Barthelemy.

" A great proportion of the citizens of Athens passed their time in the different tribunals, and received a salary of three oboli, that is, fourpence-halfpenny a-day. The average price of the *setier* (twelve bushels of Paris) of corn, whose value is the least uncertain standard of comparison, was thirteen French livres, (10s. 10d. English), that is, a little more than the half of the medium price with us. A citizen of Athens could thus, with the daily pay annexed to the most important functions of the republic, purchase a measure of corn, which would at present cost sevenpence-halfpenny English. In order to form an idea, therefore, not indeed of the public magnificence, nor of that of some individuals, but of the ease and luxury of the ordinary class of citizens, we must represent to ourselves what they would be at Paris, if the salary of the public functionaries was fifteen *sous* a-day.

"Many of them (the Athenians) went barefooted. The common people were clad in cloth which had received no dye, and which could therefore be re-whitened. The rich preferred coloured clothes:* they held in considerable estimation those which had been dyed scarlet, by means of small reddish grains, and in still higher those of a purple dye."

Silk, which is subjected to the most varied processes of dyeing, comes originally from China. It was, say the Chinese annals, the wife of the emperor Hoang-ti who first engaged in spinning the cocoons which are naturally found on trees. Silk was carried thereafter into Hindostan, and thence into Persia, Greece, and Rome. But it arrived here at a very late period. Some have concluded, from a verse in the Georgics of Vir-

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* Voyage de Jeune Anacharsis.

gil,* that its use was known at Rome in the time of Augustus. We find less doubtful indications in Pliny. Silk bore still so high a price in the time of the emperor Justinian, that it was sold for its weight of gold.† Lastly, some monks brought from India to Constantinople eggs of the silk-worm, and established there the method of rearing them, and of spinning the down of their cocoons.‡

It appears to have been in the time of the Crusades that silk-worms were introduced into Italy.

The art of dyeing webs seems to have been unknown in Greece before Alexander's invasion of India. Pliny relates, that the sails of his vessels were there dyed of different colours. Hence the Greeks possibly borrowed this art from the Indians.

India is indeed the nursery of that knowledge and those arts which were subsequently diffused and improved among other nations. Fortunate accidents might be readily multiplied in a country rich in natural productions; which requires little labour to supply the subsistence of its inhabitants; and whose population was promoted by the profusion of nature, and the simplicity of manners, ere the tyranny of conquerors had exercised their ravages; but religious prejudices, and the unal-

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* *Velleraque ut foliis depectant tennia Seres.*

† Voltaire, Essai sur les Mœurs, &c.

‡ Procop. lib. iv. cap. 17. De bello Gothico. Georg. lib. ii.

terable division of castes, soon shackled industry. The arts have been thenceforward stationary in India; and it would appear, that in the time of Alexander dyeing had attained nearly the same state as at present, in regard to cotton goods; for silk was still unknown there, or at least very scarce.

The beautiful colours which we observe on the Indian goods, to which the name of *Perses* was originally given, because it was through the trade of Persia that it first reached us, might lead to the belief that the art of dyeing was there pushed to a great degree of perfection. But we learn from the description which Beaulieu gave, at the request of Dufay, of operations performed in his presence,* that the processes of the Indians are so complicated, tedious, and imperfect, that they would be impracticable elsewhere, from the difference in the price of labour. European manufactures soon surpassed them in correctness of design, variety of shade, and simplicity of manipulation. If they have not yet rivalled the vivacity of two or three of their colours, this must be ascribed merely to the superiority of some colouring substances, or perhaps to the very length and multiplicity of the operations.

We may therefore conclude, that the art of dyeing was less extended and less improved

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* *Traité sur les Toiles Peintes,* in which we observe the manner of fabricating printed calicoes in India and in Europe. The opinion given in the text is confirmed by the more exact details found in Bancroft *on Permanent Colours.*

among the ancients than among the moderns; but the former possessed a dye which has been lost or neglected, and which was the most eagerly desired object of luxury,—this was purple. Its processes have, however, been better preserved in historical monuments, than those of any other colours.

We shall not dwell on the tales with which it has been attempted to embellish the origin of the purple dye. There is a great probability of the discovery having been made at Tyre, and that it contributed much to the opulence of this celebrated city.

The liquor which was employed to dye the purple, was derived from two principal species of shells. The larger bore the name of the *purple;* and the other was a species of whelk. Both were subdivided into several varieties. They were further distinguished by the greater or less beauty of colour which they could afford, and according to the coasts where the fishing was carried on.

The colouring juice of the *purples* is contained in a vessel which is found in the throat. Only one drop of liquid was obtained from each shellfish. The whelks were bruised: These contained a very small quantity of a red liquor, verging on black. (*Nigricantis Rosæ.*—Plin.)

When they had collected a certain quantity of the colouring liquor, they added to it a proportion of sea-salt. They then macerated for three days; after which five times as much water was added. This mixture was kept at a moderate heat, separating from time to time the animal matters which rose to the surface. These operations lasted ten days. They now tried, with a little white wool, if the liquid had taken the proper hue. The stuff was subjected to different preparations before it was dyed. Some passed it through lime water; others prepared it with a species of *fucus*, which served, like some of our astringents, to render the colour more durable. We do not know precisely the marine plant to which the ancients gave the name of *fucus;* but it was of such extensive use in their dye-works, that the word became a generic name for all kinds of colouring substances, (dye-stuffs.) Pileur d'Apligny conjectures, that it might be a species of *archil* or *rocella*, which is found on the coasts of Candia;* others, again, prepared the cloth with alkanet.

The juice of the whelk did not yield of itself a permanent colour; but it increased the brilliancy of the colour of the other shell-fish. The purple of Tyre was made in two operations. They commenced by dyeing with the juice of the *purpura;* after this they gave it a second dye with the juice of the whelk, whence Pliny calls it *purpura dibapha.* In other processes, the liquors of two species of shell-fish were mingled; thus, for 50 kilogrammes of wool, 200 kilogrammes of the liquor of the whelk and 100 kilogrammes of

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* Essai sur les Moyens de perfectionner l'Art de la Teinture.

that of the *purpura* were taken. An amethyst colour was thereby obtained. Sometimes a body or basis was given with the *coccus,* which is our *kermes,* and after that the dye was completed with the juice of the *purpura.* Finally, they combined some of the preceding methods, and thereby obtained a great variety of purple hues, which were distinguished by different names. That of Tyre possessed, according to Pliny, the colour of coagulated blood; the amethyst purple had that of the stone so called; another species resembled violet, &c.*

It seems that some kinds of purple preserved their colour a very long time: Plutarch relates, in the Life of Alexander, that the Greeks found in the treasury of the king of Persia a great quantity of purple, of which the beauty was not affected though it was 190 years old.

The very small quantity of liquor which was extracted from each shell, and the length of the dyeing process, gave to the purple so high a price, that, in the time of Augustus, a pound of wool dyed in Tyrian purple, could not be had for less than 1000 *denarii,* about 700 French livres, (L. 28 sterling.)

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* Those who wish to acquire more extensive information on the purple of the ancients, may consult among the moderns the following works:—*Fabii Colomni lyncæi purpura; G. Gottl. Richter, Progr. de purpuræ antiquo et novo pigmento;* Reaumur, Mem. de l'Academie, 1711; and especially a learned work of M. Bischoff, entitled, *Versuche einer geschichte der faberkunst, &c.* 1788.

The priests, who sought always to take advantage of what might make an impression on the people, attributed, in early times, a sacred character to the purple. It was a colour pleasing to the Deity, and which must be reserved for his worship. Although the true purple has been lost for a long time, the pride of the name has been preserved in our sacerdotal hierarchy.

Purple was almost every-where an attribute of exalted birth, and of dignities. It served as a decoration to the first magistrates of Rome. But the luxury which was afterwards carried to excess in this capital of the world, rendered the use of it common to opulent individuals, until the emperors reserved to themselves the privilege of wearing it. It soon became the symbol of their inauguration. They appointed officers who were charged with the superintendence of this dye in the manufactories, where it was prepared for them alone, principally in Phœnicia. The punishment of death was decreed against all those who might have the audacity to wear purple, even should they cover it with another dye.

The penalty annexed to this whimsical kind of high treason, was undoubtedly the cause which made the art of dyeing purple disappear, first in the West, and much later in the East, where this art still existed in vigour in the eleventh century.

There was extracted from *coccus,* now known under the name of *kermes,* (an account of which may be seen Sect. iii. Part 2.), a dye, which was hardly less esteemed than the purple, and which was sometimes associated with it, as we have already mentioned. Pliny relates, that it was employed for the robes of emperors. The name of scarlet was usually given to it; but it was sometimes confounded with purple.

It was only in the age of Alexander and his successors, according to Pliny, that the Greeks sought to give some perfection to black, blue, yellow, and green (dyes).

Among the Romans, newly married women wore in the early times a yellow veil. This colour was appropriated to matrons.

In the games of the circus, four parties were distinguished by their colours: green, *color prasinus;* orange, *rufatus;* ash-colour, *venetus;* and white.

We may judge of the qualities of these colours by the substances which they employed. As Bischoff has made very extensive researches on this subject, I shall give, after him, an enumeration of the ingredients which entered into the art of dyeing in those times, independently of the *coccus* and the purple shell-fish.

1. Alum; but we may see in the first part of this work, (Sect. v.) that very probably the ancients were not acquainted with our alum in a state of purity.

2. Alkanet. Suidas relates, that this substance served likewise as a pigment for women.

3. The blood of birds, which was employed by the Jews.

4. The fucus. That of Crete was preferred. It was usually employed to give a basis or ground to good colours.

5. Broom.

6. Violet. The Gauls prepared from it a colour which resembled one species of purple.

7. Lotus medicago arborea. Snail trefoil, (Luzerne en arbre). The bark served for dyeing skins, and the root was employed in dyeing wool.

8. The bark of the walnut tree, and the rind of the nut.

9. Madder. It is not known whether the madder of the ancients be the same plant as ours, or some other root of the same family.

10. Woad. (*Glastum.*) This plant was certainly employed by the ancients; but it is doubtful if they gave it the same preparation as we do.

They made use of the sulphate of iron, and of that of copper, for dyeing black, especially skins. Nut-galls, of which the most valued came from Comagena, served as the astringent. They used, as a substitute for it, the seeds contained in the pods of an acacia peculiar to Egypt. They also employed the bark of pomegranate and of some other astringents.*

Although the ancients may have used some substances of which no memorial is preserved, it is easy to see that the acquisitions which we have made, especially since the discovery of America,

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* Ameilhon, Mem. de l'Instit. Litter. et Beaux Arts, tom. iii.

give us a great superiority with regard to several colours. But is the regret frequently expressed for the loss of the purple, well founded? Are we not able to rival the beauty of this highly famed colour?

The shell-fish which furnished the colouring liquor of the purple, exist probably in as great abundance as formerly. They have been sufficiently characterized to enable us to recognize them. In fact, Thomas Gage relates that there was found near Nicoya, a small Spanish town of South America, shell-fish possessed of all the properties described by Pliny and the other ancient writers. It appears, even, that some use was made of these shell-fish for dyeing cotton on the coasts of Guayaquil and of Guatimala.* Cole discovered some of them in 1686 on the English coasts; Plumier found a species of them at the Antilles; Reaumur made several experiments on the *buccinum* which he found on the coasts of Peru; Duhamel made also several on the colouring juice of the shell-fish which bears the name of *purpura*, which he found in abundance on the coasts of Provence. He observed that this juice assumes a purple colour only by the action of light, as Reaumur had already remarked respecting the colouring juice of the *buccinum*; that this juice, at first white, assumes a yellowish-green colour, which deepens, verging on blue; that, finally, it is seen to redden, and

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* Histoire Philosophique et Politique du Commerce des Indes, liv. vii.

in less than five minutes to become of a very vivid deep purple colour.* Now, the purple of the ancients possessed these characters.

Moreover, we have a very detailed description of the manner in which the fishing was conducted of the shell-fish which served for purple, in a work of an eye-witness, Eudocia Macrembolitissa, daughter of the emperor Constantine VIII. who lived in the eleventh century.†

Our indifference, therefore, in procuring the purple, and in profiting by the researches which some moderns have successfully made, probably proceeds from our having acquired more beautiful and less costly colours. Many learned men are of this opinion.‡

In fact, the kermes afforded a colour which was esteemed by the ancients as almost equal to the *purple* (purpura), and which contributed to that distinguished by the name of *color hysginus.* Now, we understand the management of the kermes in probably a more advantageous manner than the ancients did, because we possess a pure alum, which disposes the stuff to receive a finer and more permanent colour; and yet our dyers

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* Mem. de l'Acad. 1736.

† Eudocia Macrembolitissa was married to a Constantine, and after his death to Romanus III., who was elected emperor in 1068. Her work is to be found in a collection published by M. d'Anse de Villoison, under the title of *Anecdota Græca e regiâ Parisiensi et e Venetâ S. Marci bibliothecis deprompta,* T. i. 1781.

‡ Bischoff, Versuche, &c. Goguet de l'Origine des Lois, Arts, et des Sciences, 2 partie, liv. ii.

have been obliged to renounce its use almost entirely, notwithstanding the solidity of its colour, because it cannot, in point of beauty, bear a comparison with the colours now produced from cochineal.

Supposing the slight difference which may exist between the colour of the kermes, and that of the purple of Tyre, to be compensated by the advantage which we derive from our alum, we might regard this purple, which was so precious that the Cæsars reserved it to themselves under penalty of death, to be similar to that blood-red which we observe in ancient tapestries, for the production of which kermes was employed.

The supposition, that the colour which we derive from kermes is preferable to that which the ancients obtained from it, can be supported by the testimony even of Pliny; for he insinuates that it had little permanence; but the colour which is now given by means of kermes, to wool prepared with alum, is of the greatest durability.

Soap, the discovery of which is ascribed to the Gauls, appears to have had no other use among the ancients than that of a pomade for cleansing the hair, or for staining it with any colours which they chose to mix with it. This substance is, however, of such utility, that it must give us a superiority in bleaching, and in some parts of dyeing. They supplied its use, in the scouring of wool and whitening of cloth, by a plant which Pliny calls *radicula*, which was termed *struthion* by the Greeks, and which some consider as our *saponaria;* as also by another plant, which Pliny designates as a species of poppy. Homer paints the princess Nausica and her waiting-maids treading their dresses with their feet in ditches, in order to bleach them. From other evidence we learn that wood ashes were mingled with them; and also, that some earthy boles were employed.

We have acquired from the New World several dye-stuffs, cochineal, brazil wood, logwood, annotta. We owe the superiority of our dyes especially to the preparation of alum and to the solution of tin, which lends such lustre to several colouring substances. Silk, which has become so common with us, and which takes such lively and brilliant dyes; the rapid movements of commerce, which place the productions of China and the Indies within the enjoyment of even the common people; an active and enlightened industry, stimulated by the rivalship of the different nations of Europe, who endeavour to counterbalance their instruments of power; all these circumstances set an immense interval between the luxuries most familiar to us, and those of the most opulent individuals among the ancients. Europe, however, before acquiring this superiority, experienced all the devastations of barbarism.

In the fifth century the arts became extinct in the West; soon thereafter, almost every trace of intelligence, reason, humanity and industry, disappeared. A few decayed arts, indeed, were preserved merely in Italy. Muratori quotes a manuscript of the eighth century,* in which we

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* Diss. de Textrina et Vestibus sæculor. rudium Antiq. Ital. vol. xi.

find some descriptions of dyes, chiefly for skins, and some processes of the other arts; but the Latin, which is almost unintelligible, and some chasms in the writing, prevent us from forming a just idea of these processes.*

The arts were better preserved in the East, whence were derived, till the twelfth century, the objects of luxury which a few of the great were able to procure. During the Crusades, the Venetians reared their power on the frenzy of the age: their fleets took charge of the victualling of our fatal emigrations; their commerce became enriched; the arts were established among them, enlightened by the manufactures of the Greeks; and from this city they were propagated into the other parts of Italy. In 1338, 200 manufacturers were employed in Florence, who fabricated, it was said, from 70,000 to 80,000 pieces of cloth, forming an object of commerce worth 1,200,000 golden crowns.

The discovery of *rocella* was accidentally made by a merchant of Florence about the year 1300. Having remarked that urine gave a fine colour to a species of moss, he made experiments, and learned to prepare *archil.* He kept this discovery secret for a long time. His descendants, of whom a branch still remains, according to the

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* I shall quote literally a description of alum, which seems to prove, that only aluminous stalactites, or a volcanic earth impregnated with alum, was used. DE ALUMEN. *ALUMEN antem metallum, est terra floriens de eritarin. Eritarin terra est alba, facilis ad pisandum.*

report of Dominique Manni, have retained the name of *Ruccelai,* from the Spanish word *oreiglia,* which that species of moss bore.

The arts long continued to be cultivated in Italy with increasing success. In 1429 appeared at Venice the first collection of processes employed in dyeing, under the name of *Mariegola dell' Arte de Tentori.* A second edition of it, much enlarged, was given in 1510. One *Giovan Ventura Rosetti* formed the project of giving more extent and utility to this description. He travelled into the different parts of Italy and the neighbouring countries, where the arts had begun to revive, to learn the processes which were there pursued; and he published, under the name of *Plictho,* a collection, which, according to Bischoff, is the first wherein the different processes were assembled, and which must be regarded as the primary impulse towards that perfection which the art of dyeing has since reached.*

It is to be remarked, that in the work of Plictho there is no mention made of either cochineal or indigo; so that in 1548 these two colouring substances were probably not yet employed in

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* *Plictho dell' Arte de Tentori, che insegna tenger panni, tele banbasi e sede, si per l'arte magiore, come per la comune. Venezia,* 1548. This work has been translated into French under the title of *Suite du Tenturier parfait, ou l'art de teindre les laines, soies, fils, peaux, poils, plumes, &c. comme il se pratique à Venise, Gênes, Florence, et dans tout le Levant, et la manière de passer en chamois toute sorte de peaux; traduite de l'Italien. Paris,* 1716.

Italy. Pliny indeed speaks of a substance which came from India, and to which the name of *Indicum* was given; but no use was made of it except for painting. It is, however, very probable, that the Indians used it in dyeing; it appears, even, that the first which was employed in Europe was brought from the East Indies by the Dutch. The cultivation of it was first established in Mexico, and thence in the other parts of America, where it has acquired qualities superior to what comes to us from India.*

For a long time Italy, and particularly Venice, possessed almost exclusively the art of dyeing, which contributed to the prosperity of their manufactures and their commerce; but by degrees this art was introduced into France. Giles Gobelin made an establishment in the place which bears his name. This enterprise was regarded as so rash, that the name of *Gobelin's Folly* was given to the establishment; and the success which it obtained so astonished our ancestors, that they believed Gobelin had entered into a compact with the devil.

The discovery of the scarlet dye may be regarded as the most remarkable era in the art of dyeing, not only by the lustre which distinguishes it, but also by the brilliancy which we can impart, by means of the same process, to several other colours. We have seen that the ancients gave

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* The indigo imported into Great Britain from Calcutta now, is in general superior to the South American.—T.

the name of scarlet to the colour which they obtained from kermes, and which was very inferior in beauty to what we designate by the same appellation.

Some Spaniards having observed that the inhabitants of Mexico made use of cochineal for colouring their houses and dyeing their cottons, informed the ministry of the beauty of this colour; and Cortes received, in 1523, an order to promote the multiplication of the precious insect which produced it. The colour which cochineal gives naturally is, however, a pretty dull crimson.

A little while after the cochineal became known in Europe, the scarlet process, by means of the solution of tin, was discovered. It is stated, that about 1630 Cornelius Drebbel observed, by an accidental mixture, the brilliancy which the solution of tin gave to the infusion of cochineal. He communicated his observation to his son-in-law, Kuffelar, who was a dyer at Leyden. He soon improved the process, kept it secret in his workshop, and brought into vogue the colour which bore his name.*

Soon thereafter, a German chemist, called *Kuster*, *Kuffler*, or *Kepfler*, found out also the scarlet process by means of the solution of tin. He carried his secret to London in 1643. A Flemish painter named *Kloeck* or *Jean Glucq*,

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* Grundriss der farbekunst. Sigismond. Friedrich Hermstadt.

procured the knowledge of it, and entered into partnership with a family of the name of *Jullienne*, the last of whom died in 1767.* This process was subsequently diffused over Europe. *Kloeck* travelled in the East, which, since the time of the Greeks, had preserved a remnant of manufactures; and he naturalized in Flanders the art of dyeing on wool and silk, which flourished there for a long time. M. Francheville fixes the death of this man, who was so useful to his country, towards the year 1550.†

The employment of indigo, which has been likewise a great acquisition to the art of dyeing, experienced more difficulty in its establishment than that of cochineal. It was severely prohibited in England under the reign of Elizabeth, as well as logwood, which was ordered to be burned whenever it was found in a manufactory. This prohibition was removed only in the reign of Charles II.

The use of indigo was equally proscribed in Saxony. It was treated in the ordinance issued against it (which reminds one of the decree against tartar emetic), as a corrosive colour, and food for the Devil. *Fressende Teufels.*‡

This is a grand example of the abuses into which an unenlightened administration, easily misled by the suggestions of personal interests,

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* Notice sur la manufacture nationale de Tapisserie des Gobelins, par Guillaumeau.

† Mem. de Berlin, 1767.

‡ Bischoff, Versuche, &c.

may fall. The blue dyers, who were in possession of the process with pastil and woad, represented, that indigo would ruin the commerce of these two substances, which were native productions. This motive, which would be still specious in the eyes of several persons, readily determined the issuing a prohibition, which was soon to be eluded, at the expense of paying a tribute to the industry of other nations. The prejudice against indigo was also communicated to France; and in the Instructions of Colbert it is forbidden to put above a certain proportion of it into the woad vats.

Colbert gave to French manufactures, which had remained languishing under the stormy administrations of Richelieu and Mazarin, an impulse which soon advanced them beyond the progress of other nations. He called forth the most expert artists; he recompensed every talent; he established several manufactories; and it may be remarked, that those of Vaurobais and Sedan were designated, in the letters-patent which were granted them, under the name of fine cloths of Dutch and English fabric. He published, in 1672, a code of instruction for dyers, which merits attention.*

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* *Instruction generale pour la teinture des laines et manufactures de laines de toutes nuances, et pour la culture des drogues ou ingredients qu'on emploie.* This work was reprinted in 1708, under the following title:—*Le Teinturier parfait, ou instruction nouvelle et generale pour la teinture des laines et manufacture de laine de toutes couleurs, et pour la culture des drogues ou ingredients qu'on y emploie.*

There are presented in this, first the motives which give importance to the object under consideration :—" If the manufactures of silk, wool, and thread, are those which serve principally to sustain and give value to commerce, dyeing, which communicates to them that beautiful variety of colours which makes them agreeable, imitating whatever is most lovely in nature, forms the soul, without which the body would have but a feeble existence.

" Wool and silk, which, in their natural colours, shew rather the rudeness of the age, than the genius of man, and the refinement of our days, would command but a moderate trade, if dyeing did not impart to them that elegance which makes them be sought after and desired even by the most barbarous nations.

" All visible objects are distinguished or rendered desirable by their colours, which must be not only beautiful to give commercial currency to the stuffs, but also good, that their durability be equal to that of the fabrics to which they are applied."

In placing alongside of several salutary regulations, instructions for cultivators and artists, Colbert did homage to that feudal spirit, which multiplying with fiscal views the shackles of commerce, manufactures, and agriculture, had impressed throughout nearly the whole of Europe the idea of regarding these bónds as indispensable. Instead of restricting himself to measures which should serve to guarantee the fidelity of the fabrics and the goodness of the colours,—instead of developing the germ of that honour which belongs to commerce, and which promotes its interest, he pushed the prohibitory regulation to the point of requiring, that the dyeing of black cloth should be begun by the dyers in the grand tint, and finished by the dyers of the little tint. —(*Teinturiers en grand teint, et en petit teint.*) The former were allowed to have in their possession only a certain number of ingredients, while the latter were also restricted to a certain number. Neither the one nor the other were permitted to have brazil wood, &c. It is true, indeed, that the sad effects of these prohibitions were tempered by the facility of evasion, as well as by the premiums awarded to those who made some advancement in their art, and whose discoveries being subsequently communicated to the public, produced modifications in the regulations. French manufactures lost their pre-eminence by the revocation of the edict of Nantes, which scattered them over the rest of Europe, leaving desolation in our factories.

Since this period, the department of administration charged with the superintendence of our arts and manufactures, has been constantly occupied with the means of repairing our losses, and of making our industry flourish. It has employed that plan in particular, which, with a judicious liberty, is the most efficacious of all, viz. the diffusion of instruction and scientific knowledge.

Dufay, Hellot, Macquer, were, in succession, charged with the duty of presiding over the art of dyeing; and to their labours we owe precious improvements. Dufay was the first who formed sound, though incomplete ideas, on the nature of the colouring particles, and on the forces by which they adhered to cloth. He examined some processes with sagacity, and established the surest tests which could at that time be formed, for determining in a ready and practical manner the goodness of a colour. Hellot published a methodical description of the processes which are practised in the dyeing of wool, which forms still the best treatise we possess on this subject. Macquer gave an exact description of the processes executed on silk: he made known the combinations of the colouring principle of Prussian blue; he tried to apply its use to dyeing; and he furnished a process for imparting to silk brilliant colours by means of cochineal.

The solicitude of administration has had, in the judgment of foreigners, the success which it deserved. Anderson ascribes to the perfection of our dyes the superiority which some French manufactures have preserved over those of the nations which possess the finest wools;* and Home (Lord Kames) thus explains himself:—"It is to the Academy of Sciences that the French owe the superiority which they enjoy in several arts, and especially in that of dyeing."† Several

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* History of Commerce.

† Essay on the Bleaching of Cloth.

distinguished philosophers, indeed, have followed with equal success the example set by the Academy of Sciences.

Macquer had undertaken to publish a general treatise on dyes, of which he gave the prospectus in 1781; but the languor which for a long time announced his dissolution, prevented him from executing it. He who replaced Macquer in the administration of commerce, endeavoured, in the first edition of these Elements, to connect the theory of the phenomena presented by the art of dyeing, with the great discoveries which had effected at that period a revolution in chemistry; to make the application of it to the practice of this art; and to pave the way for a new career of advancement, by a more exact analysis of the properties of the substances which serve as agents in dyeing, or which have relations with the qualities of colours.

ELEMENTS

OF

THE ART OF DYEING.

PART I.

OF DYEING IN GENERAL.

SECTION I.

OF THE GENERAL PROPERTIES OF COLOURING SUBSTANCES.

CHAPTER I.

Of the Theory of Colours, and of the distinctive Properties of Colouring Particles.

The physical theory of colours may appear foreign to a work, in which we are to consider only the properties which distinguish them, in reference to the agents which are employed in their application to the stuffs which receive them, and to the circumstances which produce in them changes or modifications. It may however be interesting, and possibly useful to the discussions on which we are about to enter, to establish a connexion between the phenomena which the colouring substances produce, and those which the great Newton has analyzed in his Optics.

We shall begin, then, by examining if the theory of Newton, concerning the colours assumed by transparent liquid or solid bodies, such as air, water, glass, according to the difference of tenuity of the plates which they form, and according to their respective density, can be applied to bodies constantly coloured, such as the colouring substances which are the objects of dyeing.

In order to represent the ideas of Newton, and the consequences to be drawn from his observations, we shall enjoy the advantage of being guided by the treatise of Haüy, where physical knowledge is concentrated with equal elegance, clearness, and precision.*

" In proportion as the transparent parts of bodies vary in size," says Newton, " they reflect the rays of one colour, and transmit the rays of another colour, for the same reason that thin plates and bubbles reflect the light, or transmit these rays; now, this is the principle of the uniform colours of all bodies."†

Newton, however, supported this induction merely by the experiments which he made on colourless substances. Delaval endeavoured to discover proofs of it in the operations which che-

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* Traité Elementaire de Physique, tome xi.

† Optic. lib. ii. part. 3. prop. 5.

mistry causes bodies to undergo, and in those of the art of dyeing.* Some doubts had been offered about this application of the theory of Newton, in the first edition of this work; since which time Bancroft has opposed to it a great number of facts.† We shall avail ourselves of these several observations in the discussion which we are about to undertake, solely in the view of recalling to this interesting object the attention of those who can follow the traces of Newton. We must begin by forming an exact idea of the opinion which it is proposed to examine.

"In every body the particles are separated from each other by small interstices, which we call pores, and which contain different subtile fluids. These particles having a determinate thickness, repel the rays, which, in penetrating them, are found in a fit (*retour*) of easy reflection, and the body thus assumes the colour, either simple or mixed, analogous to that of the reflected rays, and which depends on the degree of tenuity of the particles.

"In fact we have seen, that coloured rings are produced in the plates of solid bodies, as well as in those of liquids or fluids; and since every little

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* Experimental Inquiries on the cause of the changes of colours in opaque and naturally coloured bodies. Letter to the Earl of Morton, on the relation between the specific gravity of several metals and their colours. This last work was honoured, in 1765, with a medal by the Royal Society.

† Exper. Researches concerning the philosophy of permanent colours.

space comprised in one of these plates reflects or refracts the light, it follows, that if this plate were divided into a multitude of small fragments, each of these would still produce the same effect as when it was in continuity with the others. Now, as the particles of a body may be likened to the separated fragments of a plate, whatever may be said of this plate is exactly applicable to them also.

" In speaking of the particles of bodies, it is not meant to designate their smallest molecules, or those which we call integrant molecules. In order to conceive what ought to be understood by the particles which reflect the light, we may suppose, with Newton, that the integrant molecules, already separated from one another by the pores, form, by means of the union of a certain number of them, other molecules of the second order, separated by more extensive pores; that these, in their turn, compose molecules of the third order, with interstices always more considerable; and thus in succession. Now the particles which reflect the light in the ordinary state of a body, have a certain thickness, whence result separations to a certain extent between them: these particles are then considered as insulated, relatively to the adjoining ones. The *media* which intercept them, namely, the subtile fluids which occupy their pores, and the air which surrounds their outer surface, perform the function of two glasses, between which the plate of air in the experiment of Newton is comprised; for example, in a plate of mica of a perceptible thickness, there are particles of a certain order, which possess the property of reflecting the rays of a yellowish-white, and these exist naturally at sufficient relative distances for the light to act upon them, as if they existed alone. If we divide this leaf into leaflets, to a certain degree of tenuity, we insulate the particles of another order, which will reflect other colours, as is confirmed by observation.

"We have spoken, under the article *divisibility*, of a plate detached from a piece of mica, whose degree of thinness was such, that its primitive colour, which was yellowish-white, had passed to the most intense blue."—*Haüy.*

Yet, whatever tenuity be given to carmine or indigo, by bruising, as Bancroft observes, the colour peculiar to each is not affected. We merely brighten it, by multiplying, according to Monge, the surfaces which reflect the white.

It may, indeed, be replied, that these substances are composed of homogeneous particles, which, notwithstanding the greatest division at which we can arrive, produce the same effect as when they formed a continuity, whilst the mica has particles of a certain order, which possess the property of reflecting the rays of a yellowish-white; while on dividing a plate into thin *folia* to a certain degree of tenuity, we insulate the particles of another order, which reflect the blue.

We shall here venture to offer some observations.—

1. This manner of supposing mechanical arrangements, in order to employ them in the explanations of physical properties, without directly proving them, may easily serve to prop hypotheses otherwise entirely destitute of probability.

2. This supposition of particles of different orders, which may reflect different colours in a homogeneous body, does not accord with the opinion of Newton, who ascribed all the colours obtained from plates of Muscovy talc, which is merely a mica, to the thickness which he mechanically gave to these plates; and who compares these colours to those produced by soap bubbles, according to the very variable thickness which they assume. By this opinion, indigo and carmine ought certainly to afford different colours, according to the tenuity of their parts; but we shall presently observe a circumstance, where it is difficult to suppose that the particles of indigo preserve, along with their colour, the same dimensions and the same density.

It is admitted, that a solvent must intervene in the dimensions of the molecules which reflect the colours; and this effect is employed to explain some changes of colours produced by acids and alkalies. "We may easily explain, on the principles laid down, the colours produced in certain liquors which are colourless, by the mixture of one of these liquors with the other, or the changes of colour which a liquor naturally coloured suffers in the same case. Thus, nitric acid dropped into alcohol, in which an infusion of roses has been made too feeble to communicate any hue, developes instantly a colour similar to that of the roses before infusion. The same acid, mingled with tincture of litmus, changes the blue into a lively red. Syrup of violets becomes green by the addition of an alkali. In all these mixtures, the union of the molecules of the two liquids forms mixed molecules, whose thickness is different from that of the component molecules, and occasions the reflection of the colour analogous to this thickness."

Newton specifies more particularly the cause of the changes of colour produced by acids and alkalies. "It is known," says he, "that saline menstrua are very proper for dissolving certain substances, and it is also known, that some of them precipitate what others dissolve; and as it is the nature of acids to attenuate and dissolve, and that of alkalies to thicken and precipitate, if the colour of the syrup of violets were of the second order, an acid liquid attenuating its particles would change this colour into a red of the second order."

Delaval has also tried to explain the action of acids and alkalies, by ascribing to the first the property of attenuating, and to the second that of inspissating. Let us examine, therefore, if the properties of acids and alkalies, and those of the solutions which they effect, authorize these explanations.

If, in the effect which they produce, the union of the two liquids forms mixed molecules, whose thickness is different from that of the component molecules, and determines the reflection of the colour analogous to this thickness, there must be a remarkable difference in this respect between barytes, which has a great specific gravity and a great fixity, and ammonia, which is, on the contrary, specifically very light and of an elastic disposition: there ought to be found a similarity of effect between some acids and some alkalies; yet barytes and ammonia produce the very same change. Sulphuric or phosphoric acid does not act differently from carbonic acid, on the substances whose colour they can alter.

The supposition advanced by Newton, that alkalies augment the thickness of the molecules, and that acids attenuate, will not appear well founded to those who direct their attention to the properties of the solutions of colouring substances in acids or alkalies: the solution by alkalies properly presents, in the greater number of cases, more decided characters of attenuation than that which is due to acids, and it is for this reason that they destroy, in dissolving them, the greater part of the colours which have been fixed upon stuffs. It is only, therefore, for explaining certain changes of colour, that to alkalies is assigned a property which cannot be reconciled with observation.

We are now to examine a circumstance, where, notwithstanding a great difference introduced into the density, and a great attenuation of the colouring substance, this preserves unchangeably its colour. We shall confine ourselves to one example, although we could adduce many of the same kind. It is from indigo that we shall take it. If we dissolve indigo in sulphuric acid, we may dilute the solution by successive additions of water, so that it requires at least, according to the observation of Bergmann, 20 *pounds of water in a cylindric vessel of glass, 7 inches diameter, to destroy the effect of the smallest drop of the solution.* The molecules which always reflect the blue, ought however to pass through all the dimensions which exist between that of the solution of indigo, possessing much specific gravity, and that of water; they ought to suffer a greater and greater attenuation. Further, we may substitute the acetic acid for the sulphuric, by precipitating the latter with acetate of lead. A portion of the indigo falls with the sulphate of lead. This precipitate, which ought to have molecules much thicker, as well as the liquid which holds the indigo in solution merely by means of the acetic acid, possess equally the same blue colour.

Newton concluded from his observations, *that the corpuscles which produce black, must be smaller than any of those which produce other colours.*—His theory appears to us to lead even here to a result, which proves that a false application has been made of it. In fact, ink consists of molecules, which are a metallic compound in a state of precipitation, and which of consequence, according to the very idea of Newton, are placed in circumstances that announce the greatest compactness. If we dilute it with much water, the black passes to blue or violet. When the solution of indigo in sulphuric acid is much condensed, it appears absolutely black; by dilution with water it becomes blue; that is to say, by diminishing its condensation, or by doing the contrary of what the theory requires.

Hitherto we have discussed the opinion on the supposition that the colouring molecules act, by virtue of the form which belongs to them, in the liquids in which they are in solution, as we see it stated in the following passage of Haüy. "With regard to transparent and even coloured bodies, they seem to offer a middle term between limpid and opaque bodies. Their molecules reflect the rays of the colour under which they are presented to the eye, and at the same time these bodies transmit, throughout all their extent, other rays, which usually have the same colour as the reflected rays. Thus the molecules situated at the surface reflect one part of the rays which arrive at this surface, and transmit the rest; other molecules situated a little lower, reflect one part of the rays which have escaped the first reflection, then transmit the others; and thus in succession, to the last surface, where there still arrive a sufficiently great number of rays passing into the air, to give the body placed between the eye and the light a very sensible transparency. It thence results, that the greater thickness the medium has, the deeper is its colour, which agrees with observation.

" This supposition will not accord with the opinion which we must form of chemical combinations possessing liquidity, and in which all the properties become common among all the parts by their reciprocal action, whilst the equilibrium of the action is not disturbed. The figure which belongs to the different molecules allows no influence to be perceived till they approach the term where they must pass to the solid state: It is then, for example, that water, which tends to congeal, acquires an expansion due to the effort which it makes, in order that its molecules, in losing their liquidity, may assume an arrangement determined by their surfaces.

" Experiments made by Delaval appear to prove, that the effects attributed to the distinct parts of the colouring substances in solution, do not depend on their individual reflection. He filled a flask, of a square form, with a coloured liquid, after having covered three of its sides and the bottom with a black paint; and he observed, on looking to the liquid by the free face, which formed a right angle with his window, to prevent the reflection from the posterior surface, that the above liquid appeared black, whatever might be its proper colour. Glasses having the same form, and differently coloured, equally appeared black when they were covered with a black cloth, with the exception of one face which was left free, to admit the incident light. If their mass be considerable, they thus also appeared black; but their fragments, applied to a white ground, exhibited the colour peculiar to them."*

He thence concludes, that coloured liquids and glasses are seen in their proper colours only by rays reflected from their posterior surfaces; so that it is the rays which have traversed the coloured liquid or glass, which give the sensation of colour by transmission or reflection.

He makes a remark, whose application is found in this place. "If a small quantity of colouring substance is mixed with a medium which has no colour, the mass appears dyed with the colouring substance. But if we add a great quantity of this colouring matter, the mass appears black; consequently, in ascribing to the colouring substance the power of reflection, we advance a contradictory and inexplicable proposition; for we affirm, that the more of the substance, having the power of reflection, the incident light encounters, the less light is reflected; so that if the colouring substance be very abundant, there is no longer any colour but a black."

In order to extend this theory to opaque coloured bodies, Delaval supposes that they are always composed of two substances, one of which is white, and the other, which is coloured, possesses transparency, so that the rays of a certain colour which traverse it, are reflected by the white surfaces that they meet. When white molecules do not separate those which are coloured, it is enough

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* Mem. of the Liter. and Philos. Soc. of Manchester, vol. ii.

if there be present any medium whatever possessed of a different density; as Newton has shewn that two transparent substances, of a widely different density, produce an opaque body. Delaval thus explains the colour of gold and metallic oxides.

This explanation is very specious, and satisfies the greater number of observations. Nevertheless its application appears to us too general, because it requires us to suppose, between the coloured molecules of the metals, the existence of a *medium*, which the other properties do not indicate, and because other causes may produce the effect here ascribed to it.

In recapitulating what has been said, we find, that in order to explain the different phenomena presented by coloured bodies, 1st, we consider, in a general manner, *the colouring molecules of a body as insulated, relatively to those which adjoin them, and the media which are interposed; viz. the subtile fluids which occupy their pores, and the air surrounding their exterior surface, as two glasses, between which is comprised the plate of air, as in the experiment of Newton.*

2. It is admitted, however, that in the solutions which experience changes of colour by the action of acids and alkalies, the union of the molecules of the two liquids forms mixed molecules, whose thickness is different from that of the component molecules, without explaining the uniformity of effect of those acids and alkalies which differ most in their specific gravity, fixity, and volatility.

3. It is presumed, on the contrary, that in the solutions, combinations, and precipitations, where the substances preserve the same colour, there occurs no alteration in their dimensions, applying to the colouring parts the theory of No. 1., although the state in which they exist be equally the effect of a reciprocal action, and although there be equally a combination.

In all the cases of transparency, the colouring molecules are supposed to act individually on the rays of light; and experiment seems to prove, that the reflection of bodies which are not opaque, takes place only at their anterior and posterior faces.

The effects observed in the solution of water in air, and in its precipitation, appear to us capable of illustrating the properties of solutions relatively to light.

When damp air has been compressed in a globe, according to the experiment of Kratzeinstein related by Saussure,* and when we restore the freedom of communication, this air, which, placed between the eye and the light, exhibited at first only a pure transparency, causes vapours to be perceived, which have the colours of the rainbow at the moment when the compression is removed; and it resumes its transparency by a new compression.

This phenomenon is not difficult to analyze. When the air, saturated with humidity in a state of

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* Essai sur l'Hygrom. § 209.

compression, is suddenly liberated, it produces by its dilatation a degree of cold, which causes the precipitation of a part of the water which it held in solution. Compression produces a contrary effect, by the heat which accompanies it.* Saussure remarks, that the phenomenon due to the vapours lasts only an instant, because the temperature becoming fixed, the state of solution becomes equally so.

Light then experiences no peculiar reflection or refraction from the water or air while the solution exists; and it is only when these two elements acquire a peculiar existence that this effect begins. Is it not natural to ascribe to other solutions what is here observed in that of water? On the other hand, can we compare the constant properties of coloured substances, with the variable and transient effects owing to the refraction and reflection of the molecules in simple juxtaposition?

Delaval made a great many experiments to prove, "that the more considerable the density of constantly coloured bodies is, the greater also is their power of reflection (every thing else being equal) for reflecting the least refrangible rays; that, on the contrary, when they have less density, they can proportionally reflect only the less refrangible rays; and consequently they must exhibit different colours, according to the order of their density."

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* Stat. Chim. tom. i. p. 163.

He makes choice particularly of metallic bodies to prove, " that they differ as to colour, exactly in the same gradation as in density; the densest body being red, that which is immediately of a less density being orange-yellow," &c.

A little attention, however, is sufficient to convince us, that there is no relation between the specific gravity of metals, or of glasses coloured by their oxides, and their colours. Delaval regarded, with Newton, the solution of metals as a simple division of their molecules, without regard to their oxidation, the theory of which was then unknown, and on which principally depend the changes of colours in their solutions and oxides. To establish his opinion, and to make the peculiar colour of every metal coincide with its specific gravity, he selected that state of solution and oxidation which best suited his views. We refer to the treatise of Bancroft for a detail of the facts hostile to the opinion of Delaval.

Newton ascribed the colour of white metals " to their excessive density, by virtue of which they seem to reflect almost all the incident light, unless, when dissolved in suitable menstrua, they be thereby reduced into very small parcels (particles), when they become transparent."*

If, from the density, we judge of the effect which silver ought to produce on light, its solution in nitric acid, which can take up a great quantity of

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* The brilliant white of potassium and sodium, bodies of little density, seems adverse to this idea of Newton.—T.

it, and can be diluted with water as much as we please without decomposition, ought, in passing through different densities, to acquire the property of reflecting different colours. It remains, however, colourless and transparent, although, according to the observation of Wollaston, the refracting quality of the metallic solutions varies with their different degrees of concentration.* It ought to tally with the density and attenuation of the solutions or precipitates of cobalt, nickel, and manganese, which, like silver, void of colour in the metallic state, acquire it very intensely and very variously in their oxidation and precipitation.

The considerations now presented lead us to believe, that we ought not to confound the fugitive colours produced by the reflection of plates, which follow the laws described by Newton, with the colours which continue, notwithstanding the changes of density and thickness. These appear to depend on properties, in which the peculiar affinity for the different rays of light has an influence which resists that of the dimensions and the density. On examining the facts, we perceive that condensed oxygen exercises a great power in this species of affinity. A variable proportion of it, affecting in an insensible manner the specific gravity of the metallic oxides, produces in them great changes of colour. In like manner, a little oxygen, conveyed by muriatic

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* Phil. Trans. 1802. Ann. de Chim. tom. xlvi.

acid to colouring substances, either makes their colours disappear, or produces in them considerable alterations; whilst other combinations, for example that of alumina, which precipitates the greater number of colouring substances in the form of lakes, and which, according to the ideas of Newton and Delaval, ought to give considerable density to these substances, preserves meanwhile their proper colour, merely concentrating it by the condensation which the earth occasions.

The very experiments of Newton prove, that the peculiar affinity of different substances has a great influence on their relations to the rays of light, since, according to him, their refractive power is proportional, not merely to their density, but also to their inflammable disposition. This proposition ought not to be taken with too great latitude. For phosphorus, which is very inflammable, has no great refrangency. It follows however, from the very observations on which the doctrine rests, that there is a great difference of action, according to the affinity of the bodies for the rays of light.

The interesting experiments of Dr Blair likewise prove the peculiar power of the affinity:— When light passes from any medium whatever into a vacuum, the red rays are the least refrangible, and the violet are at the other extreme; but if light passes from one medium into another, he shews, that it is the quality or particular nature of these media that determines which of these rays shall be the most refrangible, or if they shall be equally so. The green rays occupy the middle of the spectrum in the dispersion occasioned by crown glass; they are found among the least refrangible by the dispersive action of flint glass; but in muriatic acid these rays are found, on the contrary, on the side of the violet or the most refrangible. It thence happens, that the order of the colours is reversed in the secondary spectrum, formed by a combination of crown glass with the liquid.

If we depart, in these considerations, from the consequences to which physical observations have led; if we believe that we must resist, in this particular, the authority of Newton, and that of his illustrious interpreter, it is with regret; for we feel how important it is to connect all the effects due to the reciprocal action of bodies, and we hope that future experiments will fill up the space which here seems still to separate natural philosophy and chemistry. Meanwhile, we shall confine ourselves to the results of this last part of the science, which treats of the properties of bodies.

In the metallic oxides, and in several mineral substances, all the parts are equally coloured; but this is not the case with vegetable or animal substances. The colour in the latter is usually owing merely to particles, which are mixed or combined with those constituting the bodies themselves; and vegetables contain sometimes different colouring molecules at different periods of their growth, or in their different parts.

The colouring molecules of vegetable and animal substances are almost the only ones employed for the purpose of dyeing; but they are often modified by the use of *intermedia.* Such are the substances designated in this treatise by the name of colouring particles, *(parties colorantes.)*

These colouring particles do not exhibit, in their composition, the simplicity of mineral substances, nor does oxygen affect their colours in the same way. We shall examine, in one of the following chapters, in what manner this principle acts upon them so as to alter their nature.

Some chemists have regarded iron as the cause of all vegetable and animal colours; and Adolphus Becker employed, in support of this opinion, considerations derived from the property which this generally diffused metal possesses, of assuming a great number of colours in the states of oxide, solution, and vitrification.*

Iron, in fact, appears to be contained in all vegetable and animal substances, but in extremely small quantity. Oak, one of the vegetable substances which ought to yield the largest residuum, leaves in its combustion only 1-200th of its weight of ashes; and these ashes do not contain 1-200th of iron. Can the rich and splendid colours, with which vegetables are enamelled, be explained by so minute a proportion? Is there in reality any relation between the changeable-

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* Specimen sistens experimenta circa mutationem colorum quorundam vegetabilium a corporibus salibus, cum corollariis; auctore J. F. Adolpho Becker, 1779.

ness of some of these colours, by acids, alkalies, and air, and the uniform succession of colours which iron assumes according to its degree of oxidation?

The opinion which we are combating might indeed be supported by the suffrage of Bergmann, who supposed he had proved that indigo owes its colour to the iron which it contains;[*] but we may be permitted to reply, that it is easy to shew how this great chemist had deceived himself on this subject. By means of the alkaline prussiate, he obtained, from the ashes of an ounce of indigo, from 30 to 32 grains of prussian blue; and he estimates the iron which this contains at 18 or 20 grains. But in other places he proves, that the iron contained in a substance forms at most but the fifth part of the prussian blue which we procure from its solution, and every-where else he employs this valuation. We must therefore reduce to six grains, the iron he obtained from an ounce of indigo. In the experiments which follow the above, he proves, that the greater part of this iron may be dissolved by muriatic acid, without the colouring particles being affected; so that the larger share of this metal does not enter into their composition. From this it clearly follows, that the colouring particles of this substance must contain a quantity of iron so small, that it can have but little influence on its colour.

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[*] Analyse Chimique de l'Indigo. Mem. des Savans Etr. tom. ix.

The means of chemical analysis which we possess, are so far from enabling us to determine the composition of the colouring particles with sufficient precision, for shewing to what principles they owe their properties, that we often observe a very different composition giving rise to a colour of the same kind. The particles of indigo differ much from those which colour several flowers blue. A great number of yellow substances afford colours almost similar in appearance, which notwithstanding differ much in their properties.

There are simple colours, and there are others arising from the mixture of these colours, which are consequently compound. Newton has given a general rule for forming any colour whatever, by means of other prismatic colours. Le Blond has proved, that we may procure all the colours which the art of the painter can desire, by the mixture of red, blue, and yellow.* Dufay has shewn, that the same effect may be obtained in dyeing; and he has thence concluded, that there was in nature only three primitive colours, which gave origin to all the rest. This opinion has been embraced by several philosophers; but it does not appear to be sufficiently established.

Between simple colours, and colours formed by the union of different rays, there is this difference;—the former, viewed through the prism, retain

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* L'Harmonie du Coloris dans la Peinture, reduite en pratique.

their simplicity, while the latter are decomposed. The green produced by the rays of this colour, suffers no decomposition by the prism. It has, therefore, the character of a simple and primitive colour. But the compound green is separated into yellow and blue.

Although the green formed in dyeing results from a mixture of blue and yellow, we must not consider all the greens as combinations of the two species of colouring particles. Thus, the green oxide (hydrated oxide) of copper cannot be owing to molecules of a different nature; and the green of plants is undoubtedly produced by a homogeneous substance, in the same way as the greater number of hues which exist in nature. This colour owes then its origin sometimes to simple rays, and sometimes to an union of different rays; and some other colours are in the same predicament. Were the green of plants due to two substances, one of which is yellow and the other blue, it would be extraordinary if we could not separate them, or at least change their proportions, by some solvent. There are, however, some substances which contain colouring parts of different species; madder, for example, as we shall see in the second volume. (Note A.)

The green, which we assume as an example of a truly compound dyeing colour, shews that the colouring molecules cover only one part of the surface of the stuff, although this may appear of a full and uniform colour; for, after the stuff has been dyed blue, the yellow parts fix themselves on it, and produce the green; and although the dyeing has been begun with yellow, if a yellow of little permanence be employed, it may be destroyed by air, and especially by chemical agents, while the blue remains unaffected; which proves that it is on the stuff, and not on the indigo, that the yellow particles have been principally fixed.

Hence we see, that in order to procure the sensation of a simple colour, the rays of the different colours require merely to be approximated. In fact, we may produce an uniform colour by the exact mixture of wools of different hues; and in painting we obtain simple colours by the mixture of different ingredients, which do not chemically combine.

The colouring particles form different combinations, and they are applied either alone, or previously combined with other substances, to wool, silk, linen, or cotton. The art of dyeing consists in employing the affinities of the colouring particles so as to extract, dissolve, and thereafter apply and fix them to the substances to be dyed, which will be distinguished in this treatise by the name of *stuffs*, whatsoever may be their nature and their form.

It has been proposed to arrange colouring particles into extractive and resinous; but this division conveys only incomplete and false ideas of their properties; for there are colouring particles which, being insoluble in water, might be regarded as resinous, and yet they do not dissolve in alcohol. Such are, the red portion of carthamus (safflower), which dissolves merely by means of an alkali; and indigo, which, insoluble both in water and alcohol, becomes soluble in alkalies only under certain circumstances; but it dissolves readily in sulphuric acid.

The colouring particles which are soluble in water cannot be compared to the mucilaginous and extractive parts of vegetables, since the property of dissolving in water, like these substances, gives no idea of the properties which it is essential to discover in them; such as their relations to the chemical agents employed in dyeing, to air, to light, and to animal and vegetable substances.

It is, moreover, an abuse injurious to the progress of sound theorizing, to seek an explanation of the properties of colouring substances in the mucilaginous, resinous, earthy, saline, and oily parts which may be supposed to enter into their composition, as Poerner particularly has done.

We have just seen, that in trying to account for the causes of colours, and the nature of the colouring particles, two inconveniencies have arisen: the one, from the attempt to explain the action which the molecules of colouring substances exercise on the rays of light by their density and thickness, without having any means of determining these circumstances, and without taking into view the affinity arising from their chemical composition; the other, to compare, from some slight relations, the colouring particles with the mucilages and the resins, and to seek to explain their properties by the parts supposed to enter into their composition; whereas their colouring properties ought to be determined by direct experiments, and not be explained by an imaginary composition. We depart from true theory, which is solely the result of observation, when we ascribe to laws purely mechanical the adherence of the colouring particles to the substances which they dye, as well as the action of mordants, and the difference between permanent and fugitive colours. Hellot, to whom otherwise we are indebted for the best practical treatise extant on dyeing wool, has fallen into a complete illusion on this subject, and his theoretical ideas have often influenced his observations and the principles which he has laid down, as we may ascertain by the perusal of his work. We may judge of his theory by the following passage:—"I believe it may be laid down as a general principle of the art now treated of, that the whole invisible mechanism of dyeing consists in dilating the pores of the bodies to be dyed, in depositing within them particles of a foreign matter, and in keeping them there by a species of coat (*enduit*), which neither water, rain, nor the rays of the sun, can affect; in selecting colouring molecules of such a tenuity that they may be retained sufficiently incased in the pores of the subject, laid open by the heat of boiling water, then contracted by cold, and farther coated with a species of cement (*mastic*), which is left in the very pores by the salts chosen to prepare them. Hence it follows, that the pores of the fibres of wool, from which we have fabricated or are going to fabricate stuffs, ought to be cleansed, enlarged, coated over, then contracted, in order that the colouring atom may be preserved in them nearly as a diamond in the collet of a ring." *

We have reason to be surprised that Macquer should have adopted the ideas of Hellot. "Here would be the place," says he, "to explain the manner in which mordants act in dyeing, and to develop the cause of fast and fugitive dyes; but these objects have been treated with so much sagacity by M. Hellot, that I think it my duty to refer my reader to him."†

Dufay, however, had already perceived, that the colouring particles were naturally disposed to contract a stronger or weaker adhesion with the fibres which received them;‡ and he remarks very properly, that without this disposition the stuffs would not take a colour similar to that of the dye-vat, or divide equally with it the colouring particles; whereas the liquor of the bath becomes sometimes as limpid as water, giving up all its colouring matter to the stuff; "which seems," says he, "to indicate that the ingredients have less attraction for the water than for the particles of the wool." He adds, that several other phenomena may be accounted for in the same way; but that such an explanation leaves

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* L'Art de la Teinture des Laines, p. 42.

† L'Art de la Teinture en Soie, avant propos, p. 8.

‡ Observations Physiques sur le Melange de quelques Couleurs dans la Teinture. Mem. de l'Academ. 1737.

still much to be desired, and that he would abandon it without difficulty were a more probable one proposed.

Bergmann is the first who referred the phenomena of dyeing entirely to chemical principles.* Having dyed wool and silk in a solution of indigo, in sulphuric acid much diluted with water, he explains the effects which he observed in this operation, by ascribing them to the precipitation occasioned by the greater affinity of the wool and the silk for the blue molecules, than of these molecules and the acidulous water. He remarks, that this affinity of the wool is powerful enough to deprive the liquid entirely of its colouring particles; but that the feebler affinity of the silk can only diminish the proportion of these particles in the bath; and he shews, that on these different affinities depend both the permanence and intensity of the colour.

This is, in fact, the legitimate manner of viewing the phenomena of dyeing, which are true chemical phenomena.

A short while thereafter Macquer adopted this theory, and made just applications of it to the action of mordants, and particularly of alumina.†

Whatever may be the physical cause of colours, the colouring particles, which it is the object of the art of dyeing to apply to stuffs, possess che-

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* Analyse de l' Indigo. Mem. des Savans Etrang. tom. ix.; Mem. envoyé pour le prix proposé en 1776, et dans les notes sur le traité de Scheffer.

† Diction. de Chim. 2d edition, au mot *Teinture*, 1778.

mical properties distinguishing them from other substances dependent on the affinities which their particles collectively exercise, as well as on the reciprocal action of these particles, and on their constitution, which disposes them more or less to assume the solid or the liquid state.

By virtue of these properties, they dissolve in different liquids, they combine with acids, alkalies, oxides, with some earths, and especially alumina; they frequently precipitate the oxides and alumina from the acids which held them in solution; in other circumstances, they even form super-compounds with the salts; sometimes they unite immediately to the stuffs; more frequently they form with these substances a combination much more intimate through an *intermedium*, or even they do not combine with it except through the *intermedium;* the intermedium modifying their colour, their other properties, and even their composition.

The difference in the affinity of the colouring particles for wool, silk, and cotton, is sometimes so great, that they refuse to combine with one of these substances, whilst they combine very well with another; thus, cotton takes no colour in the bath that dyes wool scarlet. Dufay got a piece of stuff made, the warp of which was wool, and the weft cotton; he passed this stuff through the fulling-mill, to ensure the same preparation to the wool and cotton; but the wool took the scarlet dye, and the cotton remained white. It is this difference of affinity which makes it necessary to vary the preparations and the processes, according to the nature of the substance which we wish to dye of a particular colour.

If the effects of the *intermedia* employed in dyeing, and if the fixation of the colouring particles on a stuff by itself, or by means of an intermedium, be owing to the combinations which are formed, we must still refer to chemical combination the changes produced, by acids and alkalies, in several vegetable colours, which chemists employ for verifying the nature of different substances. We may compare the resulting compounds to neutral salts, which possess qualities distinct from those of their components, but in which one of the components may be in excess, so as to cause its properties to predominate. This state of combination is observed between the colouring particles of cochineal and the acidulous tartrate of potash, or cream of tartar. On evaporating slowly a solution of this salt in a decoction of cochineal, crystals are formed, which retain a fine ruby colour, much more intense and more lively than that of the liquid in which they were formed.

The reciprocal action of acids and alkalies being much greater than that which they exercise in particular on the colouring particles, they can mutually saturate each other, and then the resulting compound has little effect on the colouring particles; so that the changes which had been produced by one of the substances disappear when it is neutralized by an antagonist substance.

Blue colours are not the only ones which can pass to red by the agency of acids, and to green by that of alkalies; the most part of the red colours, that of the rose, for example, are exalted by acids, and pass to green by alkalies; and some green colours, such as that of the decoction of burdock, according to the testimony of Nose,* and the green juice of the buckthorn berries, (*rhamnus catharticus*) according to Becker, redden also with acids.

This property, common to the most ordinary colours of vegetables, appears to prove that there is a close analogy between the greater part of their colouring matters; nor is it without foundation that Linnæus † thought the red colour owing to an acid, of which he maintained the existence; but there are also several vegetables which contain a free acid, without possessing a red colour.‡

In the combination which the colouring molecules form with the stuff, they preserve only a

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* Versuch eineger Beytrage zur Chemie.

† Amænitatum Acad. tom. iv.

‡ There are flowers whose colour appears to be naturally modified by a very feeble acid, without being decidedly red: such is the flower of violet, whose violet juice becomes blue when we leave it for some time in a tin vessel, probably because the acid which it contained combines with a portion of oxide on the surface of the tin; such also is the flower of the mallow, which becomes blue by simple drying. The primitive colour is restored by the addition of a very small quantity of acid. *Observ. Physico-Chim. sur les Couleurs, par Opoix.* Journal de Physique, tom. viii.

part of their original properties; on being associated with alumina, with the oxides, and some other substances, they are somewhat modified; but the properties of the latter combinations are further modified when they unite with the stuff.

These modifications are analogous to what is observed in other chemical combinations; but they are subject to a peculiar degradation from the action of air and light; sometimes, on the contrary, they receive from these agents a new lustre or a different shade: there are also agents which, after combining with the colouring particles, alter the colour which they first produced, making it pass to yellow, and then destroy it; such in particular is oxygenated muriatic acid; it acts by means of the oxygen which it yields, and consequently differs in nothing except intensity from that of the atmospheric air.*

It follows, from what has been stated, 1. That the colouring molecules have affinities which produce their solution and their combination, the effects of which, combining with those of their own constitution, form the differences that distinguish them from each other.

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* This theory is no longer tenable, since it is known that dry chlorine does not blanch dry litmus paper. When moisture intervenes, muriatic acid is formed, and oxygen evolved; to the action of which body on the colour the bleaching effect is to be ascribed. Water is the source of the discoloration, both in the ancient and the modern process of bleaching.—T.

2. That they unite directly with the stuff, or by the aid of an intermedium; but the stuff has relations with them according to its nature.

3. That, in combining with a substance, they experience a change which modifies their colour, besides the modification resulting from the shade peculiar to the substance to which they combine.

4. That the colouring molecules differ not only from one another by these different dispositions, but likewise by the ulterior changes which they may suffer from the action of other substances, and particularly from that of the air and light.

In order to establish, on these grounds, the principles of the art of dyeing, so as to explain the peculiar phenomena which it presents, to guide ourselves in its practice, and to obtain the surest, easiest, and most economical processes, either for executing known operations, or for fulfilling the demands of the consumers, and improving the art, we shall in this section examine more particularly the effects arising from the action of substances which serve as *intermedia*, and those produced by the agents which may affect the nature of the colours.

But stuffs possess different relations with the colouring particles, and they must receive preparations preliminary to the operations of dyeing: under this point of view, we shall examine them in the second section.

The third section will be devoted to the art of bleaching linen and cotton by the oxygenated muriatic acid, (chlorine).

We shall be occupied, in the fourth, with the manipulations of dyeing in general, and the means by which we can ascertain the goodness of colours.

We shall present, in the fifth, a summary account of the principal ingredients employed in dyeing, in reference to dissolving, modifying, and fixing the colouring particles.

After having thus exhibited, in the first part of this work, the general facts which are to be applied to particular operations, we shall detail, in the second part, the processes of dyeing, arranging them into *genera* and *species* of colour. Here we shall examine every colouring substance; we shall apply to the different dyes the principles established in the first part; we shall unfold the processes of the art, and, independently of the explanations, we shall endeavour to improve it by direct experiments. We shall then try to harmonize the results of experiment with the principles of chemistry; but we shall stop whenever these principles cannot conduct us to satisfactory explanations, or we shall confine ourselves to conjectures, to be verified by the future advancement of the science.

CHAPTER II.

Of Mordants.

The term *mordant* is given to those substances which serve as *intermedia* between the colouring parts and the stuffs which they dye, either for facilitating or modifying their combination. This word is rendered appropriate by the use which even the ancients made of it.* We may distinguish, under the title of *alteratives*, the ingredients which are employed merely with the view of changing the shade.

Mordants merit the greatest attention. It is by them chiefly that we diversify the colours, give them more brilliancy, fix them on the stuffs, and render them more durable.

A mordant is not always a simple agent, but in the mixture composing it different combinations are sometimes formed, so that the substances which have been employed do not act immediately, but by the resulting combinations.

Sometimes the mordant is mingled with the colouring particles; sometimes the stuff is impregnated with it before being exposed to the dyeing bath. On other occasions these two methods are combined. We may dye in succession with liquors which contain different substances, the last of which acts only on the parts with which the

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* Ameilhon. Mem. de l'Institut. Litter. tom. iii.

stuff has been imbued by the preceding operation. One solution, which is to yield its basis to the stuff, has need of heat; another requires the operation to be made in the cold. The mordant is frequently an oxide; in which case its properties may vary, not only according to its actual condition, but also according to the action of the substances with which it is associated, and even according to the circumstances of the operation. It is by the determination of all these conditions that chemistry can particularly direct the art of dyeing, can establish its processes in a constant manner, removing from it whatever is useless or prejudicial, and transferring to one kind of dyeing what is found efficacious in another.

We shall describe, in the fifth section, the essential properties of the chemical agents of which the greatest use is made in the quality of mordants: we shall determine, in the second part, the particular effects which they produce on every species of colouring substance, detailing every fact which experience has taught concerning those operations of dyeing in which they are employed. At present we shall confine ourselves to the development of the general observations which have been made on their action.

There are colouring substances on which acids and alkalies appear to have but a feeble action, which are soluble in water, and combine immediately with stuffs; such are several dun colours, extracted from woods and roots, and the husks of the walnut. These substances serve, therefore, the purpose of dyeing without the aid of any mordants. There are some, again, which dissolve only by alkalies, as, in particular, the safflower. Its colouring part quits the alkalies, and fixes on the stuffs, when those are saturated with an acid. The anotto, which dissolves easily by means of an alkali, abandons it to combine with the stuff, without the necessity of employing an acid. When indigo is deprived of oxygen, it becomes yellow, and is then soluble in alkalies. Stuffs may abstract it also from the alkalies, and then it resumes its blue colour, through the agency of oxygen. Dyes made with these colouring substances have no need of auxiliaries. But the greater number combine only in small quantity with the stuffs, when a base does not serve as an *intermedium* to their union. They adhere feebly to it, and resist much less the causes of destruction.

The substances employed as mordants should therefore furnish a base which attaches itself to the stuffs and to the colouring particles, and which resists their redissolution and destruction. As to those substances, however, which occasion merely some modifications in the colours, it is sufficient for them to be retained in small quantity in the combination formed between the stuffs, the mordant, and the colouring matter. Hence, although alteratives act equally by combining, they should be distinguished, however, from mordants, which serve to fix the combination.

Acids can in general dissolve the colouring substances, but as they do not themselves possess the property of combining with the stuff, they cannot serve as bonds of union; on the contrary, they usually carry off the colouring particles which had been retained by the stuff, and they contribute to the colour which is fixed, only in the quality of alteratives, by uniting in small quantity to the coloured combination.

The alkalies, among which we must comprise the earths that produce saturation with acids, can combine with the most part of colouring substances; but, in order to ascertain the effects which they ought to produce according to their differences, and to compare them with those due to the acids, we must direct our attention to the properties of the combinations which depend on those of their elements.

While reciprocal affinity produces an union, the dispositions of the substances to solidity or liquidity are preserved in the combinations, with the differences proceeding from the condensation which they experience.*

It thence results that the alkalies, which possess much solubility, ought to form soluble combinations with the colouring substances which have an affinity for them; but those which have little solubility ought, on the contrary, to produce insoluble combinations.

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* Essai de Statique Chimique.

These considerations, which are supported by the results of the reciprocal action of acids and alkalies, and by the properties of the combinations in general, lead us to distinguish the effects of the different bases. Potash, soda, and ammonia, cannot serve as *intermedia* to fix the colouring substances on stuffs; but they may, as well as acids, effect the solution of colouring substances on which they have an action. Their affinity with the stuffs should also tend to operate their solution. It is only as alteratives that these alkalies can enter into coloured combinations. If they produce some precipitation in the watery solutions of colouring substances, it must be merely by separating a body much more soluble from another in itself slightly soluble, or by occasioning some change in a substance of somewhat unstable composition.

The other alkalies, namely, lime, barytes, strontites, and magnesia, which possess little solubility, or a much greater tendency to solidity, appear fitter to serve as mordants. In fact, these alkaline earths have sufficient affinity to form, with colouring substances, combinations which are precipitated from their solution; but they considerably affect their colours by their alkaline properties. They possess too weak an affinity to enter into an insoluble combination with the stuffs; so that, far from promoting the union of the colouring particles, on the contrary they obstruct it, forming insulated precipitations.

Magnesia, which is insoluble, afforded the prospect of being usefully employed as a mordant. In order to try it, acetate of magnesia was mixed with an infusion of brazil wood. A precipitate took place of a dull violet colour. After ascertaining the faculty it possesses of falling down with colouring substances, cotton was impregnated with the above salt, as is done with acetate of alumina; but this cotton took no more colour than if it had received no mordant. Wool treated with acetate of magnesia, did not derive from it the property of fixing the colour of madder; no more did silk. It appears, then, that the alkalies in general can serve only as solvents or alteratives; but in this latter quality, those which have the least solubility should be the most efficacious. The same thing is true of the acids; whence the utility of the supertartrate of potash in several processes.

The body which possesses in an eminent degree the properties suitable for a mordant, is alumina. Insoluble when it does not experience the action of acids or alkalies, it has a strong disposition to combine with the colouring particles; it does not act on their colours as the alkalies do, but it preserves very nearly their natural hue. It separates also much more easily from the acids which hold it in solution, than the alkaline bases do.

To be convinced of this property which alumina possesses, of combining with the colouring particles, we have only to agitate alumina, precipitated from the sulphate of alumina by an alkali, with an infusion of brazil wood, when all the colouring particles separate from the water, and remain fixed in the earth. It is this combination which forms some lakes, and particularly the *stils de grains.*[*]

This is not the method, however, in which it is directly employed for the composition of the most part of lakes.

A decoction of the colouring substance from which we wish to obtain a lake, is mixed with a solution of the sulphate of alumina. There is usually formed a precipitate, which carries down a portion of the colouring substance. With some colouring matters, however, no precipitate ensues. To cause, or to complete it, the acid of the salt is saturated with an alkali, when the alumina falls down, retaining in combination with it the colouring substance. It is this precipitate, whose colour varies with the substance employed, which forms the lakes, after sufficient washing to carry off the saline particles. For the *stils de grains,* the decoction, mingled with the sulphate of alumina, is passed through a calcareous carbonate, which serves, at least in part, to decompose the sulphate of alumina ; or through a clay, whose action on the sulphuric acid contributes also to the decomposition of the alum, and to the precipitation of the lake. What occurs here by the

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[*] Traité Theorique et Pratique sur l'Art de faire et d'appliquer les Vernis, &c. par Tingry, tom. ii.

action of the alkali or the clay, which tend to seize the acid, is effected in dyeing by an opposite action, by the affinity between the stuff and the coloured alumina.

The affinity of alumina for the different stuffs may be easily proved. If an animal substance be dissolved by an alkali, and if with this solution alum be mixed, the animal substance precipitates in combination with the alumina. The same combination is formed when, after mixing gelatin with a solution of sulphate of alumina, an alkali is poured into it.

The combination of alumina and the animal substance may be sur-compounded (*sur-composée*) with a colouring substance. For example, when, in the preceding experiment, the decoction of a colouring substance, such as brazil wood, is mixed with the solution of sulphate of alumina and gelatin, the coloured precipitate thus obtained represents the combination which is formed with the stuffs in those dyes where a mordant is employed.

Although it cannot be proved in the same manner, that alumina enters into combination with linen and cotton, yet the effects which aluminous mordants produce upon these substances, leave no doubt that a combination with alumina is formed. Hence, by means of aluming, colouring substances which could not be fixed, or would be speedily destroyed, quit their solvent, form with the alumina more saturated and durable colours, and even when the colour has disappeared, the stuff still retains the alumina, which can fix new colouring substances, and impart to it the requisite properties. Bancroft relates, that having impregnated with acetate of alumina one part of a cotton web, while the rest of it had no mordant, and having dyed this cloth with saffron, he exposed it on the grass: The colour soon disappeared on the part which had received no mordant, and some time afterwards on the portion which had been imbued with the mordant. He then dyed the cloth anew with saffron, when the exposure on the grass produced the same effect. Finally, after a third dyeing, the mordant still gave the same faculty to the portion of the cloth to which it had been applied. Hence alumina remained fixed, notwithstanding the three dyeing operations.

It is manifest, therefore, when a stuff acquires, by means of an aluminous salt, the properties dependent on alumina, that it can decompose this salt and combine with its alumina, whilst the acid which held it in solution is disengaged and remains in the bath; but we must not thence conclude, that no portion of the acid remains in combination with the stuff, so as to have some influence on the colour. (Note B.)

Metallic oxides possess with several colouring particles such an affinity, that they abandon the acids which kept them in solution, to precipitate in combination with the colour.

On the other hand, all the oxides possess the property, of combining with animal substances;

which several combinations may be formed, by mixing with the metallic solutions an alkali saturated with the animal substance.*

It is not therefore surprising, that the metallic oxides can serve as bonds of union between the colouring particles and animal substances; but they differ greatly in this respect. Let us examine on what peculiarities these differences depend.

Although all the oxides have a disposition to combine with the animal substances, they differ much in this particular; so that, especially when the animal substances form a solid texture, there are oxides to which they can hardly unite. Supposing the same degree of affinity, those oxides which form a stronger combination with the acids ought to abandon them with more difficulty; and again, the same oxide ought to be more easily precipitated from feeble acids than from such as act with more energy. Hence it is not astonishing that there are only some metallic solutions which can be employed as mordants, and that in conformity with the purpose intended.

Some metallic substances carry into their combinations only a white and colourless base; others modify, by the association of their own colour, that of the colouring matter; but in several oxides the colour varies according to the proportion of oxygen fixed in them, or according to other un-

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* Mem. de l'Academie, 1784.

determined circumstances. The latter oxides could not serve as a base to durable colours, whose lustre would be easily affected by these ready alteratives, unless it were russet hues, whose slight changes would be imperceptible.

The oxide of tin surpasses all the others in its property of becoming fixed on woollen and silken stuffs, but especially on the former. It readily abandons the acid which holds it in solution to combine with them, so that it is sufficient to impregnate wool and silk with solution of tin, although they should be then thoroughly washed; a process which does not answer with other metallic solutions.

Tin slightly oxidized has, in reality, only an ashy colour. But since it has a great affinity for oxygen, it takes enough of it in the ordinary solutions to pass to the white colour; or it may complete its oxidizement even during the operations of dyeing. It retains its oxygen with force, and hence, when highly oxidized, its oxygen exerts but little action on a colouring matter. The oxide of zinc appears to possess analogous properties, but it has much less affinity with stuffs and with colouring particles; while, on the other hand, it retains the acids more powerfully, and is thereby much less fit for a mordant.

The affinity of the oxides for substances of a vegetable nature appears to be much weaker than for animal substances; whence it happens, that metallic solutions are not well adapted to serve as mordants for colours in cotton and linen. An exception must, however, be made in favour of the oxide of iron, which may be applied in a very solid manner to these substances, even when it is precipitated from its solutions. To this purpose Chaptal makes an interesting observation.* He states, that a solution of iron disturbed by precipitation may be cleared up by moving cotton and linen through it. We must, however, observe, that the oxide of iron differs in colour according to its state of oxidation; and that the action which it exercises on the colouring substance varies, as we shall see, according to that state. The oxide of copper has also some affinity for linen and cotton, so that its solutions may be employed in some processes. Oxide of manganese announces a similar disposition.

It follows from what we have now stated, 1. That the acids and the alkalies are not fit for mordants, that is to say, for *intermedia* or bonds of union between the stuffs and the colouring substances, although those of sparing solubility can produce species of lakes with colouring matters: 2. That of all the earthy substances, alumina is the one eminently endowed with the properties of a mordant, from its affinity with colouring substances and with stuffs, and from its feeble attraction to acids: 3. That among metallic substances we must distinguish those which afford a white base to the colouring substances, and those which affect the colouring matters by their own colours.

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* Mem. de l'Instit. tom. iii.

Among the former, which are fit for light and splendid colours, the solutions of tin hold the first rank, from the affinity of the oxide for the stuffs of an animal nature, and for the colouring substances, as also from its weak attachment to acids. The force with which it retains oxygen contributes to its qualities. Among metallic substances, whose colour produces modifications, iron is of the most extensive employment; but its effects vary according to its state of oxidation.

When the colouring particles have precipitated an oxide from its solvent, the latter has usually the power of dissolving a portion of the combination of the colouring substance with the oxide, and the liquid remains coloured, although the precipitation be facilitated, and rendered more complete, by the presence of the stuff. The effects depend therefore in part, not only on the proportion, but also on the species, of acid which acts as a solvent to the oxide. This observation is applicable to acids which hold alumina in solution; but the acids, alkalies, metallic solutions, and even the neutral salts, may serve as alterants.

We observe, that by varying the mordants we may greatly multiply the shades obtainable from any one substance, especially with the co-operation of the alterants. It is sufficient merely to vary the method of applying them. Thus we shall obtain different effects, by impregnating a stuff with a mordant, or by mixing the mordant in the dyeing bath; by making the operation with heat or cold, with the continued contact of air, or without its intervention; by means of a solution in a strong acid, or of one in a feebler or more volatile acid.

Drying favours the combination of the bases which have an affinity for the stuff, because the water which produced the solution resists, by its own affinity, the action of the stuff that tends to bring it to the solid state.

But the circumstances by which we ought to be regulated vary according to the qualities of the stuff, which, by a disposition whose cause cannot always be assigned, requires sometimes the aid of heat, whilst a stuff of a different nature combines better in the cold.

Finally, the processes which a stuff should receive in succession, to attain the proposed end, sometimes decide the choice of the solution of the mordant, and the manner of applying it. This is particularly observable in reference to cloths for printing, which should be able to pass through several operations, without suffering injury from any one of them.

This beautiful art (calico printing), which was introduced into Europe only in the middle of the last century, has made the most rapid progress, having arrived at a perfection not only very superior to the condition in which it has remained for so many centuries in Hindostan, but it has become one whose processes possess the greatest precision, and are susceptible of the most complete explanation.

The perfection to which it has been carried among us, principally by the active and enlightened industry of the celebrated Oberkampf, recently seconded by that of Widmer, is owing in part to the necessity of insulating the processes, in order to succeed, not only in varying the colours and the shades, but likewise in securing to them a permanence which may resist the operations requisite to give due whiteness to the intervals which separate the printed spots. Hence it has been possible to observe and ascertain the effects of every operation; and hence every colour has been subjected to the severest trials; whereas the other processes of dyeing often confound together different effects, involving them in a fleeting lustre.

Since the processes of this art are well fitted to give an exact idea of the effects of mordants, and of the different circumstances which modify them, we shall here trace an outline of it.

The mordants possessed of great solubility, whose acid, capable of being volatilized, is united to its base by a feeble affinity, are preferred for calico printing, because, as they can be put upon the cloth in a greater state of concentration, and can be more completely decomposed upon it, more intense and substantial colours may be obtained. Their solubility gives them the further advantage of not rendering the mordant clotty, by a species of crystallization when it is inspissated, or unequable during its desiccation on the cloth.

The acetate of alumina and the acetate of iron possess these properties, and are sufficient to produce, with different colouring substances, the greater number of the diversified hues observable in printed goods.

To prepare the acetate of alumina, three parts by weight of alum, and one of acetate of lead, are dissolved in eight parts of hot water. An eighth part of potash, and as much chalk, are afterwards added. The oxideof lead contained in the acetate, forms, with the sulphuric acid of the alum, an insoluble salt, which precipitates; while the base of the alum, or the alumina, remains in solution, combined with the acetic acid. Since in this, the generally adopted process, the proportion of acetate of lead is not sufficiently great to effect the entire decomposition of the alum, the chalk and potash are added, which serve to decompose a portion of this salt, whose crystallization in the inspissated mordant might have rendered its employment prejudicial. We may produce, without the addition of the chalk or potash, an acetate of alumina, which has not this inconvenience, by putting along with the given proportions of alum and water three and a half parts of acetate of lead.* (Note C.)

The acetate of iron is made by the direct solution of pieces of rusty iron in acetic acid, the

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* There is an error in these proportions of M. Berthollet: 60 parts of alum are equivalent to about 100 of acetate of lead.—T.

vinegar of commerce. (The crude vinegar, called *pyrolignous acid,* is now usually employed for this purpose in Great Britain.—T.)

The mordants are thickened with different kinds of gum, starch, or flour. They should be sufficiently so to preserve, in the impressions on the cloth, the outlines of the objects engraven on the plate, but not so much as to hinder their leaving the plate equably in their application to the cloth. This receives as many different impressions as there are different mordants; but no more are applied at a time than are to be coloured in the same dyeing bath.

When the cloth is in this condition, it is left for several days, stretched in the workshop, exposed to a moderate heat in a chamber, called in the calico manufactories *the hot-room* (or stove). This heat, by favouring the volatilization of the acetic acid, accelerates and completes the decomposition of the mordants, as well as the combination of their bases with the cloth. On coming out of this chamber, it is passed into a boiler, which contains cow-dung diffused through hot water. The effect of this operation is to dissolve the substance made use of for thickening the mordant, as also the portion of this mordant which, not having combined with the stuff, and being diffused in the dye-bath, would soil it, both by the combination which it would form with the colouring matter, and by the action of the acid which it might deposit upon it. Thus a twofold injury would accrue to the cloth, by the impoverishment of the dye-bath, and by the covering of the portions which should remain white, with the combination, difficultly detachable, of the superfluous mordant with the colouring matter. Widmer conceives, that there is formed, besides, in the dunging, a triple combination of the animal matter with the alumina and the cloth, which improves the beauty of the colours. This opinion is the more probable, since water alone does not produce the effect of the dunging; in which process an examination, not however very elaborate, has not enabled us to perceive any other substance capable of acting, except a matter analogous to bile. (Note D.)

Before being dyed, the cloths ought still to be carefully washed and beetled, to secure the removal of all the combined mordant. Water and mechanical beating are here employed. (The wash-wheels of our print-fields answer this purpose admirably.—T.) They are then introduced into the dye-bath, where the whole surface becomes coloured; but the colours are much deeper on the parts impressed with the mordant. The colouring matter thus enters into a triple combination with the mordant and the stuff, thereby acquiring the faculty of resisting external agents much more than when it is insulated or combined with the stuff without any *intermedia*. (Note E.)

On this peculiarity are founded the processes employed for restoring, to the parts of the cloth which have received no mordant, the white colour which they possessed before this dyeing. To produce it, the goods are boiled in water along with bran, they are then exposed on the field, observing to lay on the grass the surface of the cloth that bears the colours. By the alternate repetition of these operations, the colouring matters uncombined with the mordants are changed in their composition, dissolved and detached; whereas those which are actually combined, far from suffering change, acquire more lustre, and thus the figures alone remain coloured. (NOTE F.)

This destruction of the colouring particles by exposure in the field, and ebullition with bran, is effected in the same manner as that of the colouring particles of flax, and is explained in the same way. The difference of the process consists solely in the substitution of bran for alkalies; because these would dissolve a portion of the colouring substance fixed by the mordant, and would alter its colour; whereas the bran having a much weaker action on this substance, affects merely the colouring particles, rendered soluble by the action of the air. The identity of the effects of this process with those of common bleaching, has led Widmer to substitute for this method the employment of chlorine, modified by an alkaline solution. Haussman has used this plan with success; and it is known to be practised in many English manufactories.* (NOTE G.)

From madder, with acetate of alumina more or less diluted with water, are obtained the deep

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* See Section III.

reds, and their different shades, down to a delicate rose colour; with acetate of iron, from black to lilac, passing through all the intermediate violet hues; and finally, with the mixture of these two mordants, in different proportions, the amaranths, the mordores (brown-reds), the browns, and the puce-coloured. By substituting woad for madder, we procure, with the first of the above mordants, the yellows; with the second, only dull olives; but with their different mixtures, we have agreeable olive and bronze colours. Combining the action of these two tinctorial substances in their turn on each of these mordants, very diversified mingled hues are obtained. When we treat of the particular processes of dyeing, we shall enter into more details concerning those which relate to the dyeing of printed goods.

The following are, in general, the steps of the operations of this art. To apply to cloth the most soluble and most easily decomposed mordants; to promote their drying and decomposition; to remove, by animalizing the cloth at the same time, whatever has not entered into combination with it; to dye, and to restore to the portions not printed the purest white. To these operations the whole process is reducible. It evidently proves, that linen and cotton are susceptible of combination with the bases of the mordants; that this combination possesses a great affinity for colouring matters; and that it communicates to them the property of being much more unalterable by the ordinary agents of their destruction.

Some colours, however, may be directly printed upon cloth, with all the solidity and lustre of which they are susceptible: Such, for example, is that of indigo, known under the name of *pencil blue,* because it is usually applied with this instrument; that called *rust-yellow,* because it is obtained by printing-on slightly oxidized oxide of iron, resulting from the decomposition of two parts of sulphate of iron with one of acetate of lead, diffused in eight parts of water. These are styled *colours of application.* They possess the great advantage of requiring no operations except those of printing and washing. The colours now mentioned, which have been long used, are very durable, and so much the simpler as they have no need of a mordant; but the number of those possessed of this property are very limited. In others, we must attach to the stuff, at the same time, a mordant and a colouring matter, capable of combining together, and of thus uniting with the cloth. This method, analogous to that used for wool and silk, of dyeing in a bath composed of the mordant and the colouring substance, has been hitherto successfully applied in only a very few cases, in consequence of the weak affinity which cotton and linen have for colouring substances united to mordants.

There is another method, still little known, of producing upon cloth, at little expense, a diversity of colours. It consists in applying to the cloth, previously impregnated with the mordants and the dyes, substances which, serving themselves as mordants, modify the shade which the colouring matter has given, with that already existing on the cloth; or to apply some others, which, carrying with them an acid capable of dissolving this mordant, and already combined with a colouring matter, thus substitute a new mordant for that which is on the rest of the cloth, and add also a colouring matter to that which was there before. By a similar process, a white may be induced on dyed goods. Oberkampf formerly employed, and then abandoned this process. Widmer has since improved it much, and applied it to colours which presented the greatest difficulties. The English manufacturers make great use of it; they employ for this purpose an acid, sulphate of potash, and lemon juice. This composition may answer for cloth which has received little mordant, but it is doubtful if it can serve for others.* (Note H.)

CHAPTER III.

Of Astringents in general, and particularly of the Gallic Acid and Tannin.

Astringents deserve peculiar attention, not only because they are of great use in dyeing, but

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* The principle of Mr Thomson's patent is excellent for this purpose. Dyed cloth topically impressed with a thickened solution of any vegetable acid, tartaric for example, is passed through a solution of chloride of lime.—T.

because by this title is distinguished a property common to a great many vegetables.

Perhaps there is no property in vegetables concerning which such vague ideas have been currently received. A slight relation in taste has frequently been deemed enough to rank them in the class of astringents; and every substance has been commonly regarded as astringent or acerb, which turned a solution of iron black. This effect has been presumed to arise from one identical principle residing in all the bodies that produce it. Experience has subsequently shewn, that two species of astringents ought to be admitted, viz. tannin and gallic acid. Before describing the distinctive properties of these two substances, it is proper to consider the gall-nut, which contains them both, the properties of which have been particularly examined, as it is of great use in dyeing.

The gall-nut is an excrescence found on the young branches of the oak, and chiefly of that species called *rouvre*, which grows in the Levant, Istria, and the southern departments of France. This excrescence is produced by the puncture of an insect, which deposits eggs in the small incision which it makes in spring. The juice which exudes from this wound becomes thick, accumulates, and serves as a shelter to the young insect, till such time as it can make its escape. When there is found no outlet for it, it is found dead in the gall-nut. Sometimes, after it has quitted its cell, other insects come to occupy it.

Different kinds of nut-galls are distinguished; some of them are white, others yellow, green, brown, red. Some are of an ash-colour, and even blackish. They vary much in size, and are round or irregular, light or heavy, smooth or covered with tubercles. Such as are small, blackish, granular, and dense, are the best. These are known under the name of Aleppo galls, imported from that town, from Tripoli and Smyrna. In dyeing, galls are usually distinguished into white and black.

Nut-galls dissolve almost entirely by long ebullition in water. Sixteen drams yielded Neumann fourteen drams of extract. Alcohol extracted only four grains from the residuum, which weighed two drams. The same quantity treated at first with alcohol, and then with water, afforded 12 drams and 2 scruples of spirituous extract; the residuum weighed half a scruple more than in the preceding experiment. The spirituous extract has a stronger and more disagreeable taste than the other.*

Lewis, Macquer, Monnet, and the Academicians of Dijon, made different experiments to determine the properties of the astringent which is contained in nut-galls. They observed, that the black colour afforded with solutions of iron

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* The Chemical Works of Caspar Neumann, &c. by William Lewis.—From 500 gr. of Aleppo galls Sir H. Davy obtained by aqueous infusion 185 gr. of solid matter, of which 130 was tannin, mucilage 12, gallic acid about 31, calcareous earth and saline matter 12.—T.

depends on a combination formed between the astringent and the iron. To the suspension of these black molecules, the black colour of ink is owing. If the solution be diluted with much water, these molecules fall down under the form of a deep blue powder. It is these which are fixed on cloth dyed black.

We shall, for the present, confine ourselves to these results, because the properties which the astringent presents on different occasions, and in different circumstances, will be better known by an acquaintance with the two substances here included under the same name.

To Scheele the discovery of the gallic acid is due. We shall here introduce the description which this great chemist gave of the method by which he extracted this acid, and of its properties.

" I passed through a coarse sieve one pound of nut-galls, and infused this powder in a *kanne* (two pints three quarters French) of pure water, in a glass globe, leaving it to act for four days, during which it was frequently stirred with a glass rod. I filtered this liquid,* which was limpid, and which had the colour of French wine. I left it freely exposed to the air, in the same glass globe, covered merely with grey paper. This was done in June. A month afterwards I

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* " If hot water be employed, or if the mixture be digested with heat, the infusion is not limpid: this determined me to employ cold water, and digestion in the cold." Journ. de Phys. 1787.

looked into this infusion, and found it covered with a thick pellicle of mouldiness. In other respects it had formed no precipitate, but it had no longer its former astringent taste, and was more acid. I returned this infusion into the same balloon, covered in the same way with paper. Five weeks thereafter I examined it anew, when it was fully half evaporated: I found a precipitate in it two fingers thick, and at top a mucous pellicle; it had lost all its styptic taste, and it still coloured vitriol of mars black. I filtered the infusion, and left it exposed to the air. By the following autumn the greater part was evaporated away; what remained was mixed with much precipitate. I united these precipitates, and poured cold water upon them. After they had fallen down, I decanted off the water, and then poured on as much hot water as was necessary for their solution. I filtered the whole. The liquid, which was of a yellow-brown, was evaporated at a gentle heat. During the evaporation, one part of it precipitated like a fine sand, and another formed at the bottom in radiated crystals. This salt was grey; and, notwithstanding repeated solutions and crystallizations, it was impossible for me to obtain it whiter.

" This salt of gall-nuts comports itself in the following manner:—

" 1. It has an acid taste, causes effervescence with chalk, and colours infusion of litmus red.

" 2. An ounce and a half of boiling water is required for dissolving completely half an ounce of this salt; but whenever the solution cools, the whole forms a concrete mass, composed of small crystals. Half an ounce requires twelve ounces of cold water for its solution.

"3. It dissolves very easily in spirit of wine; for half an ounce of this salt, only one-half of boiling spirit is necessary; but if cold spirit of wine be employed, then for half an ounce two ounces of spirit are required.

"4. It readily inflames in a crucible placed in an open fire, melts with the diffusion of an agreeable odour, leaving a charcoal which is difficultly reduced to ashes.

"5. Distilled in a retort, it becomes at first fluid, and affords an acid phlegm. No oil passes over, but at the end a white sublimate rises, which attaches itself to the neck of the retort, and remains fluid as long as it is hot, but afterwards crystallizes. Much charcoal is found in the retort. This sublimate has nearly the smell and the taste of benzoic acid, or salt of benzoin; it dissolves equally in water and in spirit of wine; it reddens infusion of litmus; and what is remarkable, it precipitates metallic solutions with their different colours, and the vitriol of mars black.

"6. The solution of the salt of gall-nut poured into the solution of gold, renders it of a dull green, and eventually throws down a powder which is the gold revived.

"7. The solution of silver becomes brown, and deposits, with heat, a grey powder, which is revived silver.

“ 8. The solution of mercury is precipitated of an orange-yellow.

“ 9. The solution of copper affords a brown precipitate.

“ 10. The vitriolic solution of iron becomes black; the more the water is charged with it, the deeper is the colour.

“ 11. Lead dissolved in vinegar is precipitated white.

“ 12. Bismuth gives a precipitate of a lemon-yellow.

“ 13. Molybdic acid becomes of an obscure yellow, without any precipitate taking place.

“ 14. Platinum, zinc, arsenical acid, tin, cobalt, and manganese, experience no change.

“ 15. The (saline?) solutions of lime, magnesia, alumina, and barytes, are not decomposed; but lime water causes an abundant grey precipitate.

“ 16. The salt of nut-galls is changed into oxalic acid when nitric acid is distilled from it in the usual way.

“ The white precipitate obtained when acetate of lead is thrown down by nut-galls, may be again decomposed by vitriolic acid, and the salt of nut-galls is thus obtained in its greatest purity. Since the infusion of nut-galls precipitates the acetate of lead, I thought that I might be able to procure this salt in a manner still more expeditious; but this did not succeed with me, for when I had decomposed this precipitate by means of vitriolic acid, I recovered my infusion of galls with its ordinary astringent taste.

" If gall-nuts be distilled with a violent heat, an acidulous phlegm is obtained, the smell of which is not disagreeable ; no oil passes, but towards the end a volatile salt rises, like that obtained from the salt of gall-nuts distilled, and which has the same properties. (No. 5.) It hence appears, that this salt exists ready formed in the infusion of gall-nuts, although we cannot obtain it in the way of ordinary crystallization, for it is so intimately united with some mucilaginous principle or other matter, that it cannot be separated from it without some interior movement or fermentation."

Before prosecuting the examination of the properties of gallic acid, to which, since the experiments of Scheele, chemists ascribed exclusively the effects of astringents, we ought to describe another substance, tannin, which has some properties in common with it, but differs in other respects.

The art of tanning had been conducted by a blind routine, till Seguin shewed that astringents contained a peculiar substance, which, in combining with skin, gave it the properties of tanned leather, and that the tanning effect arose from the combination thus formed. To regulate this art, he had only to determine the circumstances necessary for forming that combination, and for giving it the requisite qualities.* He proved that

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* Journ. de Manuf. et Arts, tom. iii. ; Annal. de Chim. tom. xx.

animal glue had the property of forming a similar combination with tannin; for on mingling a solution of strong glue with an astringent infusion, a substance fell down analogous to tanned leather. By this test he could ascertain the quantity and quality of tannin in an astringent substance, so as to trace and measure its effects in the operations of tanning.

Since then, chemists have investigated the means of separating the tannin from the gallic acid. For effecting this object, Proust suggested the muriate of tin, which, whatever be its state of oxidation, is decomposed by tannin, but not by gallic acid. The tannate of tin which falls down, is thereafter decomposed by sulphuretted hydrogen, when the tannin is pure.† But this skilful chemist has himself admitted, that his process was imperfect; for one portion of the tannin remained in solution, while some of the extractive matter accompanied the portion which precipitated.‡

Fiedler pretended to separate the gallic acid from the tannin by means of alumina precipitated from its sulphate;§ but on carefully repeating this process, we have observed, that the gallic acid combined also with the alumina, and we have not been able to separate it by this method. When gelatin precipitates tannin, the gallic acid, which remains liquid, retains a portion of it; for

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† Ann. de Chim. tom. xxv.

‡ Ibid. tom. xli.

§ Journ. de Van. Mons. tom. i.

these two substances exercise a mutual action which opposes their separation, and we have in vain tried different processes for removing this obstacle.

Gallic acid and tannin alike precipitate the solutions of iron. Proust presumes that they cannot combine with the iron, unless it be in the last stage of its oxidation. This opinion has been discussed elsewhere.[*] We shall content ourselves with remarking here, that tannin, and especially gallic acid, form with iron a solution of a black-blue colour, as Delaval and Priestley observed with infusion of nut-galls. There is a decomposition of water; but the iron can thus be brought only to the lowest degree of oxidizement. The solution of protoxide of iron in acetic acid, is likewise rendered black by tannin or gallic acid. These facts are sufficient to prove, that if the slightly oxidized sulphate and muriate of iron do not produce a black colour with tannin or gallic acid, this effect depends only on the stronger action which the acids in this case exercise on the protoxide of iron, and Proust himself points out this cause; but whatever happens, it is not the less true, as he thinks, that these metallic salts are of use in dyeing, only in so far as they are highly oxidized; or, that the oxide of iron absorbs oxygen while it is in the dyeing bath, or during the airing which the stuffs receive on coming out of the bath.

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[*] Essais de Statique Chim. tom. ii.

The same chemist has very justly remarked the difference between the precipitates produced by tannin and by gallic acid. "The red sulphate is precipitated by tannin of a somewhat dirty blue; the deposite is copious, coarse, and black when it is dry. On comparing the precipitate which the sulphate affords with gallic acid, we find that it is very different. The latter is extremely fine, and floats for a long time in the water. It is perfectly black. While the gallate of iron is soluble in acids, the tannate of iron is decomposed by them, parting with its iron while the tanning matter falls."

Lastly, he has observed, that tannin was not a uniform substance; but he regards that obtained from catechu, dragon's-blood, sumach, and yellow-wood, as possessing properties sufficiently well marked to form distinct species.

Vauquelin has equally found a difference between the tannin of gum-kino, and that of ordinary tan.* He remarks, that it precipitates iron of a green hue, like that of cinchona and rhubarb.

This difference among the tannins is very perceptible on making comparative experiments with catechu and gall-nuts, or oak-bark. It may be remarked, even on comparing the precipitates obtained from gelatin, and those astringents whose properties are most similar, such as gall-nuts and sumach. The tannate produced with

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* Annal. de Chim. tom. xlvi.

sumach falls down less readily; it is less friable, and less coloured than that afforded by the gall-nut.

There is such a difference among astringents as to prevent their properties from being considered as identical; there is a like difference among the tannates produced from the different animal substances and the same kind of tannin; for this property of forming a combination with tannin does not belong exclusively to gelatin. Albumen also possesses it; but the tannates which it forms are much more friable and less coloured than those due to gelatin.

From the preceding statement it appears, that astringents may owe the property of colouring black to the two distinct substances, gallic acid and tannin; and that the latter, far from being identical, has properties which differ more or less in all the vegetables which contain it. One mode of distinguishing substances containing tannin alone, is by examining if the precipitate obtained be readily formed, so as to leave the supernatant liquid colourless. This happens when the tannin of catechu, for example, is precipitated. But if we add a little gallic acid to the solution, the supernatant liquid retains a black colour for a long time. Different astringents examined in this manner, and among the rest oak-bark, appeared to us not to contain gallic acid. Besides gall-nuts, sumach alone exhibited evidence of the acid of galls. That bark must, however, contain but little; for when it is subjected to the process of Scheele, none of it is obtained. But all the astringents afforded with blue test paper marks of acidity, which are even somewhat considerable in catechu, although the presence of gallic acid in it cannot be suspected. Hence, the acidity is not a proof of the existence of the gallic acid, but may be owing to tannin, or a foreign acid.

White gall-nuts, subjected to the process of Scheele, afford pretty soon an abundant deposite, less coloured than that yielded by black gall-nuts. Nor has it the crystalline appearance, though it is the gallic acid which forms this deposite; nor is it in a state of combination. We think it probable that the latter kind of gall-nuts contain a greater quantity of it; though our experiments do not enable us to affirm that this is certainly the case. We have compared the relative quantities of tannin afforded by these two species of gall-nuts, when they are precipitated by gelatin; we have obtained apparently the same quantity of precipitate from both, so that we cannot yet point out wherein that difference consists which distinguishes these gall-nuts, as is observed in the operations of dyeing.

A portion of the gallic acid exists certainly in the gall-nut; but may not some of it be formed in the long space of time which Scheele's process requires? We are hitherto unable to answer this question; but we are led to suppose, that the tannin is in a great measure destroyed, or that it suffers an alteration which permits the gallic acid, which was in a state of combination with it, to crystallize; for Scheele remarks, that the infusion of gall-nuts loses all its astringent taste. A portion of the tannin is, however, preserved from this change by the action of the gallic acid itself, which retains it in its precipitation and crystallization.

It is this portion of tannin retained by the gallic acid, as obtained by the process of Scheele, which affects its colour, and prevents its properties from being properly insulated. Repeated crystallizations only make it brown, by the decomposition occasioned by the heat. We have tried different methods of purifying this acid; that which succeeded best, consists in treating it with oxide of tin, newly precipitated from its solution by an acid. The gallic acid then loses its colour, the tannin which altered it being retained by the oxide, and it crystallizes in very white needles. In this state, it is perfectly similar in its properties to that obtained by sublimation. We have seen that Scheele observed this sublimate, but Deyeux has described it more in detail. He prescribed the precautions which the distillation of the gall-nut requires to obtain this acid sublimate, and he remarked that one part passed over in the liquor, whilst another was decomposed by the fire. Hence, notwithstanding every care, but a small quantity can thus be obtained. Deyeux supposes, that when this acid is exposed to distillation, as well as its combinations with the oxides, pure oxygen gas is disengaged, and much charcoal is left behind. But we obtained only carbonic acid during this distillation, which we conducted with the greatest care, with the view of ascertaining the extraordinary result which had been announced.

The oxide of tin, by means of which gallic acid is purified, appears to retain a portion of it, and to lessen its quantity a little; but we have not observed that decomposition of which Proust speaks,* probably because it takes place only in the portion combined with the oxide of tin, of which we neglected the examination; and as he treated the infusion of nut-galls directly with the oxide of tin, the quantity of tannin was capable of causing the combination of all the gallic acid associated with it, which does not happen when we thus treat gallic acid retaining but a small portion of tannin.

Gallic acid may also be purified by means of albumen, which, on coagulating with heat, separates the tannin with it; but it retains at the same time gallic acid, and a portion of the albumen remaining liquid along with the gallic acid, causes this to be difficultly separable by crystallization. Hence the first method is preferable.

Gallic acid, in its state of purity, excites an effervescence with the alkaline carbonates, and assumes, on combining with potash and soda, a greenish-blue colour, which becomes so deep by heat, that the liquid appears black at a certain

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* Annal. de Chimie, tom. xlii.

degree of condensation. But it is green if we dilute the liquid, or if we put it into a tube of small diameter. It takes a blue colour with lime, barytes, and strontites; but on adding a greater quantity of acid, the colour becomes red, after passing through several shades. Though it forms precipitates with these alkaline earths, the liquid continues coloured. This acid can scarcely be exposed to ebullition, without assuming a brown shade, and suffering a degree of decomposition.

The observations now presented, concerning the properties of gallic acid, differ from those of Scheele, since, according to him, this acid forms soluble salts with all the alkaline earths, excepting lime water. The reason of which is, that his trials were made with solutions in the acids, so that the acid present did not suffer these naturally insoluble salts to precipitate. We conceive, that this acid forms with all the oxides insoluble salts, whenever this insolubility is not overcome by the action of an acid or an alkali.

The affinities of tannin appear to differ very little from those of gallic acid, at least in the combinations connected with the art of dyeing. The differences of their effects appear naturally explicable from those of their solubility.

All the species of tannin seem to surpass gallic acid in their tendency to solidity; for, in the first place, they form an insoluble substance with gelatin, while gallic acid remains in a liquid combination with it; but albumen, which has more disposition to coagulate than gelatin, can afford a solid combination with gallic acid. 2. The combination of tannin with the solutions of iron, forms a precipitate whic his speedily separated and deposited, whereas gallic acid produces merely a transparent liquid, whose colouring molecules settle slowly, and only in particular circumstances. 3. Proust has observed, that the alkaline carbonates, and the most part of the very soluble neutral salts, possess the property of precipitating tannin from its solutions, in consequence of the great affinity which they have for water, provided that the proportion of water be not too great.* Sulphuric acid acts in the same way. 4. The same chemist has observed, and the observation was given in the first edition of these Elements, that when several successive decoctions of gall-nuts are made, the last are destitute of gallic acid.

It is only, indeed, by this superior tendency to form solid combinations, that the properties of tannin appear to differ, in reference to dyeing, from those of several colouring substances, in which it exists in merely a lower degree. Thus the solution of logwood and brazil wood does not form a precipitate with gelatin; but it produces one with albumen when aided by heat. The solution of yellow-wood (fustic) yields a precipitate with gelatin; wherefore it contains a substance analogous to tannin, according to the observations of Chaptal and Proust.† The portion which is not precipitated affords a lighter and livelier yel-

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* Ann. de Chim. tom. xxxiv.

† Mem. de l'Instit. tom. ii.

low; but this portion is itself separated in a concrete form with albumen. On the one hand, several substances employed as astringents have the property of dyeing different shades of fawn and yellow; on the other, the colouring substances which have a deep colour, produce also a black colour with solutions of iron; and the blacks on printed goods are commonly obtained from madder.

The astringents are employed not only to make the baths of the black dye, but also to prepare stuffs by the operation called *galling*, which consists in impregnating the stuffs with the astringent principle of nut-galls, as will be afterwards stated.

It became necessary to determine what part the gallic acid and tannin might each have in this operation. To throw light on this subject, we impregnated with gallic acid specimens of silk, wool, and cotton, and then passed them through a solution of iron. None of these specimens was coloured black, and the cotton even took no dye; but similar specimens, impregnated in the same manner with infusion of nut-galls, took a black colour with solution of iron. On performing the contrary operation, that is to say, impregnating the stuffs first with solution of iron, we had a similar result. We next ascertained, that by means of tannin, gallic acid also entered into combinations with stuffs. Hence, in the galling, the stuff unites to both the substances which afford black with the solutions of iron. When the stuff is impregnated with tannin alone, it takes also a black colour. Both the substances associated in gall-nuts contribute therefore to the black dye; while tannin, but not gallic acid, produces an analogous effect when it alone is present. It thence follows, that as both the substances can yield a black precipitate with the sulphate of iron, we may thus judge, at least approximatively, of the effect of the different astringent substances in dyeing black.

A discussion has arisen concerning the properties of oak-bark, which, it was asserted, might be substituted with advantage for the gall-nut, even weight for weight, in all black dyeing. In proof of this it was stated, that oak-bark was substituted in the ordinary proportion for the gall-nuts which the hatters of Paris put into their dyeing baths. But this effect proceeds from the circumstance, that the dyeing of hats is produced particularly by logwood, as we may ascertain by applying to a hat any acid, the muriatic, for example, which reddens it immediately, as happens to all the colours derived from logwood. For this dye, therefore, nothing is required but a very little astringent matter, which seems useful merely to deepen by another shade the colour given by the logwood. In fact, a very small quantity of galls enters into the process commonly employed for hats. We have seen an expert hatter employ only one part of gall-nuts to thirty of logwood.

The present discussion was brought before the Academy of Sciences. The report of its commissioners contains details which may be useful, because they state the proportion of the astringent principle obtained from different substances, and the comparative effect which they produce in dyeing black. For this reason we shall give an extract of it.

The commissioners, Lavoisier, Vandermonde, Fourcroy, and the author of these Elements, compared in their experiments, nut-galls, oak-bark, the raspings of the oak taken from the interior of the wood, the raspings of the alburnum (white bark) of the oak, logwood, and sumach, in order to determine the proportion of the dyeing principle contained in these substances. They took in succession two ounces of each, which they boiled for half an hour in three pounds of water. This first water was followed up by a second, which underwent the same ebullition, and thus they continued till these substances seemed to be exhausted. They mixed together the decoctions which they had obtained. They employed a very clear solution of sulphate of iron, the proportion of sulphate and water in which was exactly determined. They judged first of all of the quantity of the astringent principle, by the quantity of sulphate which each liquor could decompose, and next by the weight of the black precipitate, which was more or less speedily deposited, adding to it a sufficient quantity of water. In order to stop precisely at the point where the addition of the sulphate became superfluous, it was necessary to proceed very slowly with the precipitation towards the end, pouring in the solution of the sulphate only drop by drop, and halting at the moment when a new addition of this substance no longer augmented the intensity of the black colour. When the liquid is too opaque, and when the change of colour can no more be distinguished, a small portion of it was diluted with a good deal of water. To this was added from the end of a glass tube a little of the solution of sulphate of iron, and it was thereby observed if the point of saturation had been attained. Afterwards, when it was wished to make the precipitate fall down in order to be collected, the liquor was diluted with a great deal of water.

This operation deserves attention; because it is an easy means of determining in dye-houses the just proportions of astringents and solutions of iron; but we must bear in mind, that the solutions of iron ought to be highly oxidized, in order to produce the greatest effect. Although this consideration was not attended to in the experiments of which we are about to state the results, these merit no less confidence, because the same sulphate of iron was used in all the trials.

To saturate the decoction of two ounces of nut-galls, three drams and sixty-one grains of sulphate of iron were required. The dry precipitate weighed seven drams and twenty-four grains.

The decoction of oak-bark was of a deep yellow colour. A small quantity of sulphate of iron gave it a dirty reddish hue; a more considerable addition made it pass to a brown-black. Eighteen grains of sulphate of iron were necessary to saturate the decoction of two ounces of this bark. The precipitate collected and dried was in coarser particles, and more difficult to divide. It weighed twenty-two grains. The *liber* of the oak presented very nearly the same results.

The decoction of the raspings of the heart of oak required one dram and twenty-four grains of solution, and afforded one dram and twenty-four grains of precipitate. The decoction of the alburnum of oak produced very little precipitate.

The decoction of sumach assumed a violet red colour, when there was added to it a little of the solution of sulphate of iron, of which it required two drams and eighteen grains. The precipitate perfectly resembled that from the nut-galls; but an accident hindered its weight from being ascertained.

The decoction of logwood was coloured sapphire-blue by the addition of the sulphate of iron. On exceeding the point of saturation, the blue became greenish and dirty. The quantity necessary to reach the point of saturation, was two drams and twelve grains. The circumstances of colour which we have now mentioned, may differ according to the state of oxidizement.

Trials of dyeing were thereafter made on patterns of woollen cloth. These shewed, that the quantities of astringents fitted to give, with an equal weight of the same cloth, a black colour of like intensity, were proportional to the quantities of astringent principle, which had been determined by the experiments on each species; but the black obtained with the different parts of the oak, did not resist boiling so well as that produced with nut-galls.

If the astringents submitted to trial in the preceding experiments, whose results agree with those of Lewis and Beunie, prove that they cannot be compared weight for weight with gall-nuts, and if sumach alone approaches their effects, we must not thence conclude, that they cannot be employed in dyeing black. But we conceive that it would be much more advantageous to make use of them in galling, than in the dyeing bath, because the black molecules which tannin forms with the oxide of iron, are too quickly insulated and precipitated. We have made a pretty deep black, by treating wool, and even silk, in this manner, with oak-bark.

It is said in the Memoirs of Stockholm for 1763, that we may substitute for nut-galls *uva ursi*, gathered in autumn and dried with care, so that its leaves continue green.

If gallic acid, the different species of tannin, and several other colouring substances, such as logwood, brazil wood, and madder, afford with the solutions of iron blacks more or less deep, there must be something in common in the mode of acting of these substances, whatever may be in other respects the difference of their properties. It is our present object to determine this.

Monnet, and the academicians of Dijon, formerly remarked, that the solution of gall-nut revived the metal of the solutions of gold and silver. Scheele observed, that gallic acid produced this effect; and Proust has verified this property, not only in tannin, but also in several other colouring substances. We are warranted to conclude from these facts, that the astringents, and even the colouring substances in general, possess the property of carrying off oxygen from those substances which can yield it easily.

An observation of Proust informs us, that the astringent produces a similar effect on the solutions of iron. This celebrated chemist evaporated a solution of iron highly oxidized, after precipitating it with nut-galls, and he observed that the liquid, after the evaporation, yielded crystals of the green or slightly oxidized sulphate. It thence results, that the black molecules which fall down contain iron in only the lowest degree of oxidation, since they leave in this state even that which they could not abstract from the acid.

The black molecules then contain the iron in a black state (protoxide). On the other hand, the astringent, in thus absorbing oxygen, must experience the same changes that it suffers when it is combined with oxygen; but the infusion of an astringent deepens in colour, and becomes brown by simple exposure to air; and we shall see in the following chapter, that it undergoes the same changes which a slight combustion produces, taking this word as signifying a diminution of its oxygen and its hydrogen, so that the carbon becomes predominant.

The astringent ought to experience this effect in a high degree, because it contains a great deal of carbon; for gall-nut leaves, after distillation, more than three-eighths of its weight of charcoal. But when we employ a highly oxidized sulphate, it appears from the experiments of Proust, that a portion of the tannin is altered in its nature by a too energetic action of the oxygen.

We see now, how the black molecules may result from a combination formed of black oxide of iron and a substance which must assume by degrees the same colour; why astringents, although differing in their other properties, ought to produce an analogous effect; and finally, why colouring substances of very different kinds afford, with solutions of iron, colours approaching more or less to the black hue.

We may observe, that the gallic acid exhibits in its action on solutions of iron a small difference, which seems to announce, that it possesses in a less degree the property of abstracting oxygen from iron. Tannin produces a black colour in a sulphate, so little oxidized that the gallic acid does not change its hue, unless it remains exposed to the air.

On comparing all the observations advanced on astringents, we may draw the following conclusions:—

1. Gallic acid cannot serve by itself for the black dye, but it may contribute to the effect caused by the tannin, either by combining with the stuff, or by becoming fixed in the dyeing bath on the galled stuff.

2. Tannin may serve, without the aid of gallic acid, for the black dye. The different species of tannin possess in this respect different properties as to the quality of the black, which can be determined only by direct experiments. Astringents, besides the quality of the black which they afford, differ also in the quantity. Thus oak-bark, and the other parts of this wood, contain far less astringent matter than gall-nuts.

3. It is especially for the galling that those astringents which do not contain gallic acid may replace the gall-nuts, because the black molecules which these form fall down too slowly; and besides, the quantity which must be employed to replace the gall-nuts would be too considerable, and would embarrass the dye bath. Sumach is, among the astringents at present known, the one which approaches the most to gall-nuts, and which is the fittest to replace them.

4. With regard to ink, in which the colouring particles must not precipitate, no known astringent can be substituted for gall-nuts, not even sumach, as Lewis has proved in his excellent observations on this preparation, which deserve to be somewhat dwelt upon.[*]

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[*] Lewis' Exper. Essay on the Commerce of the Arts.

If too large a proportion of sulphate of iron be added to the galls, the ink becomes speedily brown, and then passes to yellow, because the astringent is destroyed by the action of the oxygen which the sulphate of iron affords, or progressively attracts from the atmosphere; for we shall see, that oxygen eventually destroys those colouring substances with which it is combined in too great quantity. When this accident happens from age, Lewis found, that an infusion of gall-nuts passed over the altered characters restored them; and Blagden has indicated a means still more efficacious, which is the prussiate of an alkali.* Lewis ascertained, that the best proportion for ink was three parts of gall-nuts to one of sulphate of iron; that cherry gum and plum-tree gum were as good as gum arabic for giving the necessary consistence, and for keeping suspended the black molecules which tend to fall; and that decoction of logwood, employed instead of water for the infusion of the gall-nuts, improved the beauty of the ink.

We have remarked, that both gallic acid and tannin gave to iron the property of decomposing water, and of forming by this means a solution of iron, which passes from blue or violet to black. Delaval says, that he produced with the solution of this metal and an infusion of nut-galls, the deepest

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* A solution of ferroprussiate of potash, faintly acidulated, or sulphuretted hydrogen water, are the best restoratives of the characters of faded ink.—T.

black, and the most indelible ink.* He adds, that on plunging into this tincture silks and woollen stuffs, without adding any acid to it, he obtained them of the deepest and most indestructible black colour. Proust also says, that he would prefer, both as to durability and beauty, the ink made by dissolving iron in an infusion of gall-nuts, to that which is prepared with the sulphate of iron.† He remarks in the same place, that the combination of gallic acid and tannin with iron, is not changed into prussiate of iron by the prussiate of potash; an observation which had already been made by the academicians of Dijon.

We have mentioned, that Lewis had observed that a decoction of logwood increased the beauty of ink. It is observed, especially in the black dyes, that an addition of logwood gives more lustre to black; and we shall see, that it is advantageous to fix a blue colour on stuff which is to be dyed black. Now, logwood forms with the oxide of copper, added to black dyes, a blue colour, which contributes to the beauty of the black by the mixture of that hue.

We must here remark, that the black of the dyes is produced only by the condensation of molecules, which when more diffused enjoy a particular colour, such as blue, dun, or violet. But the mixture of two substances, whose diluted colour is different, yields a more intense black. This effect is readily observable in the mixture of

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* Experimental Inquiries.

† Ann. de Chim. tom. xxxv.

two liquids of a deep colour, even when no precipitation occurs by their mutual action. On this occasion we shall adduce an observation of Hooke, quoted by Newton: "If we take two coloured liquids, the one red the other blue, in sufficient quantity for them to appear very dark, although each apart be pretty diaphanous, they will cease to be so on their mixture; for the one transmitting only red rays, and the other transmitting only blue rays, none will any longer pass through the two liquids mixed together."*

The result is not, however, exactly such as Newton states it, provided the two liquids are not of a nature to produce a precipitate. The colour transmitted is always different from the two insulated colours, and always deeper; but if the mixture appears opaque in a vessel of a certain size, it will appear still transparent in a vessel of a smaller diameter.

We perceive therefore that it must be advantageous, for obtaining an intense black, to mingle different astringents, the black of which is derived from different colours. Perhaps gallic acid may thereby augment the black occasioned by the tannin; and perhaps it would be beneficial to employ a mixture of different kinds of tannin in galling.

We have hitherto considered tannin only in reference to black dyes; but its use is not confined to this kind of dyeing: it exerts on several other

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* Optics, tom. i.

colouring particles an affinity analogous to what we have observed between it and gallic acid; whence it serves to fix them on stuffs, and to communicate stability to them. In this point of view, it may be compared to mordants; but as it possesses in itself a colour which has a tinge of yellow or dun, and as the effect of one colour must be to modify and darken that peculiar to another colouring substance, the use of astringents as a mordant does not suit bright colours, particularly those of little intensity.

CHAPTER IV.

Of the action of different Substances, particularly of Air and Light, on Colours.

Hitherto we have considered the colouring molecules only as substances forming different combinations, by which their properties are modified; but they may yield more or less easily to the action of other substances, which destroy the combination thus formed, or which by a sur-composition deteriorate their properties. They may suffer the alterations produced by external agents, either from the mutual action of their principles, or of the substances which form a combination with them.

The power of resisting vegetable acids, alkalies, soap, and, above all, the action of air and light, constitutes the durability of a colour; but this property has a very unequal standard, according to the nature of the colour and the species of stuff; for in certain silk dyes the same permanence is not required as in those of wool.

There is no obscurity in the action of water, alkalies, acids, and soap: a solution is effected by means of these agents, or a small portion of acid or alkali unites to the combination which forms the colour; for this is not destroyed, but merely changed, and can be restored by removing the acid or the alkali.

This is not the case with the action of air and light. Till lately, it was not known in what this action consisted; but we are at the present day much farther advanced in this theory, which we proceed to detail.

Scheele had observed, that oxygenated muriatic acid (chlorine) rendered the vegetable colours yellow, and he ascribed this effect to the property which it possesses, of seizing the phlogiston which enters into their composition.

The author of the Elements proved,* that the properties of oxygenated muriatic acid arose from the oxygen, which it readily yielded to the substances exposed to its action; that it commonly brought the colouring particles to a yellow hue; but that, by a continuance of its action, it destroyed their colour, though he did not determine wherein this action consisted.†

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* Mem. de l'Acad. 1785.

† For the theory of blanching by chlorine, see Note to page 62.—T.

With regard to the action exercised by oxygen on the colouring particles, Fourcroy afterwards made several observations, which throw much light on the changes which they experience, especially when their aqueous solution remains exposed to the air, or when it undergoes ebullition. He remarked, that, by the action of the air, vegetable decoctions formed pellicles, which lost their solubility, and progressively changed their colour. He traced the gradations of colour thus obtained, and concluded from his observations, that oxygen entered into the composition of these colouring particles; that when it combined with them their hue changed; that the more of it they absorbed, the more fixed their colour became; and, that the mode of procuring unchangeable colours for painting was, to select those which had been exposed to the action of oxygenated muriatic acid.*

The author of these Elements sought to determine more peculiarly wherein the action of the air consisted, when it combines with the colouring particles, especially by examining the operation of oxygenated muriatic acid upon them.†

We shall copy literally what had been stated in the first edition of these Elements, because Bancroft, whose authority has great weight with us, has attempted to refute the theory there established, and because we are desirous of enabling

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* Annal. de Chimie, tom. v.

† Annal. de Chimie, tom. vi. Mem. sur l'action que l'acide muriatique oxigéné exerce sur les parties colorantes.

our readers to weigh his reasons, and the grounds of our opinion.

"We must distinguish, in reference to the effects of the air, between the colours of metallic oxides and those of the colouring particles. I have proved, that the modifications of the former are owing entirely to the different proportions of oxygen; but I have been led by my observations to a different opinion concerning the modifications of the other colouring particles.

"I have observed, that the oxygenated muriatic acid exhibited different phenomena with the colouring particles; that sometimes it discharged their colour, rendering them white; that more frequently it caused them to become yellow, dun, brown, and black, according to the intensity of its action; and that, when their colour seemed to be discharged or blanched, heat, or the lapse of time, was sufficient to render them yellow.

"I have compared the effect produced by oxygenated muriatic acid, when the colouring particles are rendered yellow, fawn, or brown, with the effects of a slight combustion; and I have shown that they were identical, that they were owing to the destruction of the hydrogen, which, combining with oxygen more easily, and at a lower temperature than charcoal, leaves this predominant, whence the natural colour of charcoal is blended more or less with that which pre-existed.

"This effect is very perceptible, when sugar, indigo, or the infusion of nut-galls or of sumach, is submitted to the action of oxygenated muriatic acid. The sugar and indigo assume a deep colour, and afford unequivocal traces of a slight combustion. The infusion of gall-nuts and of sumach forms a black deposite, which is charcoal nearly pure."

These phenomena are analogous to those observed in the distillation of an organic substance. In proportion as its hydrogen is disengaged under the form of oil, or in the state of gas, the substance turns yellow, and eventually only a black charcoal remains. If we expel the hydrogen of an oil by heat, it becomes brown.

Other experiments which I have made on alcohol and ether have satisfied me, that oxygen united to muriatic acid possessed the property of combining with the hydrogen, which abounds in these substances, so as to form water.

When, therefore, oxygenated muriatic acid renders a colour yellow, dun, or brown, this effect is caused by the colouring substance suffering a slight combustion, in which a greater or less part of its hydrogen has formed water; whence the carbon becoming predominant, communicates its peculiar colour.

I have shewn, that the art of bleaching goods depended on this alteration of the colouring particles by the oxygen of the atmosphere, the dew, and oxygenated muriatic acid. The colouring particles of flax become soluble in the alkali of the leys, which must be alternated with the action of the oxygen. We may afterwards precipitate from the alkali these colouring particles, which when dried and collected are black. They therefore prove the truth of this theory, both by the colour they have assumed, and by the quantity of carbon they afford in their analysis.

"The alkaline solution of the colouring particles of the cloth, which is blackish-brown, loses nearly its whole colour on pouring into it a quantity of oxygenated muriatic acid; and the same effect may be observed with several other substances, which have derived a colour from a commencement of combustion.

"A cloth may appear white, and yet become yellow in process of time, especially if it be exposed to certain degrees of heat, when the oxygenized particles have not been removed by a sufficiently efficacious ley. In like manner, the green particles of vegetables are blanched by the oxygenated muriatic acid, but become yellow on ebullition.

"These facts prove, that oxygen may whiten or render pale the colouring particles with which it combines, whether it has begun to produce on them the effects of combustion, or whether it may produce these effects but slowly, and especially when this combustion is subjected to a certain degree of heat.

"It is very probable that, in every case, one portion of the oxygen unites with the colouring particles without combining particularly with the hydrogen, and that thereby the colouring particles of the flax have become, from the action of the oxygen, more soluble in the alkalies than they previously were.

"The action of oxygen has an undoubted influence, in several other circumstances, on the changes effected in the colouring particles of vegetables. These particles are formed chiefly in the leaves, the flowers, and the inner bark of trees. By degrees they experience a slight combustion, either by the action of the atmospheric air which surrounds them, or by that of the air carried into the interior of the vegetables by particular vessels; whence it happens, that the most part of trees contain colouring particles of a dun hue, verging more or less on yellow, red, or brown, which, by means of this combustion, thicken, and are eventually thrown out of the vascular fibres of the bark, of which I have found them to form the greater proportion.

"These observations teach us in what manner the air acts on colouring substances of an animal or vegetable nature: it first combines with them, making them weaker and paler, and gradually establishes a slight combustion, by which the hydrogen in their composition is destroyed; they pass to yellow, russet, dun; their affinity with the stuff seems to diminish, they are detached from it, they are carried off by the water; and all these effects vary, and are finished more or less quickly, and more or less completely, according to the nature of the colouring particles, or rather according to the properties which they possess in their actual state of combination.

" The changes which occur in colours, arising from the combination of the colouring particles with the metallic oxides, are a compound effect of the change produced in the colouring particles and the metallic oxide.

" The light of the sun accelerates greatly the destruction of colours; it ought then (if the theory which I have laid down be just) to favour the combination of the oxygen, and the combustion thereby produced.

" Sennebier has given a great number of interesting observations, concerning the effects which light occasions in the different substances, and particularly in colours; he ascribes these effects to a direct combination of the light with these substances."*

The influence of light on the colour of woods has been long ago remarked. In obscurity, they retain their natural state; but when exposed to light, become yellow, brown, and pass into other shades. Sennebier observed the differences exhibited by several species of wood in this respect. He found that the changes were proportional to the vivacity of the light; that they took place even under water; that moistened woods, how-

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* Mem. Physico-Chimique sur l'influence de la lumière solaire, &c. tomes ii. et iii. This philosopher, to whom physics is under so many obligations, has adopted, in a great measure, (Physiol. Veget. tom. v.) the ideas exposed here; and among which we must distinguish between the positive consequences of observation, and the applications that are yet merely conjectural.

ever, suffered changes less rapidly than those which were dry; that it required several folds of ribbon to preserve a wood entirely; that black paper was sufficient, but with paper of other colours the alteration was not prevented. A simple envelope of white paper was insufficient, but two intercepted the action of the light.

"This skilful philosopher extended his experiments to a great number of vegetable substances. They may serve to clear up several phenomena of vegetation, with which I have at present no concern. But to prove wherein the action of the sun on colours consists, it would be sufficient to examine the phenomena exhibited by the solution of the green particles of vegetables in alcohol.

"If this solution, which is of a fine green colour, be exposed to the light of the sun, it speedily takes an olive tint, and then is discharged in some minutes. If the light has little vivacity, the effect is much slower; but in perfect darkness, the colour is preserved without alteration, or at least the alteration is very tardy. Sennebier says that an alkali restores the green colour; but if the liquid has experienced all the discoloration which it can undergo, the alkali produces no change on it. He remarked, that in azote or phlogisticated air the colour was not affected, and that it suffered no change if the flask was full.

"I inverted over mercury a flask half filled with the green solution, and exposed it to the light of the sun. When the colour was discharged, the mercury was found to have risen in the flask, and consequently the vital air had been absorbed, the oxygen having combined with the colouring particles. I have not observed the deposite of which Sennebier speaks; the liquid remained transparent, and of a clear yellow colour.

"I evaporated this liquor; its colour soon deepened, becoming brown; and the residuum was black, and in a carbonaceous state.

"The light acted therefore by favouring the absorption of oxygen and the combustion of the colouring matter. At first, the marks of the combustion are not perceptible, the liquid preserving merely a feeble yellow colour; but the combustion is soon consummated by the action of the heat, when the liquid turns brown, and leaves a black residuum. If the vessel in which the liquid is put contains no oxygen gas, the light has no action on the colouring particles. The azotic gas suffers no diminution.

"The circumstance of ribbons and a simple white paper not protecting from the action of light merits attention. It can penetrate through envelopes which appear to us opaque, so as to exert its energy at greater or less depths.

"Beccaria, and after him Sennebier, have compared the effects which light produces on ribbons of different colours; but the differences which they observed ought to be ascribed to the nature of the colouring substances with which the ribbons were dyed, rather than to the colours themselves; for a ribbon dyed with brazil wood will lose its colour much more speedily than one dyed with cochineal, though the shade be the same.

" Although light greatly accelerates the combustion of the colouring particles, and though its presence even appears necessary for the destruction of some of them, yet this effect takes place in other circumstances without the aid of light. Having placed several plants in darkness, in contact with oxygen gas, I observed that some of them absorbed it. I also observed, that the rose changed and took a darker tint without the contact of the air, undoubtedly because it contains a little oxygen, whose state of combination becomes afterwards more intimate ; but several species of flowers preserved their colour perfectly well in azote.

" I placed tincture of litmus in contact with oxygen over mercury, in darkness, and in the sun-light : the first was preserved very long without alteration, while the gas experienced no diminution ; the second lost much of its colour, it became red, the oxygen gas was in a great measure absorbed, and a little carbonic acid was formed, which undoubtedly produced the change of the blue colour into red.

" This observation may give some idea of the changes of colours occasioned by a peculiar disposition of the principles existing in a vegetable substance, when it experiences, by combination with oxygen, the effects of a slight combustion, which may generate some acid, as in the leaves which redden in autumn previous to their turning yellow, and in the streaks observable in flowers of languid vegetation.

"It is therefore proved, that light promotes the absorption of oxygen by the colouring particles, and that a combustion thus takes place, the ordinary effect of which is a predominance of carbonaceous particles.

"To the same cause must be ascribed the decay remarked in stuffs themselves by the action of light. "Among several examples which I might adduce," says Dufay, "I shall mention only a curtain of fugitive crimson taffeta, which had remained long stretched behind a window: all the parts which were opposite the panes of the glass were entirely deprived of colour, whilst those which corresponded to the wood of the casement were much less faded; and further, the silk itself was almost destroyed in the discoloured parts, where the curtain could be torn with the slightest effort, whilst it retained elsewhere nearly its usual strength."*

"The colouring substances resist, therefore, the action of the air in a greater or less degree, according as they are more or less disposed to combine with oxygen, and to suffer from its action a combustion more or less speedy, more or less considerable. Light favours this effect in several circumstances; its concurrence is essential; but the insulated colouring particles are much more subject to this combustion than when

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* Mem. de l'Academie, 1737.

they are combined with a substance such as alumina, whether this defends them by its incombustibility, or whether the force of affinity binds them up, so to speak, and enfeebles their action on other substances; and in this principally consists the utility of mordants. Finally, the latter combination acquires still greater unchangeableness when it is intimately united with the stuff.

"Thus the colouring matter of cochineal is easily dissolved in water, and its colour is quickly affected in the air. When combined with the oxide of tin, it is much more lively, and scarcely soluble in water; but it is still readily altered by the air and by chlorine. When it exists in triple combination with woollen stuff, it resists these agents better.

"From these observations we are not to conclude, that all the yellow colours proceed from the carbonaceous portion of the colouring substances; different compositions may afford the same colour. Thus indigo is entirely different from the blue of our flowers, from the blue of oxide of copper, and from prussian blue.

"Nor do I assert that oxygen may not unite in a small proportion with some colouring particles, without weakening their colour, or changing it to yellow. We shall find in the chapter on indigo, that this substance possesses a green colour when combined with an alkali, lime, or a metallic oxide; but that it resumes its colour, and separates from these solvents, on recovering a small portion of the oxygen which it had lost.

The liquor of the *buccinum*, which served for dyeing purple, is naturally yellowish; on being exposed to the air, and particularly to the sun, it passes speedily through different shades, and finally assumes that colour which was deemed so precious by the ancients.*

" It may be regarded even as a general fact, that colours assume more brilliancy by combining with a small portion of oxygen. It thence happens that the stuffs, as they come out of the bath, ought to be agitated in the air, and sometimes withdrawn from the bath at intervals, in order to expose them to the atmosphere. But the quantity of oxygen which fixes itself, thus contributing to the lustre of the colour, is very inconsiderable in some cases, and the degradation of shade soon begins.

" The action of the air affects not only the colouring particles and the stuff, but also the metallic oxides which serve as an intermedium to them; because the oxides, which are at first deprived of a portion of their oxygen by the colouring particles, may recover some of it. Hence the oxides, whose colour varies with the proportion of their oxygen, exert an influence on the changes experienced by the stuff. The alteration of the colouring particles must also contribute to this effect.

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* Decouverte d'une Nouvelle Teinture de Pourpre, &c. par Reaumur; Mem. de l'Academie 1711. According to the testimony of Eudocia, the purple took its lustre, and arrived at its perfection, only by exposure to the sunbeams.

"I have stated, that the colouring particles, in a state of combination, were less liable to be affected by the action of the air than when they are insulated. This is a circumstance very commonly observed. There are, however, particular exceptions. Alkali produces a contrary effect. I half filled a phial with an infusion of cochineal, and exposed it to light over mercury; another phial, similarly situated, contained an infusion of cochineal made with a little tartar; and in a third, some alkali was added to the infusion. The second phial suffered least alteration in the same space of time, accompanied with the least absorption of air.

"In the third, the liquid became at first brown, then the colour disappeared, and the absorption of the air, although inconsiderable, was greater than in the two others. By evaporation it assumed a brown colour, and the residuum was yellow-brown.

"I have made similar experiments on several colouring substances: the alkali deepened their colour, which grew more and more brown; and it likewise favoured the absorption of the air. Madder alone seemed to form an exception; its colour, which at first became deeper, was more durable than that of the infusion without alkali.

"The usual effect of alkalies on colouring particles is conformable to what they produce on several other substances, such as sulphur. They promote the absorption of the air, because they have a strong affinity for the substance which results from this absorption.

" From this operation of alkalies, I explain a fact observed by M. Becker.* When alkalies have rendered a vegetable infusion green, we see it pass by degrees to yellow, if it be left exposed to the air; and when the yellow is once established, acids can no more bring back the primitive colour. But this effect does not occur when we abandon in the same way, for some time, a vegetable colour which has been turned red by an acid. We must, however, except those acids which act by giving up their oxygen; for the colour is equally destroyed in that case."

Bancroft advances, in opposition to what we have thus stated: 1. That the colouring substances experience, from the action of acids and other bodies, an alteration which cannot be compared to combustion. In the preceding explanations, however, the question is merely about the kind of alteration which depends on the action of oxygen.

2. That oxygen, far from destroying colours, is sometimes necessary to them; for example, to indigo. Is not this what we have said? But we distinguish between the cases where it becomes an element of the colour, and those where its action is destructive.

3. That the changes of colours produced by the air cannot be ascribed to the charcoal, which

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* Specimen, &c.

becomes predominant, because several substances contain much charcoal without having a colour similar to what is ascribed to its excess, and because the colour of charcoal itself is due to oxygenation.

We have attempted to demonstrate, that the changes produced by the air when its action is favoured by light, are especially owing to a combination of the hydrogen of the colouring substance with oxygen, whether this be absorbed from the atmosphere, or be present in less intimate combination, either in the colouring substance itself, or in the oxide united with it; and that the effect was similar to a slow combustion, in which a combination of hydrogen with oxygen was formed, so as to leave a residuum containing a redundancy of charcoal. This opinion seems to be an immediate consequence of the phenomena that have been detailed, which indicate the gradual decomposition of all bodies containing hydrogen on being subjected to this action of oxygen.

Bancroft regards charcoal as an oxide, which he compares to the oxide of manganese. We do not think it necessary to take up time in refuting his opinion * concerning the nature of charcoal. The only object is to know, if, in the circumstances under discussion, the change of colour may not have some analogy with what is observed when a vegetable substance is distilled. He pretends

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* Essai de Statique Chimique, tom. ii.

that this substance becomes in that case brown, merely by the accession of oxygen from the atmosphere. Let a distillation be made out of contact of the atmospheric air, and he will observe that the same alteration of colour takes place, either from the formation of water, or from the disengagement of a greater proportion of hydrogen, so that the properties of the charcoal become predominant.

Bancroft maintains, that the theory which he combats is founded only on the phenomena of the colouring particles of the cloth. The text which we have adduced proves the contrary, and we might easily multiply examples.

It was incorrect, according to him, to confound the effects of the combination of oxygen gas with those of the oxygenated muriatic acid ; but we do not find in his work the experiments which he announced as calculated to prove, that the oxygenated muriatic acid often produces effects contrary to those arising from the combination of oxygen.

We ought, undoubtedly, in comparing the effects of oxygenated muriatic acid with those of the absorption of oxygen gas, to take into consideration the greater condensation of oxygen in the former, and the natural effects of muriatic acid.* We should also distinguish between the

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* Translating M. Berthollet's idea into the modern language of chemistry, we would say, " Take into consideration the intense affinity of chlorine for hydrogen, the liberation of oxygen from the decomposed water, and the peculiar action of muriatic acid."—T.

effects which the oxygenated muriatic acid can produce, when it has made the whole colour disappear, as we have seen, and the effects due to the combination of its oxygen with the hydrogen of the colouring particles, as well as those arising from the difference of the colours, of which we shall speak in the sequel.

The more lively oxygenation, by means of oxygenated muriatic acid, prevents us from obtaining readily those gradations of colour which are produced by the action of the air, and which become more difficult the further they advance. Thus, conformably to the observation of Fourcroy, when a colouring substance has experienced some change by this action, it becomes, in similar circumstances, more fixed; but in this first effect, a part of its hydrogen must have entered into combination.

While we conceive that we have been able to refute the objections of Bancroft concerning at least the most usual cause of the degradation of colours by air and light, we admit, that the consequences of the opinion which we endeavour to maintain, should not have been extended to the phenomena that we are now going to examine, although this has been done with much diffidence, and without overstepping the limits of a simple conjecture.

Nitric acid, oxygenated muriatic acid, and sulphurous acid, exercise on animal substances a peculiar action, which merits examination, because it may furnish some processes to dyeing.

Brunwiser[*] having observed that woods assumed different colours on exposure to air, sought to determine the origin of these colours, and to produce them artificially. He remarked, that on moistening with nitric acid the surface of wood, principally young wood not very dry, it took a yellow colour. On performing the same operation with muriatic acid, and sulphuric acid, the wood assumed a violet colour; and he looked upon this violet as composed of a blue and a red colour. From these observations he concluded, that as all the colours are produced by the mixture of yellow, blue, and red, those which we observe in the leaves, fruits, and flowers, arise from the colouring particles which exist in the wood, but which are disguised by an alkali; that the mineral acids, on seizing this alkali, set the colouring particles at liberty; and that the fixed air, in penetrating into the leaves, the fruits, and the flowers, naturally produced the same effect, by combining with the alkali which masked them.

The author attempted to apply to the arts his pretended discovery as follows.[†] After watering chips of wood with nitric acid, he poured water upon them, filtered the liquid, and made use of it to dye wool, silk, and goat's hair, of a durable

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[*] Versuche mit mineralischen sauern geistern, aus den holzern farben zu ziehen, 1770. In abhandlungen der Baierischen akademie.

[†] Entdeckung verschiedener vegetabilischen farbematerialem seiden und wollen zeuge schon und dauerhaft gelb zu farben, 1771.

yellow; a colour due, by his account, to the yellow particles which were contained in the wood, and which had been extracted or set at liberty by the nitric acid.

De la Folie relates,* that having plunged a skein of white silk into nitric acid, or aquafortis, of the usual commercial strength, the silk assumed in three or four minutes a fine jonquil-yellow hue. He washed it repeatedly with water, that no adhering acid might remain to alter it. This colour resisted several tests to which he exposed it, and the silk retained its primitive lustre. When dipped into an alkaline solution, it takes a beautiful orange colour.

Several experiments on this process are to be found in a dissertation published by Gmelin.† He says, that he has given a fine sulphur colour to silk by keeping it for a day in cold nitric acid, or for a few hours when the acid was hot. Ebullition with soap and water impaired the lustre of this colour. It became of a fine lemon colour by keeping the silk for twelve hours in an alkaline solution; and it assumed a fine gold hue when this solution was hot.

All solutions of metals in nitric acid gave to silk a yellow colour more or less deep, as well as the solution of alumina in the same acid. But

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* Journ. de Phys. tom. iv. p. 349.

† J. Frieder. Gmelin, Prof. Gotting. de tingendo per nitri acidum, sive nudum, sive terra aut metalli saturatum serico. Erfurti, 1785.

the solution of calcareous earth and of magnesia produced no effect.

The solution of tin mixed with solution of gold yielded, according to La Folie,* a purple colour, which fixes upon silk; but Gmelin obtained by this process only a common yellow. He proves also, that the different yellows which Struve said he had obtained from different metallic solutions, depend merely on the acid of these solutions.† The only exception, perhaps, is the solution of mercury, which gave silk a copper colour.

Baumé describes a process capable of protecting silk from any alteration.‡ "A mixture of two drams of nitrous acid and one pound of alcohol is made, into which a few ounces of silk are put, mounted (*montée*), and yellow, or previously whitened, for that is absolutely indifferent. The vessel containing them is placed for about 24 hours in a water-bath heated to 30 or 40 degrees R. (100° or 120° Fahr.) The silk becomes of a dull yellowish-brown. It is now repeatedly washed in water, to remove the acid with which it was impregnated. It is then scoured with soap in the usual way; afterwards washed to free it from the soap water, and finally dried.

"If we view this silk in the sun, it shines like threads of gold. By the same process we may

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* Journ. de Physique, tom. viii.

† Bernerisches Magazin der Naturkunst und Wissenchaften, vol. i.

‡ Ann. de Chimie, tom. xvii.

give silk different shades of the above colour, and form what is called in dyeing *degradation* of colour from white to the full tint. For this purpose it is sufficient to let the silk infuse for a shorter time; the first shade is procured by one hour's infusion, and the others in proportion to their duration."

Bergman was aware of this process, when he published his notes on the Treatise of Scheffer.* He says, that ordinary aquafortis gives, in three or four minutes, to wool and silk, a bright, fine, and durable yellow; that they must be immediately washed; and the more dephlogisticated the acid (the more colourless), the greater effect it produces.

To recapitulate: nitric acid, diluted with a certain quantity of water, gives silk a yellow colour, of more or less depth, according to the concentration of the acid, the temperature, and the time of immersion: the silk must be carefully washed on coming out of the acid. This colour has a good deal of lustre. We may deepen the shade without perceptibly affecting the silk. This process may be usefully applied, not only to silk, but to other animal substances; and the colour may be modified by alkalies.

The solution (nitric) of calcareous earth, and that of magnesia, produce no effect on silk, because they do not retain an excess of acid. Solutions of alumina, and of all the metallic sub-

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* Essai sur l'Art de la Teinture.

stances, produces, on the contrary, a yellow of greater or less depth, because they all retain a greater or less excess of acid ; and it is the acid in excess which acts on the silk as free acid. It was the acid alone which coloured the animal substances yellow in the experiments of Brunwiser, and not the extracts of the wood.

The yellow colour is not owing to iron, as De la Folie pretended ; for the purest nitric acid, which consequently contains no iron, produces it as well as that in which the presence of a little of this metal may be suspected.

If silk be put into concentrated nitric acid, it speedily takes a deep yellow colour, loses its force of cohesion, and is dissolved. During this solution, the azote which enters into the composition of animal substances is disengaged, occasioning a long effervescence.* If heat be applied, much nitrous gas is formed, and the liquid at first assumes a dark colour, becoming brown. At this period, the oxygen of the nitric acid combines particularly with the hydrogen which abounds in animal substances, serving to form the oil extracted by distillation, which renders them so combustible. One part of the oxygen enters into a new combination, forming oxalic acid ; but, at the same time, another substance of a detonating quality is produced, which is yellow, and bitter, whence it has been called *amer* by Welter.†

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* Mem. de l'Academie, 1785.

† Ann. de Chimie, tom. xxix.

Welter extracted this substance not only from silk, but from other animal substances; and he observed, that it communicated to white silk a beautiful yellow, which washing with water did not impair.

It is to be desired that this expert chemist had prosecuted his trials, in order to determine more exactly both the nature of this substance and the circumstances of its production; we might perhaps be able to deduce from it the cause of the yellow colour which nitric acid communicates to animal substances, when the action of this acid is less lively than that just described. Perhaps, when it is confined to the surface of the silk, the formation of this substance on it is determined by the tendency of the silk to combination.

Oxygenated muriatic acid gives likewise a yellow colour to animal substances; but this does not seem to be a general effect. We have seen skins bleached by oxygenated muriatic acid, and this colour is always much more intense than that owing to nitric acid: thus, it appears to differ from it, and to arise merely from a feeble combination of the oxygen with the animal substance, which, when it is white, takes a nearly similar hue on long exposure to the atmosphere. It is also to be remarked, that the action of oxygenated muriatic acid weakens animal substances more easily than nitric acid, although the latter be more condensed.

Sulphurous acid exercises also a peculiar action, which deserves more consideration, as it enters into the practice of dyeing.

According to the observation of De la Folie, roses blanched by the vapour of burning sulphur, become green in an alkaline ley, and red in the acids. Sulphurous acid reddens tincture of litmus, which possesses a very fugitive colour; but it acts just like the other acids on infusions of yellow wood, brazil wood, and logwood; its vapour however is much more active, in which respect it resembles oxygenated muriatic acid.* Hence it is not judicious to substitute the use of this for the fumes of sulphur.

When silk has undergone the action of the sulphur which is to complete its whitening, sulphuric acid disengages from it an odour of sulphurous acid, although this odour was not perceptible beforehand.

From this circumstance we may conclude, that sulphurous acid has the property of combining, in small quantity, with animal substances, without experiencing decomposition; in which state it can disguise some colours, particularly that arising from a combination of oxygen. But it would seem, that in the lapse of time a more intimate union is effected between the sulphurous gas and the oxygen.

This latter effect immediately takes place when sulphurous acid is made to counteract the oxygenated muriatic acid. The yellowed silk is whitened by the sulphurous acid; and the two operations may be alternated. We shall have

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* Journ. de Phys. 1774.

occasion to speak of the use which Giobert has made of this property.

We are obliged to confine ourselves to these conjectural views concerning the action which nitric acid, oxygenated muriatic acid, and sulphurous acid, exercise on animal substances, till experience shall have conducted us to positive results.

CHAPTER V.

Recapitulation of the Theory laid down in this Section.

Substances which have constant colours should not be confounded with those which owe their variable and fugitive hues to the dimensions and density of the plates of which they are formed; or, at least, the theory of the one cannot serve for the explanation of the properties which the others possess, in reference to the colours which appear to depend on their peculiar affinity for the rays of light.

Meanwhile, till chemistry can be reconciled with physics, in explaining the phenomena exhibited by colours, we must content ourselves, in reference to the art of dyeing, with determining the affinities which characterize the colouring substances, and the physical dispositions which modify their action in every variety of circumstance.

Metallic colours must be distinguished from those which belong to vegetable and animal substances.

The colours of metals are modified and changed by oxidation, and in proportion to the quantity of oxygen combined with them.

The vegetable and animal substances, which occasionally owe to plates on their surface some plays of fugitive colours, may themselves have a peculiar colour, or may indeed owe their colours to coloured molecules which exist combined, or simply mixed, with them. It is molecules of this kind, extracted from several substances, which receive different preparations in order to serve for the purposes of dyeing.

The affinities of the colouring particles for acids, alkalies, earths, metallic oxides, and wool, silk, cotton, and flax, constitute their chief distinctive properties; but these are modified by their physical qualities, and especially by their tendency to assume the solid, or to continue in the liquid state.

In consequence of the affinity between the colouring particles, and wool, silk, cotton and flax, they combine more or less easily, more or less intimately, with each of these substances; from which arises a primary difference in the processes employed, according to the nature of the stuff and of the colouring substance.

Sometimes they unite immediately with the stuffs, but more frequently they need an *inter medium*, in order to be separated from the solvent, and to be fixed on the stuff, or at least to acquire a greater permanence.

From the affinity of the colouring particles for alumina and metallic oxides, they form compounds with these substances, in which their colour is more or less preserved, while it becomes more stable, and more insensible to external agents. This combination being formed of principles which possess the faculty of uniting to vegetable, and particularly to animal substances, has also itself this property; it enters into triple combinations with the stuff, and the colour resulting from this triple union thus acquires greater fixity, or the faculty of better resisting external agents.

The colouring particles have frequently such an affinity for alumina and the metallic oxides, that they separate them from the acids which held them in solution, and fall down with these bases; but sometimes the affinity of the stuff must determine this combination. We have to distinguish between the chemical action of the substances which dissolve the colouring particles, and those which fix them, or effect their destruction.

Colours experience great changes from the action of oxygen, which eventually destroys them; the other substances promote or obstruct this action.

Of the two principles which compose the atmospheric air, it is only the oxygen gas which acts on the colouring particles. It combines with them, and thus impairs their colour or makes them pale. But its action is soon chiefly exerted on the hydrogen, which enters into their composition, and it thereby forms water. This effect may be compared to that of a feeble combustion. Hence, the carbon which enters into the composition of the colouring particles becomes predominant, and the colour usually passes to yellow, dun, or brown; or this degradation, blended with what remains of the first colour, or with the effect at the same time suffered by a metallic oxide, produces other appearances.

Light promotes this decomposition of the colouring particles, which frequently takes place only with its concurrence; and thus it contributes to the destruction of colours. Heat favours it also, but less efficaciously than light, unless it have a certain intensity.*

The oxygen present in the colouring particles may itself undergo a combination productive of a slow alteration in the colouring particles, especially by the action of light and heat.

The oxygen which is absorbed does not, however, always and immediately produce that kind of combustion which alters and destroys the colouring particles; on the contrary, a certain absorption is usually necessary to give the colours lustre, or even to bring them out, while a larger proportion causes the colour to disappear; and it is but secondarily that the combination of

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* Statique Chimique, tom. i. p. 197.

hydrogen is formed, which produces the appearances of a slight combustion.

The colours are more or less durable, more or less fixed in the air, according to the greater or less tendency which the colouring particles have to experience that change, and to suffer it in a greater or less degree; for the resistance to this decomposition increases as it advances.

The other substances exercise their action on the colouring particles, either before they have been applied to the stuffs, or after they have been fixed on them; they thus have a different use, or they may produce destructive effects.

The substances capable of dissolving the colouring particles, serve to separate them from the particles with which they are confounded; and they prepare them, by the liquidity they communicate, for the action of the stuffs that are to fix them, or for the combinations they are to form.

The colouring particles are sometimes modified as to their colours by the action of these substances, and as they usually retain a portion of them in the combinations which they afterwards form; or as, when the compound is formed, this may take a portion of them by sur-composition, we call these substances *alterants*, in order to contrast their effect with that of mordants.

We give the name of *mordants* to substances which, combining with the colouring matters, serve to precipitate, to fix, and to render them more durable.

These two genera of substances, therefore, which exercise the same chemical action, are distinguishable by this ;—the alterants, in consequence of their physical qualities, attenuate and dissolve the colouring matters, so that only a small portion can remain in combination when the colouring substances assume the solid state; such are the acids and alkalies properly called, which, when they act with a certain energy, even deprive the stuffs of those colouring particles which were fixed on them. The power of resisting the action of them and of the air, constitutes the durability (*la solidité*) of colours.

The substances, on the contrary, which naturally tend to the solid state, communicate this property to the colouring substances with which they have an affinity, serving as *intermedia* between them and the stuffs, with which also they must have a tendency to combine.

The mordants produce this effect only sometimes, and change but slightly the natural colour of a substance; alumina, in particular, has this property. Sometimes the colour of the combination results from that of the tinctorial substance, joined to that of the mordant; such are the metallic oxides, which, moreover, alter or ameliorate the natural colour by the action of their oxygen. Thence arise their different effects.

1. The metallic oxides, to which the oxygen adheres loosely, are not fit to serve as *intermedia* to the colouring particles, because they produce in them too considerable a combustion. The oxides

of silver, gold, and mercury, are in this predicament.

2. The oxides which, on giving up more or less of their oxygen, experience considerable changes in their colour, are also bad *intermedia*, especially for light shades, because they produce variable colours. Such are the oxides of copper, lead, and bismuth.

3. The oxides which retain their oxygen with force, and which change their colour very little when they have lost a portion of it, are the most proper for accomplishing this object. The oxide of tin must be here particularly distinguished. It easily abandons its solvent; it has a strong affinity for the colouring particles, and affords them a very white base, one capable of giving brilliancy to their hues, without altering them by the mixture of another colour. The oxide of zinc possesses these properties in part.

In order to account for the colours that result from the combination of the colouring particles with the basis which a mordant gives them, we must also pay attention to the proportion in which the colouring particles are united with this basis. Thus, the solution of tin, which forms a very abundant precipitate with a solution of the colouring particles, proving thereby that the oxide of tin enters in large proportion into the precipitate, influences the colour of the precipitate, by the colour of the base, much more than the solution of (sulphate of) zinc and of alum does, which bodies usually form a much less considerable precipitate. The precipitates produced by the two latter substances, retain very nearly the natural colour of the colouring particles.

In the action of mordants, therefore, we must distinguish the combinations formed, by their means, between the colouring particles and the intermedium which they furnish to the stuff; the proportions of the colouring substance and the intermedium; the modifications of colour resulting from the association of the colour of the colouring particles with the base to which they are united; and finally, the changes which the colouring particles may suffer by the action exerted on them by that base.

Astringents do not differ essentially from colouring particles; but the latter take this name, especially when employed to produce black with oxide of iron, by restoring this metal to the state of a black oxide, and by their assuming a dark colour from the action of oxygen.

The notion of an astringent supposes, moreover, the property of combining in a certain quantity with animal substances, giving them thus solidity and incorruptibility; because these two properties are most commonly united. These again are derived from their large share of carbon, a circumstance in their composition which gives them increased tendency to solidity, and greater stability.

The natural properties of vegetable and animal substances must depend on those of their elements, and consequently on the proportions of these. These elements are principally oxygen, hydrogen, azote, and carbon. The first three, naturally very elastic, enter into solid combinations only by means of a force that subdues their elasticity. This again produces more or less effect, according to the temperature or the circumstances which may cause the repressing (condensing) force to vary. The carbon, on the other hand, must have a great disposition to assume the solid state, and to maintain its constitution.

SECTION II.

OF THE DIFFERENCES WHICH DISTINGUISH WOOL, SILK, COTTON, AND LINEN (FLAX), AND OF THE OPERATIONS BY WHICH THESE SUBSTANCES ARE DISPOSED TO RECEIVE DYES.

CHAPTER I.

Considerations on the differences between Animal and Vegetable Substances.

We must not flatter ourselves that we can account for the different results of organization. The knowledge which we have acquired, however, of the composition of animal and vegetable substances, may, agreeably to the preceding considerations, give us some idea of the cause of the different tendencies which wool, silk, cotton, and flax have to unite with the colouring particles, and with the bases which constitute their mordants.

Wool and silk belong to animal substances; cotton, flax, and hemp, to vegetable.

The principal distinction between the composition of animal and vegetable substances is, that animal substances contain the peculiar principle, *azote*, in abundance, which, in the elastic state, forms what was formerly called phlogisticated air, or phlogisticated gas, and which exists in only a very small quantity in vegetable substances. 2. Animal substances contain much more hydrogen, or the basis of inflammable air.*

From these two causes the differences observed in the distillation of animal and vegetable substances arise. The former produce much ammonia, which is a compound of azote and hydrogen; the latter yield very little, and they afford usually even a good deal of acid, the characteristic properties of which flow from oxygen. From the former much oil is obtained, whose predominant principle being hydrogen, it has a great tendency to volatilize, and to separate at a slightly elevated temperature. The latter often afford no perceptible quantity of it. The former can produce

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* Modern researches do not justify this position of M. Berthollet. Sugar and starch, by the analyses of MM. Gay Lussac and Berzelius, contain about as much hydrogen as fibrin does, and very little less than gelatin and albumen; while, by my analyses, wool and silk contain *less* hydrogen than cotton and flax.—*See Phil. Trans. for* 1822.

I subjoin the results of my analytical experiments on the four principal subjects of dyeing.

	Carbon.	Hydrogen.	Oxygen.	Azote.
Wool,	53.70	2.80	31.20	12.30
Silk,	50.69	3.94	34.04	11.33
Cotton,	42.11	5.06	52.83	
Flax,	42.81	5.50	51.70	

The first two, independently of the azote, possess a marked difference of composition, from their excess of carbon and deficiency of oxygen.—T.

prussic acid, which is a combination of azote, hydrogen, and carbon; and vegetables possess this property only in so far as they contain azote. In consequence of this composition, animal substances yield, on being burned, a lively flame, which bursts forth at the commencement; but this flame is, so to speak, speedily quenched by the charcoal that is evolved, which has peculiar characters. Their combustion is accompanied with a penetrating odour, arising from the ammonia and oil formed, which escape inflammation. They are subject to putrefaction, during which ammonia is produced, as it is in distillation, by the more intimate union of the azote and the hydrogen; whereas vegetable substances undergo a spirituous or acid fermentation. We merely indicate in this place ideas which have been developed in particular memoirs.

As animal substances contain a great deal of those principles which tend to assume the elastic state, they have less cohesion in their molecules than vegetables, and less stability in their composition. We may observe, that when they acquire solidity, they owe it most frequently to the mixture, or rather combination, of a foreign substance, such as the phosphate or carbonate of lime in the bones.

Hence, they are more subject to be destroyed by different agents, and more disposed to enter into combination with the colouring particles.

Thus, fixed alkalies, when pure or caustic, destroy animal substances, because they combine with them to saturation, and thereby lose their causticity.*

From this action of alkalies on animal substances it follows, that these substances cannot resist leys, and that alkalies must be had recourse to with much caution in the processes wherein such bodies are dyed; whereas the moderate use of alkalies is not to be dreaded with regard to vegetable substances.

Nitric and sulphuric acids have also considerable action on animal substances. The former decomposes them, with the disengagement of azote, the separation of fat or adipocere, and the formation of carbonic and oxalic acids from a portion of the hydrogen and the charcoal. The latter acid disengages from them inflammable gas, and probably azotic gas, while it reduces the other principles into the carbonaceous state.

Silk appears to approach a little towards vegetable substances, from its inferior disposition to combine with the colouring particles, and from its greater resistance to the action of alkalies and acids. This may arise either from the same principles being here more intimately combined than they are in wool, or more probably from the presence in it of less azote and less hydrogen.† But although the alkalies and the acids exert a less

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* Mem. de l'Academie, 1783.

† The organic structure, and state of condensation in animal and vegetable fibres, should be studied along with their chemical composition, in order to learn their dyeing relations. —T.

lively action on silk than on wool, we must nevertheless use them with much precaution, because the brilliancy of colour sought for in silk appears to depend on the polish of its surface, which we must beware of injuring.

Cotton resists the action of acids better than flax and hemp; and it is with difficulty destroyed even by the nitric acid.

CHAPTER II.

Of Wool.

In the cloth manufactures wool is destined to different purposes, according to the length and fineness of its filaments; but there is a wide distance between the production of fine woolled sheep and ordinary wool. Hence no little gratitude is due to d'Aubenton for fixing public attention on this important object of agricultural economy, and to those individuals who have since prosecuted, with so much steadiness and success, the project of renovating our degenerate breeds by means of Merinos.

Wool is naturally coated with a species of fat, called grease. This coating preserves it from the moths.* Hence it is not scoured till it is going to be spun or dyed.

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* Reaumur remarked, that it was sufficient to rub a stuff with greasy wool to preserve it from moths. *Mem. de l'Academie,* 1728.

In order to scour wool, it is put for about a quarter of an hour into a boiler which contains a sufficient quantity of water, mingled with one-fourth of putrefied urine. The whole is then heated as high as the hand can endure it, and it is stirred about from time to time with rods. It is now washed, and set to drain. The wool is removed thence into a large basket, placed in running water, where it is stirred, till the grease having entirely left it, the water ceases to be milky. It is then taken to be drained. In this operation it loses sometimes more than a fourth of its weight. It is of great consequence that the scouring be carefully performed, because the wool is thus alone prepared for receiving the dye.

The residuum of the first operation is preserved in a tub, to which, from time to time, some putrefied urine is added, so that the grease present in it may serve to render more soluble any thing adhering to the new wool. The ammonia of the putrefied urine contributes probably to this effect. When wool resists this operation, a little soap is added to the liquor; but it is only with much precaution that the use of soap is permitted on fine wools, because it is apt to injure them.

Vauquelin * made experiments on the nature of the grease, from which it appears to be formed, 1. of a soap, with basis of potash, which forms its chief part; 2. of a small quantity of carbonate of

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* Ann. de Chimie, tom. xlvii.

potash; 3. of a notable quantity of acetate of potash; 4. of lime, whose state of combination he could not determine; 5. of a small quantity of muriate of potash; lastly, of an animal matter, to which he ascribes the peculiar odour of the grease.

He regards the ammonia contained in the putrefied urine as not being conducive to its action, and he even advises the use of ordinary soap as better fitted to procure the desired whiteness to wools; but experience leads to results incompatible with the opinion of this skilful chemist.

Wool is dyed in the fleece, or without being spun, principally when it is to be employed for forming cloths of mixed colours; or otherwise it is dyed after being spun. It is then intended chiefly for carpets, but it is most commonly dyed in the form of cloth.

When wool is dyed in the fleece, its unconnected filaments absorb a greater quantity of the colouring particles than when it is spun; for a like reason, woollen yarn consumes more colour than woollen cloth. Cloths, however, exhibit much variety among them, according to their degree of fineness, and the closeness of their texture: besides, the difference of their dimensions, the variable qualities of the dyeing ingredients made use of, and the different circumstances of the operations, teach us not to confide in the precise doses enjoined in the processes usually described. This observation may be extended to all dyes.

For the generality of dyes, wool requires to be prepared with a bath, in which it is boiled along with saline substances, principally alum and tartar. This is called the *bouillon,* which we shall take care to describe under the different processes. But there are dyes for which wool needs none of these preparations. It must, however, be well softened in tepid water, and thereafter squeezed, or set to drain. This is a precaution which must in general be taken with all substances which we wish to dye, that the colour may more easily be introduced into them, and more equally distributed. Wool, in particular, requires heat to enable it to absorb the colouring particles; a circumstance which appears to depend on the disposition of its filaments to form a dense texture.

Monge has explained the mechanism of felting, and the effects of fulling, by the external conformation of wool and the hairs of animals. He has made interesting observations on this subject, of which I shall relate the principal.*

Nothing peculiar can be discovered on the outside of the fibres of wool and the hairs of animals by means of the microscope; yet " the surfaces of these objects are not smooth; they must be formed either of plates, which cover each other from the root to the point, nearly as the scales of fish overlap each other from the head of

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* Observations sur le Mécanisme du Feûtrage. *Ann. de Chimie,* tom. vi.

the animal towards its tail; or rather perhaps of superposed zones, as is observed in horns.

"If we seize a hair by the root with one hand, and draw it through the two fingers of the other, from the root towards the point, we experience scarcely any friction, or any resistance, nor do we perceive any noise; but if, on pinching it by the point, we make it slide equally between the fingers of the other hand, from the point towards the root, we experience a resistance which does not exist in the first case, and a tremulousness perceptible to the touch is produced, which is also manifested by an audible sound.

"We thus perceive that the contexture of the surface of the hair is not the same from the root towards the point, as from the point towards the root, and that a hair, when pressed, ought to experience more resistance in sliding and taking a progressive movement towards the point, than in sliding towards the root; but as this very contexture forms the principal object of this memoir, it is necessary still farther to confirm it by some other observations.

"If, after seizing a hair between the thumb and the forefinger, we make the two fingers slide alternately one over the other in the direction of the length of the hair, the hair takes a progressive movement in the direction of its length, and this movement is always towards the root. This effect does not depend either on the nature of the skin of the fingers or on its contexture, for if we turn back the hair, so that its point is placed where its root was, the movement ta place reciprocally in the contrary direction; th is to say, it is turned always towards the root.

" These observations, to which Monge adds some others, are all referred to the hair of his head taken as an example; but they equally hold true of horse hair, fibres of wool, and in general of the hairs of all animals. The surface of all these objects, therefore, is formed of rigid plates, superposed or tiled from the root to the point, permitting the progressive movement towards the root, and resisting a similar movement towards the point.

" This conformation is the main cause of the tendency to felting, which the hairs of all animals in general possess.

" The hatter, in fact, on striking with the cord of his bow the flocks of wool, detaches and disperses in the air each of the particular fibres; these fibres fall down over one another in all directions on the table, where they form a layer of a certain thickness. The workman then covers them up with a cloth, which he presses with his outstretched hands, working them about in different directions. The pressure approximates towards each other the woollen fibres, and multiplies their points of contact; the agitation gives each of them a progressive movement towards the root. By means of this movement the hairs interlace, and the *lamellæ* of each hair, by hooking into those of other hairs which lie in an opposite direction, maintain the whole in the compact texture which the pressure first gave. In

ortion as the tissue is compacted, the pressure
the hands ought to increase, both for the fur-
er condensation, and for promoting the progres-
ive movement of the hairs, as well as their inter-
lacement, which now meets with greater difficulty. But in all this operation the fibres of wool grapple only with one another, and not with the cloth, whose fibres, as we have already said, are smooth, and do not present the same facility in this respect.

"The conformation at the surface, of the fibres of wool and the hairs of animals, does not constitute their sole disposition to felting. It is not enough that every fibre shall take a progressive movement towards the root; it is not enough that the inclined *lamellæ*, on grappling with one another, shall maintain the texture in the state into which the compression has put it;—it is further requisite, that the fibres shall not be straight like needles; in consequence of the agitation, each of them would continue its progressive movement without changing its direction, and the effect of the operation would be, to remove them all from the centre without producing any tissue. It is necessary, therefore, that each fibre should be twisted, that the extremity which is on the side next the root be disposed continually to change its direction, to interlace itself around new fibres, and to turn back on the fibre itself, if so determined by some change in the position of the rest of its length. Wool being naturally constructed in this manner, is peculiarly well adapted for felting, and may be so employed without being subjected to any previous operation.

"But the furs of the rabbit, the hare, and the castor, are naturally straight; they cannot be employed alone for felting, without having undergone a preliminary operation, which is called *secretage;* and which consists in rubbing them, before they are stripped off, with a brush moistened with a solution of mercury in nitric acid. This solution, by acting on only one side of the substance of the hairs, alters their right-lined direction, and communicates the disposition for felting which wool naturally possesses.

"The operation of *fulling* woollen stuffs, has so close a relation with felting, that we cannot dispense with entering into some details on this subject.

"The roughness with which the fibres of wool are bristled at their surface, and the disposition which the fibres have to take a progressive movement in the direction of the root, is an obstacle to the spinning of wool and to the fabrication of stuffs. In order to spin the wool, and afterwards weave it, we are obliged to coat all the fibres with a film of oil, which, by filling up the cavities, renders the asperities less perceptible; just as a film of oil is put upon a smooth file, when we wish to render it still smoother. When the piece of stuff is manufactured, it must be deprived of this oil, which gives it a disagreeable colour, and constitutes a kind of filthiness, which would be an obstacle to dyeing. For this purpose, it is carried to the fulling-mill, where it is beat with mallets in a trough filled with water, through which clay (fuller's earth) has been diffused. The clay combines with the oil, which it renders soluble in water; both are carried off by the fresh water which the machine itself brings upon it; and at the end of a certain time the stuff is scoured.

" But scouring is not the only object of the fulling. The alternate compressions which the beetles exert on the piece of stuff, especially when the scouring is well advanced, produce an effect analogous to that of the hand-pressure of the hatter. The fibres of wool which compose one of the threads of the woof or of the warp, take a progressive movement, get introduced into one of the neighbouring threads, then into those which follow, and soon all the threads both of the woof and warp are felted together. The stuff, after having suffered a narrowing in its two dimensions, partakes of the nature both of web and felt; it may be cut without being liable to open out its threads, and there is no necessity for hemming the different pieces which enter into the composition of a garment. If it be ordinary knit wool, the stitch is no longer apt to run when it happens to escape. Lastly, the threads of the woof and the warp being no longer so well defined, or so distinct from each other, the stuff, which in other respects is thickened, forms a warmer clothing."

CHAPTER III.

Of Silk.

Silk is naturally coated with a substance, which has been regarded as a gum, to which it owes its stiffness and elasticity. The silk most common in our climates, contains besides a yellow colouring matter.

The greater part of the uses to which silk is destined, require it to be not only deprived of its colouring matter, but also of the gum. This twofold object is accomplished by means of soap. The name of *décreusage* (scouring), is given to the operation by which silk acquires its pliancy and whiteness.

The *décreusage* must not be so complete for the silks which are to be dyed as for those intended to remain white ; and it should even differ according to the colours proposed to be given. This difference chiefly consists in the proportion of soap that is employed. Thus, for ordinary colours, we content ourselves with boiling the silk for three or four hours in a solution containing 20 parts of soap for every 100 parts of silk, taking care to fill up the boiler from time to time with water, in order to have always a sufficiently large bath. The quantity of soap is increased for silks which are to be dyed blue, and more especially for those which are to be dyed *ponceau* (flesh-red), cherry colour, &c.; because these colours require a whiter ground than the less delicate ones. In treating of each colour, the proportions of soap suitable for the silk are indicated.

When silk is to be used white, it is made to undergo three operations. The first is called *dégommage* (ungumming). It consists in keeping its hanks in a solution of 30 parts of soap for 100 of silk. This solution must be very hot, but not in ebullition. When the dipped portion of the hanks is entirely ungummed, which is known by the silk assuming whiteness and flexibility, the hanks are turned about (shaken over) on the rods, in order to subject the portion which had not been plunged to the same operation; and they are then withdrawn from the bath, and fastened on pegs, in proportion as the ungumming is finished.

The second operation is the boil. The silks are enclosed in bags of coarse cloth, 12 or 15 kilogrammes of silk being put in each bag, called a *pocket* (poche). A soap-bath similar to the former is prepared, with a smaller proportion of soap; and they are boiled for an hour and a half, taking care to stir about the bags, so that those which touch the bottom may not experience too great a heat.

The third operation is called *whitening* (blanchiment). This operation is intended principally to give the silk a slight shade, which may render the white more agreeable. Different names are given to the white, according to the shade. Thus we have china-white, silver-white, azure-white, thread-white. A solution of soap is made, such that, on beating it, a froth is obtained from which we may judge if it be of a proper strength. For the china-white, which should have a somewhat red cast, a little anotto is added. The silk is then left in it till it takes the desired shade. To the other whites more or less of a blue cast is given by means of azure, which is added to the solution of the soap, though some of it has already been put into the boil.

To prepare the azure, some fine indigo is washed two or three times in water moderately hot, when it is well ground in a mortar, and boiling water is thrown over it. It is allowed to settle, and the liquid is used, which retains only the most subtile parts. This is called *azure;* for which may be substituted a little of the liquor of a fresh vat of indigo.

At Lyons, where a more perfect white is given than at Paris, no soap is employed for the third operation; but after the second, the silks are washed, sulphured, and passed through azure diffused in river water. In this method, it is of importance to employ a very limpid water.—When the silks have become very uniform, and have taken the wished-for shade, they are wrung out and dried.

The white obtained by the method now pointed out, is not brilliant enough for silks intended for white stuffs. They must still be exposed to the fumes of sulphur. This operation will be described in the article on sulphur.

Since soap appears to injure the lustre of silk, the Academy of Lyons proposed, in 1761, as the subject of a prize, to find a method of scouring (*décreuser*) silks without soap; and this prize was adjudged to Rigaut de St. Quentin, who proposed to substitute for soap a solution of salt of soda, or carbonate of soda, dissolved in a quantity of water large enough not to affect the silk. But inconveniencies must have been found in the employment of this method, which was probably too active, since no use is made of it, although it is known, and may be easily practised.

Collomb* published some observations on the bleaching of silk by the action of water alone, which merit much attention. Having perceived that a hank of yellow silk, which he had boiled about three hours in common water, had lost nearly an eighth of its weight, he repeated the ebullition twice, and carried by this means the diminution of weight to a fourth.

The silk which suffered this loss of weight, preserves, however, a yellow, or rather a chamois colour, which renders it unfit for making stuffs intended to remain white, or to receive some colours whose beauty depends on the whiteness of the ground to which they are applied; but it answers very well for colours which that tinge cannot injure. Thus the black dye which it took appeared preferable to that of silk bleached with soap.

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* Observations sur la Dissolution du Vernis de la Soie. Journ. de Phys. Août 1785.

After this operation, the silk remains very strong and sinewy (*nerveuse*); and threads of it supported weights which broke threads bleached with soap.

Eight hours of brisk ebullition are required for dissolving away the whole varnish of silk, in which it loses a little more than one-fourth of its weight; but the ebullition ought to last longer when the barometer is low, because the greater the weight of the atmosphere, the higher is the degree of heat which boiling water takes.

This consideration led Collomb to try the boiling of silk in a Papin's digester; and in fact it required only an hour and a quarter to effect the complete solution of the varnish, although the degree of heat was inferior to what produced some of the phenomena observed by philosophers in this concentrated ebullition.

The substance which the water dissolved, when evaporated, is black, brittle, and brilliant in its fracture. On distillation, it afforded the usual products of animal matter. It dissolved readily in hot water, leaving very little on the filter. The solution, which was clear, and of a greenish-yellow colour, was not sensibly affected by acids or alkalies.

The solution of alum produced in it a precipitate of a dirty-white colour; that of sulphate of copper, a black-brown precipitate; that of sulphate of iron, a brown precipitate; the nitro-muriatic solution of tin, a white precipitate; the acetate of lead, a brown precipitate.

All these precipitates are scanty, and more or less viscid. Infusion of nut-galls, and of sumach, occasioned a white precipitate.

Alcohol does not dissolve this substance even by ebullition, but only a yellow colouring portion. This solution left, on evaporation, a scaly residuum of an amber-yellow. On boiling a gramme of this substance in 100 grammes of alcohol, containing some drops of muriatic acid, its solution was effected; but, on cooling, this substance took the form of jelly.

The substance taken from silk in the scouring *(décreusage)*, is therefore of an animal nature; whence the soap water which has served for the scouring speedily putrefies. When this substance is no longer retained by its affinity for silk, it becomes soluble in water, but not in alcohol. Although it is not of a vegetable nature, the term *gum* seems sufficiently proper. The yellow colouring matter dissolves in alcohol. When this part is separated, the gum becomes brown. It would seem that this colour is caused by the heat of ebullition, since, when the yellow colouring portion only is removed, by the process of Baumé, of which we shall presently speak, the silk remains white.

In the process of Collomb, the gum is removed, carrying with it only a portion of the yellow colouring particles; while, in scouring with soap, the gum, and yellow colouring parts, are both carried off from the silk.

When silk is intended for the manufacture of blonds, laces, and gauzes, it should have its natural stiffness and elasticity. The greater part of the silk produced in our climates has a yellow colour. The white silk of China is therefore principally employed for these objects, and a few others. It is not yet positively ascertained whether the Chinese silk is naturally white, or rendered so by some unknown process. According to Poivre, this silk is bleached by exposing it to the sun. But some other circumstance is necessary; for this method has been tried without success. Baumé has published a process which he considers as analogous to the Chinese one.*

This process consists, 1. In infusing the yellow silk, or that which has not naturally a sufficiently pure white, in water heated to 25° Reaum., to destroy the mutual adherence which the threads had contracted in the winding; 2. In making this silk undergo two successive macerations, longer or shorter according to the temperature, in a mixture of alcohol containing 1-64th of its weight of muriatic acid; 3. In washing the silk with much care immediately after this operation, which, on losing its colouring part, has given up but a portion of its gum; 4. In drying this silk in a state of extension, to hinder it from crisping. The muriatic acid employed ought to be thoroughly free from the nitric acid, which gives, as we have seen, a yellow colour to animal substances. For

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* Ann. de Chimie, tom. xvii.

the same reason, such muriatic acid must be avoided as has been rendered yellow by chlorine. Hermstadt affirms, that he repeated this operation with success.

A skilful chemist, Giobert, makes objections to this process, for which he substitutes a new one. We shall remark, meanwhile, that in his experiments he employed 1-48th of muriatic acid, while Baumé prescribed only 1-64th. We shall here present the extract which has been given of his work.*

" The preparation of the acid pointed out by Baumé is very embarrassing. The green colour which the liquid assumes, the species of jelly which it forms around each filament, and still more the diminution of weight in the silk, are sufficient to indicate, that it would not be correct to view in the action of this liquid only the destruction of the colouring matter. Even in retaining a portion of its rawness *(crud)*, the silk is far from preserving so much of it as is desired in the arts ; and this process, which involves considerable expense, becomes more costly than is imagined, from the diminution in the weight of the silk.

" Crell and Brugnatelli proposed chlorine. But it is known, that silk comports itself in the same way with this acid as animal substances do, that is to say, it becomes yellow. Yet we shall presently see that it may be employed. When this

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* Bibliot. Ital. tom. i.

substance is used in the form of gas, Giobert found that the silk was soon destroyed by it.

"On employing it in the state of a pretty concentrated solution, the yellow colour becomes weaker, and apparently approaches to white; but on taking it out of the aqueous chlorine, the silk is of a yellowish colour, and this hue is more durable than its natural one.

"From this result it appears that chlorine exercises on silk a twofold action; that is to say, it destroys its colouring matter on the one hand, and on the other, it makes the same impression as on animal substances in general—a change indicated by a yellow tinge.

"This last impression is destroyed by the action of sulphurous acid; and it is in the combined and alternating action of it and chlorine that the author has attempted a new mode of bleaching.

"In the preceding experiments, and in all those where aqueous chlorine, however little concentrated, was employed, Giobert observed that the silk was considerably weakened. Very frequently, after being well washed, the filaments broke in the wringing.

"The same liquor diluted to a great degree no longer produced this effect, yet it exerted a well marked action on the colouring matter of the silk. On coming out of it, the silk retains a portion of its natural colour, and being a little oxygenated by the agency of the chlorine, it exhibits its effects and appearances.

" On passing it then into liquid sulphurous acid, also very dilute, the yellow tint is destroyed.

" Giobert has succeeded in whitening the silk completely, and preserving its raw feel, by passing it alternately through these two liquids for ten or twelve times, finishing the operation with the sulphurous acid.

" It is of the greatest importance to multiply the immersions, and not to employ strong gaseous impregnations, by which the silk would be either destroyed or considerably weakened.

" Silk bleached by this method is scarcely diminished in weight. It retains its raw feel, its flexibility, and does not appear to get stiff, while the bleaching is uniform in all its parts.

" When it was compared with the silk bleached by the process of Baumé, the latter was found to present a more agreeable gloss, while the former had merely a dead-white. This circumstance does not appear to Giobert very important, because the chief use of bleached raw silk is in the manufacture of gauzes ; and much gloss is not required in this kind of stuffs.

" The dyers believe that silk which has received the fumes of sulphur is not well adapted to receive colours. Giobert attempted to rectify this principle, with raw silk bleached by the process just detailed. This silk took every colour, and particularly the finest black."

Aluming ought to be considered as one of the general operations of silk dyeing, because without alum the most part of colours applied to silk would possess neither beauty nor permanence.

To execute the aluming there is put into a tun or tub about 40 or 50 buckets of water, and 20 or 25 kilogrammes of Roman alum, previously dissolved in a kettle-full of sufficiently hot water, stirring carefully during the mixture, to prevent the crystallization of the alum.

After washing and beetling the silks, and even wringing them on the jack and pin,* to extract the soap which they may have retained, they are plunged into the alum bath. Here they are left for eight or nine hours, after which they are twisted by hand over the tun (vat), and taken to the river to be washed.

We may pass as much as 75 kilogrammes of silk through a bath like the preceding, without being under the necessity of adding fresh alum. But when it is perceived that the bath begins to become weak, which habit teaches by the taste, 10 or 12 kilogrammes of alum are dissolved, which are put into the bath, as at first; and thus it is continually renewed, till it begins to emit a disagreeable smell. It is then thoroughly exhausted by passing the silks through it which are intended for dull colours, such as browns, chesnuts; after which it is emptied out, and a new alum liquor formed.

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* The usual frame for wringing hanks of yarn, with the aid of a screwed rod.—T.

Silks are always alumed in the cold, because, when they are alumed in a hot bath, they are apt to lose a portion of their lustre.

CHAPTER IV.

Of Cotton.

Cotton is the down or wool (*bourre*) contained in the pod of a plant which grows in hot countries. This down is separated from the seeds which it envelops by means of a kind of mill.

Climate has a great influence on the qualities of cotton, and the species of the cotton plant seem to correspond to the degree of heat.* But a great variety are found in the West India islands; and it appears from what Bennet says,† that the colonists have hitherto neglected to make a selection of those which would be most advantageous, whence they have lost a great part of the benefits which they might have derived from this valuable production.

Five species of the cotton shrub have been distinguished, which contain many varieties. Linnæus has distinguished these five species by the following names: *gossypeum arboreum*, or the

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* Essais sur les Caractères qui distinguent les Cotons des diverses parties du monde, &c. par M. Quatremere Disjonval.

† Transactions of the Society instituted at London for the Encouragement of Arts, Manufactures, and Commerce, vol. i.

cotton tree of India; *gossypeum religiosum*, a great shrub which grows also in India; *gossypeum Barbadense*, a biennial shrub cultivated in Barbadoes; *gossypeum hirsutum*, a shrub which is perennial in the hot climates of America, and annual in the cold; *gossypeum herbaceum*, which seems to be originally from Persia, but which is cultivated in the islands of the Archipelago, in Egypt, Malta, and Sicily. The Russians cultivate it even in the government of Caucasus.

To these species may be added the cotton of Siam, remarkable for the fineness and silkiness of its filaments.

According to Guthrie, there has been cultivated for some time in Germany an *asclepias, asclepias syriaca, Linn.* which yields a very silky species of cotton.* Manufactures have been established in Saxony of stuffs with this cotton, which rival silk in lustre.

The principal differences of cotton consist in the length of its filaments, their fineness, their solidity, and their colour. In the last point of view, several species are distinguished in commerce, which differ not only in their absolute value, but also in the uses for which they are intended.

The colour of cotton varies from deep yellow to white. The highest coloured is that of Siam and Bengal; with which stuffs are often made that preserve the native hue.

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* Memoirs of Manchester, vol. v. part 1.

Cotton has become, by the extent and variety of its uses, one of the principal objects of manufactures and commerce. From its manufacture being conducted with little expense of labour, India has particularly derived much of the treasure constantly poured into it.

A nation celebrated for its genius in the arts, has succeeded in compensating the difference in the rate of wages by the expedition of machinery, and has thus drawn into its bosom this source of prosperity. It must preserve exclusively the great advantages which it now derives, were other nations not to endeavour to promote, by particular measures of administration, a competition of manufacture capable of supporting a part of their population.*

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* Some respectable philosophers, while claiming freedom for commerce and industry, appear to have made too wide an application of their principles of political economy, when they inveigh against those restraints which the vigilance of government puts on the introduction of particular products of foreign manufacture.

When manufactures have acquired a marked superiority by peculiar processes, when long practice has carried these processes to perfection, and when the dexterity acquired by their workmen bids defiance to competition, we must for ever renounce them, or these advantages must be balanced by import duties, or even by prohibitions.

It is said, that we thereby force capital into other directions less natural and advantageous. This maxim is true with regard to objects in which manufactures possess natural advantages or disadvantages.

But when merely temporary disadvantages are to be countervailed, when an object of great consumption is concerned, To prepare cotton to receive the dye, it is subjected to an operation, called in French *décreusage* (scouring). Some persons boil it in sour water; but most frequently an alkaline ley is employed. In this the cotton is boiled for two hours, after which it is wrung out. It is then rinsed in the river till the water runs off clear, when it is dried.

Cotton cloth intended for printing is immersed for some time in water charged with one-fiftieth at most of sulphuric acid, after which it is washed with care in running water, and dried. The acid used in this operation dissolves the calcareous earth, and the oxide of iron, which might have injured the colours.

The aluming is given in the proportion of a quarter of alum for one part of cotton. The alum is dissolved with the precautions pointed out in the preceding article, but a solution of soda is added to it, which may be estimated at about one part of soda for six of alum. Some persons introduce a very small quantity of tartar and arsenic. The yarn is well impregnated with this solution, by working it in small portions;

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which may afford employment to a large portion of the population, it is the interest of the consumers themselves to submit to a temporary impost, which may serve as a premium to a new branch of industry, and may even create sufficient capitals to those who undertake it, by affording extraordinary profits up to a certain stage. They are in the predicament of a landed proprietor, who renounces, for some time, a part of his revenue, to establish a canal of irrigation on his estate.

after which the remainder of the bath is poured upon the whole yarn collected in a vessel. It is left there for twenty-four hours. On coming out of the aluming, it is set to purge itself in running water for an hour and a half or two hours, and it is then washed. Cotton absorbs about one-fortieth of its weight in this operation.

The galling is made with different proportions of gall-nuts or other astringents, according to the quality of the astringent, and the effect wished to be obtained.

The gall-nuts, bruised, are to be boiled about two hours in a quantity of water, which ought to be proportioned to the quantity of yarn to be galled. The bath is then allowed to cool, so that the hand may bear dipping in it. It is divided into portions, which are made as equal as possible, in order to operate with small parcels, as is mentioned under aluming; and the remaining liquor is in like manner thrown over the whole. Here it is left for 24 hours, especially when it is intended for maddering and for black; with regard to other colours, from 12 to 15 hours may suffice; after which it is wrung out and dried.

When the galling is given to stuffs that have already received a colour, it must be done in the cold, in order not to alter this colour.

Alumed cotton takes a greater increase of weight in the galling than what is not alumed; for although alumina fixes in only small quantity on cotton, it communicates to it the property of combining much better with the astringent principle, as also with the colouring particles.

CHAPTER V.

Of Flax and Hemp.

Since flax and hemp present the same properties, in reference to dyeing, they are usually confounded together in this work.

If cotton be an important object to our industry, flax and hemp merit peculiar attention, both as a territorial production, and as the most extensive source of employment to the people. This manufacture is spread over the whole country, and is subdivided into branches, from the fabrication of cordage to that of lace, and it fills up the chasms of rural labours.

One consideration which ought not to be overlooked, is, that the land most proper for hemp is that of marshes, from which the water has been drained, and that it is a production particularly adapted to small cultivators.*

Flax and hemp must undergo several preparations before they can receive a dye. The first is steeping, by which the bark of the plant is rendered separable, so as to become fit for spinning. Steeping is an operation of such importance, from the influence which it possesses on the quality

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* Instruction familière sur la Culture et le Roui du Chanvre, à l'usage des gens de la campagne, par Pertuis.

and quantity of the product, and from the deleterious qualities which it may communicate to the air, that it is proper to give some idea of the principles on which it should be conducted. The steeping of flax, in particular, has engaged the attention of practical men.

In steeping, it appears that a glutinous juice, which holds the green colouring part of the plant in solution, and which unites its cortical with its ligneous portion, suffers a more or less complete putrefaction, according to the method employed; for, as Rozier remarked,* carbonic acid gas and inflammable gas are disengaged. This substance seems to resemble closely the glutinous portion dissolved in the juice expressed from green plants, which is separated along with the colouring particles when it is exposed to a heat bordering on ebullition, and which putrefies, and yields ammonia by distillation.

Although this substance be held in solution in the expressed juice of plants, there is a probability that water alone cannot separate it sufficiently from the cortical part; and hemp which has been steeped in too rapid a stream, wants pliancy and softness.

If the steeping be performed in stagnant waters, the hemp contracts a brown colour; but, above all, it loses its durability, and exhales vapours productive of dangerous maladies. What is steeped by exposing it merely to the action of the

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* Essai sur la Culture et le Rouissage du Chanvre, par l'Abbe Rozier.

elements on the ground, is also weakened, and requires much time and manual labour.

It appears, therefore, that steeping is performed in the most advantageous manner in tanks placed on the banks of rivers, in which the water may be renewed, so much as to prevent a putrefaction hurtful to the hemp and detrimental to health, without obstructing the putrefaction necessary to render the glutinous substance soluble in water.

Rozier found, that the steeping process went on when the hemp was covered with a layer of earth, and he recommends this method; but it has been ascertained that the hemp was too easily affected in this operation.

Proset* has proposed to mix a small quantity of caustic alkali with the water in which the steeping takes place, in order to increase its solvent power, and to prevent the putrefaction; but it appears from the experiments of Home, that alkalies retard the operation of the steeping, and render the flax liable to break.†

During the maceration, as well as the previous and subsequent drying, the green colouring particles suffer an alteration, like that observed in the green substance of plants which have been exposed to the action of air and the influence of light. Their colour passes to yellow, dun, or even brown, by an agency which we have compared to that of a slight combustion.

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* Mem. sur le Rouissage du Chanvre.

† Essay on Bleaching.

That substance is partly reduced into powder, which is dispersed during the dressing, rendering this operation dangerous to those who practise it. Another portion remains attached to the fibres; but perhaps dissolved in the alkaline leys employed before the bleaching, whereby all this foreign matter ought to be separated.

For avoiding the acrid dust which rises during the hatcheling, Marcandier has recommended to macerate the fibres in small portions in hot water, to wash them with much care, and thereafter to dry them. By this means we may diminish the colouring matter, and render the flax or hemp softer and better prepared for the action of the hackle. He has even suggested the use of an alkaline solution.*

On a more complete solution of the colouring particles, is founded a process published by the Prince de Saint-Sever, to obtain fine dressed hemp.† He recommends to put the tress of hemp in a ley made with a solution of two parts of soda to one of lime, next to impregnate it with soap, to digest it for some time, then to wash it well, and lastly, to hackle it. Several processes analogous to the preceding have since then been practised, under the veil of mystery. Their results had an imposing aspect. But experience has sufficiently shown, that besides the expense which they incurred, these processes increased the proportion of tow, and the yarn obtained had less

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* Traité de Chanvre.

† Journ. de Physique, introd. tom. ii.

durability, and little advantage in beauty over the yarn yielded by the unprepared hemp.

Bralle, an old curate of the department of the Somme, occupied himself regularly for several years with the means of improving the preparation of hemp, as an object of great national interest. His first attempts consisted in steeping hemp, as soon as it was taken from the ground. On coming out of the steeping, he separated the bark from it, which easily came off. After cutting the stem near the root, and dipping it in a weak solution of black soap, he washed it with much care before desiccation. The colouring portion which would have become insoluble, except in alkalies, may also be dissolved and carried off by water assisted by a little soap. The fibre is then much whiter. By combining the action of the sun with this process, he succeeded in making it still whiter.

These operations had the inconvenience of requiring long and minute manipulations. Bralle, however, hit upon a process, by which a large quantity of hemp may be steeped in a few hours, with the advantage of freeing the stems from their bark without any waste, of preserving the length of the fibres, and consequently of producing much less tow.

The process of Bralle, whose efficacy has been verified at the *Conservatoire des Arts* on hemp intended for cordage and sail-cloth, has just been published by order of government. It consists in keeping the hemp plunged for two hours in water, containing a forty-eighth part of green soap (soft soap) in solution, which is maintained at a temperature of from 72° to 75° Reaum. (NOTE I.)

A mode has been discovered of giving to the dressed hemp, and even to the tow, a division and fineness which qualify it for the same spinning processes as cotton; so that with this preparation alone, or mixed with cotton, stuffs may be made which have a much more considerable value, than those of hemp in its natural state.

Marcandier seems to be the first who engaged in this process. He recommends to give to the tow, first of all, the preparation which he prescribed for the dressed hemp. *In carding it like wool, a fine medullary white substance is got, for which heretofore no use was known. It can be employed by itself in this state, not only to make ouates (fine cotton), which, in many respects, is better than the ordinary ouates, but it may also be spun into a very fine yarn. It may likewise be mixed with cotton, silk, wool, and even hair; and the yarn resulting from these different mixtures, furnishes, in its numberless variety, materials for new trials interesting to the arts, and to several manufactures.*

This object has engaged much attention in Germany. Hermstadt quotes several works which treat of it.* He states, that, according to Meidinger, the staple of hemp acquires the elasticity of cotton, when, after being purified by a solution of

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* Grundriss der Farberkunst.

potash and muriate of soda, it is fixed on cylinders of wood, and dried in a stove. It is also asserted, says Hermstadt, that hemp takes a fine texture when its moist fibres are put into a wooden chest, with alternate layers of wood-ashes, closing the chest with a cover, and putting it into a stove, heated not just so high as to burn the wood.

Hermstadt informs us, that the hempen webs which have received these preparations, lose the appearances of cotton by repeated washings.

In treating of bleaching with oxygenated muriatic acid, another process will be pointed out.

Flax and hemp intended to be dyed, must be subjected to the same operations as cotton, namely scouring *(décreusage)*, aluming, and galling.

SECTION III.

OF BLEACHING BY THE OXYGENATED MURIATIC ACID.

INTRODUCTION.

The art of bleaching by oxygenated muriatic acid (chlorine), is a direct application of the chemical properties of this acid; for the first knowledge of which we are indebted to Scheele, but which were developed and submitted to a regular theory in 1785.

At this period, the first attempts at applying this acid (now the element chlorine) to bleaching were promulgated. These were soon prosecuted in England by the celebrated Watt, and afterwards by Bonjour, Descroizille, Welter, Widmer, and Haussmann. A description of this art, still in its infancy, was published in the Annales de Chimie for 1789; meanwhile it continued to make some advances, which were successively published. A second description was given of it, chiefly on the data of Welter,* who had perse-

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* Journal des Arts et Manufactures. An. 3.

vered in its practice on the great scale; and those who are acquainted with this able chemist, know what confidence may be reposed in his observations.

Since then, different treatises on this process have appeared. We shall here give an idea of such of them as have come to our knowledge.

Pajot des Charmes published one,[*] which appeared in the year 8. In this, he speaks only of the first description which had been given in the Annales, and neglects one which had been made public five years before his own work, and of which several separate editions had been given.

He represents the process which had been promulgated as very difficult to execute; but the corrections which he pretended to introduce, do not appear to us to have any other effect than to diminish its precision or advantages. Thus he suppresses the intermediate vessel, which we considered to be useful. He recommends, as a very beneficial change, to substitute leaden tubes for those of glass. He mixes potash with the liquor (aqueous chlorine) to suppress its odour, the effect of which mixture had been appreciated in the original description: he regards the odour of oxygenated muriatic acid, in the way it had been prescribed, as an insurmountable obstacle; and he gives an account of the distress which he had suffered in repeating this process. He would

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[*] L'Art du Blanchiment des Toiles, Fils, et Coton de tout genre.

have become satisfied that the process might be executed without inconvenience, had he carefully followed the directions, or had he visited the establishments conducted by Widmer, Welter, or several others who used it at that period. He exclaims against the length to which the prescribed number of leys and immersions must give rise. *The limits of this number* had been said to be *between four and eight*, and we find (page 106 of his treatise) that he increases the leys to six, and the immersions to seven. He gives, moreover, a process for making sulphuric acid, by which sulphurous acid only can be obtained, &c.

Chaptal published a notice about a process long used for bleaching cotton in the southern parts of France,* which had been pointed out in our second account of bleaching. The cotton is impregnated with a solution of soda, and subjected to the vapour of boiling water in a close vessel, where this vapour suffers compression; after which it is exposed for some days on the grass. This process gave occasion to O'Reilly to publish a work on bleaching.† We shall not discuss the method which he there extols, because his assertions have not hitherto been confirmed by the experiments to which they led several operators. We shall merely remark, that in the same work he describes an apparatus as well adapted to the preparation of oxygenated muri-

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* Bulletin de la Société Philomatique. Brumaire, An. 8.

† Essai sur le Blanchiment.

atic acid; but this apparatus is such, that the vapour of the oxygenated muriatic acid, by its elastic action, would cause all the water of the intermediate vessel to spout out by the tube of safety, which in fact would soon be emptied by the same cause. Several of his details shew that he described from imagination.

We owe to Westrumb* a work on the new mode of bleaching; but this skilful chemist intimates, that he describes this art only from his own trials, without taking into account what experience had taught to actual practitioners. Rupp has given interesting experiments on this subject, of some of which we shall avail ourselves.†

We do not hope always to make the best selection in the operations which we are about to describe; but we shall be guided particularly by the observations of Widmer and Welter, who have conducted this process for several years with increasing success. We shall not advance, on views simply conjectural, even the modifications which might be contrived; but experience will undoubtedly teach us more and more to simplify, improve, and extend the usefulness of the process. Those who wish to employ it only on inconsiderable objects, by neglecting trifling interests, or by resting satisfied with partial effects, may easily simplify both the apparatus and the manipulations.

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* Bemerkungen and Vorschlage für Bleicher.

† Mem. of Manchester, vol. v.

In particular cases, bleaching may be greatly abridged, and even reduced to a few hours; but we must study, in a manufacture, to establish a series of operations, the success of which shall be proof against accidents, and which shall steadily procure employment to the same workmen, rather than accelerate any particular process.

CHAPTER I.

Theory of Bleaching.

CHEMISTRY has made such progress in our times, as to render an acquaintance with it indispensable to the practice of several arts; but the one which has for its object the bleaching of yarn and cloth by the oxygenated muriatic acid, requires, in particular, an operator to whom the science is not unknown.

Oxygenated muriatic acid (chlorine), is the agent substituted in this mode of bleaching for atmospherical air, which requires tedious exposure on the grass. For directing its preparation and effects, we must therefore be well skilled in its properties.

Muriatic acid (the marine acid of the old chemists, and the hydrochloric of the modern French school) combines with oxygen, and thereby assumes the properties of oxygenated muriatic acid; but to make this combination effective, the oxygen must have lost its elastic state. Thus it exists in the oxide of manganese (manganese of commerce) in very considerable quantity. When, therefore, one part of oxide of manganese is mixed with four parts of the fuming, or six parts of ordinary muriatic acid, one portion of the acid combines with the oxide of manganese, with the disengagement of the oxygen superfluous to this combination, which combining immediately with another portion of the muriatic acid, thus forms the oxygenated muriatic. The operation is promoted and completed by the action of heat. The oxygenated muriatic acid assumes on its separation the gaseous state, when it is soluble in water. The resulting liquid is of a greenish-yellow colour, and of a very penetrating odour. If the temperature approaches that of freezing water, the oxygenated muriatic acid gas becomes concrete, and adheres to the tube which conducts it into the water, whence it precipitates, so that the liquid is less impregnated than at a somewhat higher temperature.

It is easy to shew that the oxide of manganese contains much oxygen; for on urging it with a strong fire, it evolves a great quantity; after which the oxide can produce but very little oxygenated muriatic acid.

We may be easily satisfied also of the existence of oxygen in the oxygenated muriatic acid. We have only to expose to the light of the sun a phial filled with the above liquid, from which phial a bent tube dips under a receiver filled with water. Bubbles of air are soon disengaged, which pass into the receiver, constituting an elastic fluid, which possesses all the properties of pure air or oxygen gas. When these bubbles cease to issue, the liquid has lost its odour, colour, and all its distinctive properties. It is now water impregnated with ordinary muriatic acid. The composition and decomposition therefore equally prove, that oxygenated muriatic acid is simply a combination of muriatic acid and oxygen. But this speedy decomposition by light shews, that the oxygen very readily abandons the muriatic acid, either to assume the elastic state, or to enter into other combinations; and it is on this that the characteristic properties of oxygenated muriatic acid depend.

If vegetable colours be plunged into oxygenated muriatic acid, they disappear more or less quickly; and when there is a mixture of different colouring particles, some disappear more readily than others, the whole, however, being more or less affected. When the oxygenated muriatic acid has thus exhausted its action, it is found to be reduced to the state of ordinary muriatic acid; the colouring particles have therefore abstracted its oxygen. If we evaporate the liquid in order to examine the state of the colouring particles, we find that it yields a blackish residuum, as if its particles had suffered a slight combustion. (Note K.)

It is in this way also that colours are more or less speedily destroyed by the action of the air, especially when it is promoted by the solar beams, as was shewn in the preceding section. Hence the oxygenated muriatic acid easily and quickly produces the effects which air and light operate in a longer space of time, because the oxygen, deprived in part of its elasticity, and adhering loosely to the acid, enters readily into combination with the substances for which it has an affinity.

The filaments of flax and hemp are enveloped in colouring particles, retained in them by a true combination, and which mask their whiteness. When these colouring particles combine with oxygen, they are decomposed, so as to become soluble in alkalies. Hence the potash of the ley dissolves, and separates them from the filaments. On repeating several times the exposure on the grass, or the immersion in the oxygenated muriatic acid, and the action of the leys, we separate all the colouring particles of the filaments which remain white. By these operations the yarn loses nearly one-third of its weight.

If an acid be poured on the solution of the colouring particles in potash, and if we dry the precipitate formed, which remains upon a filter, it is blackish, and has the appearance of a body which has suffered a slight combustion, or has been carbonized. The ley, when saturated with the colouring particles, loses all its activity. What is here said of potash, is equally applicable to soda.

Yarn bleached by the ordinary process, or by that just described, has lost a portion of its strength, whence it no longer can sustain the same weight as before bleaching; but if both operations be made with equal care, the yarn bleached by means of oxygenated muriatic acid preserves more strength than that which has been treated by long exposure on the grass, because the leys have been less numerous, and the operations not nearly so long.

This mode of bleaching, then, is produced by the successive action of leys and of oxygenated muriatic acid. We must therefore describe the apparatus and operations which the oxygenated liquor and the leys require, as well as the means of promoting their action, preventing their inconveniencies, improving the whiteness, or giving to bleached objects the qualities that are desired. Lastly, we shall examine some other applications of the properties of oxygenated muriatic acid.

CHAPTER II.

Of the Preparation of the Oxygenated Liquor.

The purpose of the apparatus used in this preparation is, to disengage the oxygenated muriatic acid (chlorine), and to combine it with water. It is therefore divided into two parts,—the one which comprehends the extrication of the gas, and the other its combination with water.

For the first object, a furnace is employed, capable of containing an iron pot to serve as a sand bath. It is usually constructed of brick. The inspection of the plate will give an idea of one of these furnaces. In the sand bath is placed a matrass containing the mixture, to be subsequently described.

Matrasses from 0.38 metr. to 0.43 in diameter are preferable to those of greater dimensions, because they are less liable to break, are more easily managed, and much cheaper. The elliptical form is more advantageous than the spherical, because with an equal diameter the capacity is greater. If one matrass be inadequate for procuring the liquor which is wanted, two furnaces can be placed alongside of each other, (See fig. 1. 3, 4.) which can be put in action successively, or at the same time.

The second part of the apparatus, in which the gas is received, is the *receiver*. It has an interior diameter of 0.9 metr.; but it may be 2 metres and even more in diameter. Its sides and its bottom ought to be formed of strong oaken staves, hooped with iron, and covered with a cement.

To protect the inside of the receiver, as well as the cisterns, from the action of the liquor, they must be covered with a resinous coat, of a consistence not soft enough to run, or hard enough to break off in scales.

The interior of the receiver is furnished with three inverted tubs, (fig. 2. L L L.) destined to receive the gas extricated from the matrass. The depth of each tub ought to be 0.08 of a metre. Their connexion with one another does not admit of iron, which would be attacked by the oxygenated muriatic acid. They are secured by transverse bars fixed to the circumference of the receiver. The space between the tubs and the sides of the receiver is closed, with the exception of an opening, which permits the liquor to communicate from one tub to another, and which ought to be placed alternately on the opposite sides, as may be seen, (fig. 1, 2.)

The inferior tub, as well as the middle one, carries in its bottom a glass tube, destined to transmit into the upper the oxygenated muriatic acid gas, when the former are filled with it. This tube is 0.013 metr. shorter than the interior edge of the tub, (fig. 2. P P.)

Between the matrass and the receiver is a bottle, into which a little water is put. It has three tubulures. To one is adapted the tube of communication between the matrass and itself; from the second proceeds the conducting tube (K. fig. 2.) destined to convey the gas under the lowest tub of the receiver; the third receives a tube, open at both ends, which bears the name of *tube of safety*, because it obviates absorption. To accomplish this object, it must have, reckoning from the level of the water in the bottle, a greater height than that of the portion of the conductor tube, which plunges into the liquor of the receiver; otherwise the water of the bottle, pressed upon by the gas, would escape at its upper part. The portion of this tube which dips into the water of the bottle should also be shorter than that of the conductor tube, which is above the level of the water of the receiver; so that when the vessels become cool, and a partial vacuum is formed, the external air may enter by the tube of safety before the water of the receiver can rush in through the conductor tube.

All the tubulures are shut with accuracy, but in different ways. The *tube of safety* and the *conductor tube* are permanently fixed. With this view, they are passed across a hollow cork, which is coated inside and outside with a mixture of wax and turpentine, and forcibly pressed into the tubulure.

The tube of *communication* between the matrass and the intermediate bottle should have a stopper at each extremity; but as the stoppers must be removed at the end of each operation, they are not strongly pressed in, but merely covered with a bladder, coated with the same mixture, to protect them from the action of the gas; and they are fixed down by packthread, or rather by levers loaded with a weight at one of their ends.

Between the furnace and the intermediate bottle a deal partition is made, having an opening cut in it for the passage of the tube of communication.

It is useful to attach to the upper tub a pipe, with a bent extremity dipping into a vessel filled with solution of potash. When, by any circumstance, the gas comes to fill the cavity of this tub, the excess escapes by this pipe, and is absorbed by the potash, thus protecting the manufactory from the inconvenience which would result from its diffusion.

We may employ muriatic acid and oxide of manganese directly, or we may substitute for the muriatic acid sulphuric acid and muriate of soda, which salt, when decomposed by this acid, gives out the muriatic. The choice depends on the price of those substances at the establishment. The process which we are going to describe is the second one. It is the best, on the whole.

Oxide of manganese (manganese of commerce), when of good quality, is in black masses of greater or less size, composed of small needles of a metallic lustre. It should contain very little foreign mineral. It is reduced into powder, and well mixed with the salt, in the proportions to be presently stated.

If a manufacture of sulphuric acid be at hand, we may dispense with purchasing it concentrated, as it may be employed in the state in which it comes out of the leaden chamber, provided it have a proper degree of concentration.

Concentrated sulphuric acid, such as is found in commerce under the name of *oil of vitriol*, marks nearly 66° by the areometer of Baumé, (1.848 specific gravity). It is here presumed to be in that state.

The proportions of the ingredients which appear to us most suitable, are, 10 parts of oxide of manganese, 20 parts of sulphuric acid concentrated to the above degree, and 27 parts of muriate of soda. We do not, however, affirm, that these are the most exact proportions which can be determined. (Note L.)

If the manganese is of inferior quality, which is discovered by the residuum of the operation not retaining its black colour, the proportion of it must be increased in the following operations till a residuum be left which preserves a tinge of black.

The sulphuric acid should be diluted with an equal weight of water. Rupp and Westrumb recommend a larger proportion. This mixture is best made in a leaden vessel.

Our process is presumed to be made with 5 kilogrammes of manganese, 10 of acid, and 13.5 of salt.

After mixing the salt and manganese, they are introduced into the matrass, which is then placed in the sand bath, when the sulphuric acid, previously dilúted and cooled, is poured into it. The tube of communication is now fitted to the orifice of the matrass. The ascent of the water of the intermediate bottle into the tube of safety denotes that the openings are air-tight. This may be further ascertained, by presenting to them the moistened stopper of an ammonia bottle; for however small the portion of oxygenated muriatic acid may be which escapes, it becomes manifest by a white vapour.

We may kindle the fire in the furnace before placing the matrass in the sand bath, taking care that the heat is not so great as to expose the matrass to be cracked when set in it; or we may wait till the whole apparatus is arranged, before lighting the fire. The heat is then to be very cautiously raised, till the intermediate bottle ceases to be filled with yellow vapours, and till the conductor tube begins to grow warm. The fire must now be extinguished. An operation for the above quantities lasts from six to eight hours. We must not delay withdrawing the matrass from the sand bath till the movement of ebullition be entirely calm. The tube of communication is to be unluted, and whenever the smell is somewhat dissipated, the matrass is taken out, and placed in a basket containing dry straw. It is emptied whenever there is no danger of cracking the neck with the heat.

During the operation, the part of the matrass exterior to the sand bath must be covered with woollen cloth, pasteboard, or any similar substance capable of confining the heat.

The accidents to be feared in this operation are the boiling over, and concretion of the residuum. The former occurs during the heats of summer. It is also occasioned by the bad quality of the manganese. It may be avoided in both cases, by diminishing the doses. To guard against the obstruction of the tubes, which might arise from the boiling over, they must be made of sufficient magnitude. If, however, through inadvertency, the intermediate phial should be filled, so as to make it doubtful if the mixture can pass into the receiver, the matrass ought to be immediately removed. For if the mixture contained in it passes into the receiver, yarn turned through the liquor would take a yellow colour, which must be removed by means of sulphurous acid diluted with water.

The concretion of the residuum, which exposes the matrass to be cracked during the emptying, may be occasioned by three causes: The first is, too small a proportion of manganese; the second is, a lower temperature of the atmosphere than 7 or 8 degrees, (about 46° F.); and the third is, keeping the matrass in the sand bath some time after the operation, which happens when the heat has been pushed too far. The causes being pointed out, it is easy to avoid them.

As the temperature approaches that of freezing water, the gas occasionally takes a concrete form in the conductor tube, so as to obstruct it. To prevent this misfortune, very wide tubes must be employed.

Let us now turn our attention to the receiver. On adjusting each tube, care must be taken to cover it with water, and to extract all the air. This is done by means of a syphon introduced into the side opening, from which the water is expelled by blowing forcibly into its upper extremity.

The receiver being furnished with its tubs, and these being covered with water, with the exception of the upper one, we adapt the conductor tubes, passing them through the free space between the upper and lower tubs and the side of the receiver, and through an opening made in the board, which closes in the middle tub on the same side. This opening must be exactly shut as soon as the tubes are arranged. Lastly, the receiver is filled with water, which is not to be emptied again unless when repairs are to be made: care must however be taken every morning to evacuate the air which may exist under the upper tub, when the pipe just mentioned has not been placed in it.

From the arrangement of the tubs and the conductor pipe, it is obvious that the gas always arrives beneath the lowest tub, and the liquor must consequently be strongest at the bottom of the receiver. From this place also it must be drawn off, for which purpose we adapt to the receiver a pipe (fig. 2. Q.) of wood, sand-stone, earthen-ware, or porcelain, which penetrates to the bottom, and whose upper end is on a level with the edges of the receiver. The liquor is run off by plunging a syphon into this extremity, the longer branch of which terminates in the water of the *tub of immersion*, (fig. 2. R.) In proportion as the liquor flows out of the receiver, care is taken to replace it by the addition of water or spent liquor. (Note M.)

CHAPTER III.

Of Leys.

The defective manner in which leys are usually drawn, is the most frequent, most powerful, and yet the least suspected cause of the weakening of the substances subjected to bleaching. This part of the art, practised at all times, important both by its bad effects when ill-conducted, and by the economy which it introduces into bleaching when suitably performed, has received in modern times very little amelioration; yet it has acquired considerable improvements from more recent researches, especially those of Welter and Widmer.

It is necessary to know the exact quantity of alkali employed in each ley, so as to be able to graduate its respective force, and to proportion it to the quantity and nature of the materials to be bleached. Since the wood ashes, sodas, and the different species of potash made use of, are composed of a mixture of earths, salts, and alkalies, their weights indicate nothing; nor is the areometer a more faithful criterion, since the salts mixed with the alkali also act upon it. Hence its indications are more delusive as the proportions of the mixtures vary, not only in the different species, but as they are not constant even in any one.

Home,[*] aware of the necessity of estimating exactly the strength of leys, attempted to determine the quantity of alkali contained in the different substances employed by the bleachers, by saturation with an acid. He thus assigned the order which they ought to hold relative to their quality, and he has explained the nature of the substances found mixed with the alkali, very ingeniously making allowance in his experiments for the imperfection of the means of analysis then known. But his results have not the precision of those since published. Long afterwards, Kirwan[†] employed, for appreciating the real alkali of potashes, the comparative precipitation of a certain weight of alum, by pure potash, and by the potash under trial. Notwithstanding the precautions which he suggested for removing the causes of uncertainty attached to this mode of testing, he was not able to give it either sufficient accuracy or simplicity.[‡] Lastly, Vauquelin took the task in hand, exhibiting the proportions of the substances found in several species of commercial potashes. He estimated the proportion of alkali, by saturating with a nitric acid, of a very determinate degree of concentration, the potashes submitted to examination, and by comparing the quantity of acid necessary to its saturation with the pure potash which it had required.

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[*] Essay on Bleaching.

[†] Ann. de Chimie, tom. vii.; and Treatise on Bleaching.

[‡] Ann. de Chimie, tom. xl.

It is obvious, that since, in the art of bleaching, the alkaline parts alone are of use, the value of potashes are to each other as the quantities of acid necessary to their saturation; and consequently we become acquainted with that whose employment is most advantageous, by comparing the price of each species with the quantity of alkali which it contains. On these considerations, Vauquelin constructed the following table :—

At the time of making his experiments, the potashes of

America, containing	0.743,	was worth	70 livres.
Pearl-ashes,	0.656,		60
Dantzic,	0.524,		57 l. 10s.
Treves,	0.625,		55
Russia,	0.670,		55
Vosges,	0.385,		35

Hence he concluded, that if the consumer wished to fix the prices which he should give for each potash, according to the alkali which it contains, taking for a standard the one which the above table presents as most advantageous, he would have,—

1.	For the potash of Russia,	55	livres.	
2.	America,	61		
3.	Pearl-ashes,	54	liv.	3 sous.
4.	Treves,	51		6
5.	Dantzic,	43		
6.	Vosges,	31		12

He justly observes, that the *data* of these tables are subject to variations, which fraud may increase; but they may serve in all circumstances as terms of comparison.

The testing of potashes is useful, therefore, both for determining their commercial value, and as a guide in their subsequent employment. As the trials must be frequently repeated, it is important to have a simple manner of doing it; and under this point of view, we know none preferable to that of Welter. The process pointed out by the general administrators of gunpowders and saltpetres,* though better adapted to the end which they proposed, is not so easy of execution.

We here give the process of Welter exactly as he practises it.

The principle of the testing is saturation with an acid. But to render the different trials comparative, the acid must be of a degree of concentration which is uniform, and easily ascertained. Sulphuric acid, diluted with water till it is brought to a determinate point of concentration, answers well. By saturating a certain weight of this dilute acid with a fixed weight of fine pure chalk, dried by the heat of boiling water, the standard may be fixed. This acid is the one most readily to be had, and whose constitution is most uniform. The chalk selected for determining its concentration is a substance equally common; it does not present the difficulties which occur in procuring pure potash, and the temperature of boiling water, employed for drying it, can be very

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* Ann. de Chimie, tom. xli.

easily observed with precision. To avoid the embarrassment attending the preparation of standard acid, a quantity of it sufficient for the trials of many years may be made at once.

Were these analyses made on pieces of potashes, taken at random from the barrels, only ambiguous results would be got, because in the same barrel there are often different qualities. The experiment should therefore be made only on solutions prepared on the great scale as leys, and always with the same weights of alkali to the same number of measures of water. The most expeditious manner of making these solutions in the cold, is to suspend the potash at the surface of the water in a vessel of iron, pierced with a great number of holes, or formed of coarse iron wire. They should not be drawn off till we are certain that the whole potash is dissolved, and till by agitation the liquid is rendered uniform.

Besides these circumstances, the assay of potashes requires slips of paper stained with litmus, or any other colour equally sensible to acids, as that of mallows, radishes, &c. We should also procure a glass rod, a small glass measure, and lastly, a tube having as many times the capacity of the small measure, as measures of water have been employed to one quintal of potash.—(See Plate II.)

We fill the tube with the solution of potash, and transfer it into the goblet. We next fill the same tube with the test acid, which is also poured into the goblet; we agitate with the glass rod, and then draw a trace on one of the slips of stained paper with the extremity of this rod moistened with the mixture. If the trace do not become red, we add to the goblet a small measure of the test acid, stir, and then make another trace on the paper, alongside of the former. If the colour of the paper be not now changed, we add one measure of acid more, and continue thus till the last drawn trace is red.

If we wish to compare the qualities of several potashes, it is obvious, that we must regard as the best that which has required the greatest number of measures of acid to produce a red streak, since it is the one which saturates most acid. It is also obvious, that we might express numerically the qualities of the different species of potash, representing them by the number of measures of acid which each of them has saturated; which amounts to counting the traces formed on the paper in each trial, taking the first for as many as the tube contains of little measures, and adding unity for each of the following marks till the last, which we should not reckon, because its colour indicates that we have passed the term of its saturation.

To obtain a suitable variation of the leys, it is convenient to have solutions of potash of an uniform strength, one for example with which an equal number of measures of test acid and solution of potash are required to produce saturation. But whatever be the value of a potash, its solution may be brought to this point by adding to it, for every quintal of alkali, as many measures of water as there were measures of acid required, to effect saturation on the quantity primarily employed. Hence the number of measures of water forming the solution, ought always to be equal to that which expresses the standard (*titre*) of the potash.

If in an assay it should happen that the first trace was red, it would be necessary to add measures of the solution instead of measures of acid; and hence potash should be added to the solution to bring it to the fixed degree of concentration.

To make this more clear, suppose that we have employed 50 measures of water to dissolve one quintal of potash, (consequently the tube contains 50 times the small measure), and that we have 8 traces on the stained paper. The first counting 50, each of the following 1, and the last being red, we would say that the potash is of the standard 56; which would denote, that to bring the solution to the fixed degree, (in this case 50), we must add as many times 6 measures of water as we have employed in quintals of potash; and employing potash taken from the same cask, we should use 56 measures of water for the solution. An assay made on opening the cask, is sufficient for the whole period of employing that potash, remembering to put, every time a new solution is made, as many measures of water as the standard indicates.

The degree of concentration of these solutions does not allow them to be employed directly in the leying. Only such a number of measures is taken as is necessary to give them sufficient strength, when diluted with the water which fills the boiler and the bucking tub, and for them to have the quantity of alkali suited to the weight of the substances to be bleached. But before pouring the alkali into the boiler, it is advantageous to render it caustic; for it has been proved, (Ann. de Chim. tom. vi.), that in this state alkalies dissolve a fourth more of colouring matter than when they are carbonated. The almost general practice, however, is to ley in a mild state. It has even been pretended, in some houses, that the lime employed to render the alkali caustic, injured the stuffs. The observations which we have collected satisfy us, that this effect must be ascribed solely to the increased energy acquired by the alkali, the consequences of which may be prevented by a diminution of its quantity.

To perform this operation, the lime newly slaked is put into a large tub, the solution of potash is poured over it, they are stirred together, and, after settling, the clear liquid is to be decanted off by means of a syphon. The residuum is then to be washed two or three times, and the washings added to the ley.

One part of lime is sufficient to render two parts of potashes caustic. These proportions ought, however, to vary with the qualities of the potashes; and it is proper to ascertain that the proportion of lime is not too great, because the property which this substance possesses, of precipitating the colouring matter held in solution by the alkalies, (Ann. de Chim. tom. vi.), may render an excess of it injurious. On this account, some solution of potash is to be mixed with the liquor floating over the lime, in the tub in which the potashes are made caustic. If it become turbid, it contains lime in solution, and solution of potash must therefore be added, till it no longer yields a precipitate.

We might probably apply this property of lime with advantage, to carry off from spent leys the colouring matter with which they are charged, and render them once more fit for bleaching, by adding the proportion of alkali necessary to replace that with which the stuffs remain imbued, so as to raise the leys to the suitable standard. On the small scale, yarns have been completely bleached, by employing in this way the very same alkali in all the leys. It may be likewise beneficial, especially in places where fuel is cheap, to evaporate the spent leys, and to calcine the residua so as to destroy the colouring matter. But these operations need only be performed on the first leys, which are more concentrated than the last.

According to the experiments of Kirwan,* the use of alkaline sulphurets might be tried. They have indeed the inconveniencies of producing spots in places which come into contact with

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* Ann. de Chimie, tom. vi.

metals; but these will disappear by employing in the last leys an alkali free from the sulphurets, or by passing them at the end of this bleaching through an acidulated water. The following is the order in which this celebrated chemist has classed, according to their energy, the substances possessing the faculty of dissolving the colouring matter of flax: 1. The alkaline sulphurets; 2. Caustic potash; 3. Caustic soda; 4. Carbonate of potash; and 5. Carbonate of soda. Lime water appeared to him to dissolve but a very little of it, which he ascribes to the small solubility of the lime; but independently of this cause, it is not probable that lime, which forms an insoluble combination with colouring matter held in solution by potash, could of itself dissolve it. Kirwan observes, that sulphur did not augment the solvent faculty of lime. Higgins, however, has stated, that there is a remarkable economy in employing sulphuret of lime in bleaching. Trials on the small scale have not had the success that O'Reilly announced.—*Journal des Arts.* (NOTE N.)

The sulphurets present two inconveniencies, which must greatly diminish the benefit which their solvent faculty promises. One is, to deteriorate rapidly boilers and metallic instruments containing them; another is, to waste a considerable quantity of the oxygenated muriatic acid, if the washings have not taken it completely out of the matters that are bleaching.

The colouring matter acquires the property of being dissolved by the alkalies only in the successive operations, between every one of which whatever has become soluble ought to be removed. Experience has proved that these steps are necessary to obtain a fine white, not subject to vary; a white which cannot be attained at a single operation.* The alkali deemed necessary to dissolve the whole colouring matter of the substance we are bleaching, must therefore be divided into a certain number of leys; and as it should be proportioned according to the quantity of this colouring matter presumed to be present, less of it may be employed in the last leys than in the first.

The most general manner of leying is the following:—

The large tub is so placed, that its bottom may be near to, and on a level with the edges of a boiler, which is somewhat sunk into excavated ground, to avoid too great an elevation of the tub. A little above its bottom this is perforated with a hole, into which is fitted a small tube, that conducts the ley into the boiler. The stuffs to be bleached are arranged in the tub in horizontal layers. The boiler is then filled with water, which is poured into the tub after closing the pipe that leads into the boiler; and this operation is continued till the water stands in the tub a little above the goods, taking care to mingle

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* Annales de Chimie, tom. xi.

with each boiler-full of water a number of measures of solution of potash, equably divided, so that with the last boiler-full the whole alkali intended for the ley shall have been expended. The boiler being equably filled, the fire is kindled, the pipe of communication is opened, and the water is kept at a uniform height in the tub, by lifting it with a copper pail or bucket from the boiler, and pouring it into the tub. When the ley (thus continually lifted into the tub in proportion as it flows into the boiler) has begun to boil in the caldron, the operation (of bucking) is prolonged more or less, according to the kind of matters that we bleach, and the period of bleaching at which they have arrived. The leying being finished, it is allowed to flow off by a stopcock fitted to the bottom of the boiler; water is then poured into the tub to cool it, and expel the remainder of the ley, after which the tub is emptied.

Since the tub contains several times the capacity of the boiler, and since, independently of the time which a considerable volume of water takes to acquire a high temperature by the mixture (in rotation) of a small quantity of heated water, the ley is continually cooled by the transfer from the boiler into the bucking-tub, the ebullition in the boiler must be but very slowly brought on. However long continued the leying may be, the temperature cannot be carried higher than 72° or 73° (about 195° Fahr.) in the tub. From this arrangement it follows, therefore, 1.

That a great body of water must be heated, in order that the substances bleaching may be equably impregnated with the ley; and, 2. That we can give the leys only a heat inferior by several degrees to that of boiling water. Hence the length of the operation, as also the waste of combustibles, and the great labour: nor can the term of 80° (212° Fahr.) be obtained. Several phenomena, however, and especially the superiority found in patterns bleached in boiling leys, show how advantageous the temperature of ebullition would be.

From these considerations Widmer contrived to place directly above his boiler a tub, whose bottom was merely a strong lattice work of wood. In the middle of the boiler there is a pump which raises the ley to the top of the tub, where it is diffused by four pipes equal to the radius of the tub, and which are turned circularly by a movement adjusted to the arm (lever) of the pump. The ley is thus equably dispersed on the surface of the goods; it filters through them, and falls into the boiler. Far from being liable to cool, it preserves its temperature in this passage, because the goods are heated by the steam rising from the boiler, which cannot escape except by passing through their interstices. Two thermometers placed in an apparatus, where the boiler was two metres in diameter, one at the base and another at the top of a tub two metres high, constantly marked the same degree of heat. In three hours of an uninterrupted flowing, they both indicated 80°, (212° Fahr.) In the first trials, Widmer made use of a tub whose height was two metres, and whose diameter, equal to that of the boiler on which it stood, was only 0.8 of a metre. The ley was drawn off by a stopcock adjusted to the bottom of the boiler, and it was poured in with a bucket quicker than it could run completely away. That remaining on the top of the goods boiled strongly some minutes after the boiler was in ebullition, notwithstanding the small surface which this apparatus presented to the vapour, the cooling which the ley must have experienced in getting back into the boiler from the top of the tub, and the distance between this point and the boiler. By this method we may communicate to goods a heat superior to that of boiling water. The thermometers of the large apparatus rose to 84° (221° Fahr.); but as soon as they passed the boiling point of water, the pump could no longer raise the liquid; and we do not know how far it may be right to ley at higher temperatures. To prevent the pressure of the steam from stopping the working of the pump, Widmer next established four pipes, which opening a communication between the upper part of the boiler and that of the tub, gave a free outlet to the vapour.

This apparatus unites the advantages of leying in much less time, at a boiling heat, and with less consumption of fuel; for instead of having to heat a ley incessantly cooled by the transfer, and which occupies the capacity of both the tub and the boiler, the latter alone is filled, while the heat is preserved during the running by the agency of the vapour.

Nearly 400 pieces, of from 21 to 22 metres each, may be leyed at a time in an apparatus of the above dimensions. The longest leying lasts six hours: it consumes five measures of coals. Its efficacy is sufficiently proved by the uses to which the goods of Widmer so bleached are applied, since there can be no more delicate test for white, than the clearing the madder grounds of printed calicoes; and it has also diminished the number of operations to which he subjects the goods. We have had occasion ourselves to ascertain these good effects on cotton cloth; and we believe that they will be experienced on applying this method to the bleaching of linen webs. (Note O.)

Bosc has asserted in a paper,* on which we have some reflections to offer, that it was prejudicial to the action of the alkali to water the goods continually; an idea which he founded on his philosophical notions of bleaching. According to him, *the solution of the colouring particles in the alkali is a true combustion, effected only on the colouring matter, because it is combustible at a lower temperature than the fibres.* Our only business, therefore, is to raise sufficiently the tem-

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* Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Germinal, An. xi.

perature of the steam, so as to operate by its decomposition the combustion of the colouring particles, which thus become soluble in the alkali.

When water is decomposed by means of charcoal at a much higher temperature, there are produced carbonic acid, and an inflammable gas, holding charcoal in solution; but the charcoal which has not entered into a gaseous combination has not become more soluble in alkalies. This observation would be sufficient to prove that the explanation of Bosc is not founded on the received theories.

He makes Lavoisier say, that at 85 degrees of Reaumur, (about 223° Fahr.), *water forms a permanently elastic gas.* This illustrious chemist styled permanently aeriform fluids, those which preserve this state notwithstanding changes of temperature and pressure. The vapour of water formed at 80° (212° F.) under the ordinary pressure of the atmosphere, differs from that formed at 85° only in being more dilated, and resisting a higher (less) pressure.

He certifies, that in the apparatus which he describes, the heat is carried beyond the 100th degree of Reaumur; but at nearly 17 degrees above the term of ebullition, (250° F.), steam acquires a double elastic force. His vast apparatus should therefore be able to resist an effort superior to two atmospheres. He should have bethought himself of determining the thickness necessary to the great boiler which is to furnish this vapour, and have shewed us by what means he could fix down the different parts of the apparatus to the masonry.

In making a comparative calculation of different modes of bleaching, he regards as a matter of indifference the employment of oxygenated muriatic acid without mixture, or combined with potash and lime. We shall afterwards see how far this position is right.

When the results of different methods are compared, especially on cotton, where some days' exposure on the grass forms a part of these methods, and when it is not the object to attain the most perfect white, it is easy to be led into error, because all these methods readily yield a white, with which people may often be satisfied.

CHAPTER IV.

Of the Immersions in the Oxygenated Muriatic Acid.

If linen or cotton yarn is to be bleached, for its immersion in the oxygenated muriatic acid, we may place near the receiver a tub of the same size, but a foot lower, (fig. 1, 2. A.) It is to be two-thirds filled with water; the liquor of the receiver is then run into it by means of a syphon, as we have explained, agitating meanwhile, but without raising air bubbles. The hanks are arranged in a basket of the same height as the tub of immersion, so as to form two layers in it, leaving 0.2 metr. empty. The basket should contain from 100 to 150 kilogrammes of yarns. This basket is then raised by means of a crane or other equivalent machine, and plunged into the immersion tub; from which it is withdrawn, and replunged into it continually, so as to renew incessantly the liquid which moistens the yarn. As soon as the liquor is observed to be weakened, the basket is raised above the tub, and fresh liquor is run in from the receiver. This process is continued until the liquor retains its strength, notwithstanding the repeated immersions of the yarn. This first operation usually lasts two or three hours.

Instead of heaping the yarn in baskets, it may be plunged much more freely in the liquor, by hanging it at two rods, which pass through the middle of the hanks, and are supported by a frame of the same size with the immersion tub. There is then no danger of the yarn being bleached unequally. Less of it, indeed, enters at a time into the tubs. The mode of working is in other respects the same.

The oxygenated muriatic acid weakens and even destroys yarns, as leys do, if it be employed without precaution. Hence, when yarn is put into a very strong liquid it soon loses its tenacity. But it is very easy to avoid this occurrence, by not dipping the yarn till the liquid which comes out of the receiver be well mixed with water, or be a dilute liquor with a supportable odour. In this state of concentration, the oxygenated muriatic acid does not attack yarn, though plunged in it even for several days. We must not rest satisfied with so vague a manner of judging, especially if we wish to compare together several effects.

From the outset of his operations Déscroizilles made use of a solution of indigo in sulphuric acid, to estimate the comparative strength of his liquors; and he has since published a description of the instrument which he contrived for this purpose.* The solution of indigo ought to be prepared with seven parts of concentrated sulphuric acid, and one part of indigo, *(flore)*. These two substances are mixed in a small matrass, which is plunged for a few hours in water slightly tepid; and the solution is then mixed with 992 parts of water.

The strength of a liquor is judged of by the quantity of it requisite in order that the colour of a stated measure of this solution, in which the indigo forms 1-1000th, be destroyed or turned to a yellow hue. This trial is conveniently made with a measure glass and a goblet, similar to those pointed out for the trial of potashes.

For a first immersion, the liquor may be of such a strength that one measure of it shall deprive of colour from one-half to two measures of solution of indigo. If the odour gives annoyance, it may be diminished by diffusing some chalk and water in it. We have ascertained, that this easy method of obviating the inconvenience of the smell,

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* Journal d'Agriculture et des Arts, tom. i.

does not perceptibly impair the energy of the liquor. The strength and duration of the immersions which follow the first, are progressively less. Their number varies also according to the fineness and quality of the yarns. In general, they are limited to between five and nine.

Too weak a liquor should not be made use of, from fear of weakening the yarn; for its deficiency of action cannot be compensated by a greater number of immersions. It is easy, moreover, to avoid any accident from the liquor, by never omitting to try its strength. Attention must also be paid, not to let the yarn that is impregnated with it dry in the air; it is thereby injured, although no inconvenience happens while it is wet.

The bleaching of piece goods requires the same precautions. The finer the cloth the more economical, because it consumes less liquor; but to execute it commodiously, there must be, instead of a single tub of the size of the receiver, four tubs sufficiently large to contain each from ten to twelve pieces, twenty-four metres long. These tubs, arranged one after the other, near the receiver, are each surmounted by a reel or winch. In front of the first tub a table is placed, to which are attached at their corners the ten pieces that are to be immersed together. After bringing the liquor to the requisite degree, the end of the last attached piece is thrown upon the winch of the first tub. A workman immerses the pieces with a rod, in proportion as they pass over the winch, which is turned by a child. The end of the last piece is tied to a cord fixed to the frame-work of the winch, in order that this end, which enters last into the tub, and which finds the liquid now weakened by the pieces to whose train it is attached, may enter first into the second tub, and that the end which has been first in the preceding may, by passing last into the next, be placed in the same circumstances as the other. By giving this rotation to the goods in the tubs, with a view of changing them, and by successively passing each end first, they whiten very equally. When the pieces have been passed from the first into the second tub, new ones are introduced, which pass into the second as soon as the former have entered the third, and which pass in their turn into this, when the preceding pieces are in the fourth. At the same time, fresh pieces should be put into the first two tubs; so that as soon as the pieces shall have travelled from one tub to another, others may enter immediately into the former. When they have arrived at the fourth, and have remained the requisite time in the liquor, they are piled up on the winch to let them drain, then turned over on a wheelbarrow, to be carried to wash. Whenever the pieces are taken out of a tub, the liquor of it is tested, that it may be restored to the proper degree before introducing fresh pieces into it. Care should be taken to plunge the pieces thoroughly, and not to let any of their parts float above. The number, the strength, and duration of the immersions, vary with cloths, as with yarns.

CHAPTER V.

Of the Washings.

Whoever projects an establishment, should examine if the place where he proposes to erect it, unites the advantages of fabrication, commerce, and carriage; but, above all, he must have pure water at command; for, without this condition, he will not succeed in obtaining a fine white. Muddy water, which leaves a blackish deposite, may however be employed with success; but that whose deposite is yellow, gives always an unfavourable shade. These observations are particularly applicable to the bleaching of cotton, the white of which should have the greatest lustre.

Immediately after each operation, we must, by a careful washing, discharge from yarns and stuffs the liquor with which they are impregnated; because, if it were carried into that of the next operation, it would neutralize a portion of it, and thus impair its action. This precaution, moreover, adds much to the perfection of the white.

To wash linen or cotton yarns, a workman takes a hank in each hand, plunges them in the water, agitates, withdraws, and replunges them for three or four times, seizing the hank each time by a different point. He then puts the two hanks together, wrings them, and throws them down.

The washing of piece goods requires more apparatus, in order to be well executed. They are pretty generally washed by hand, and beat with a rod or a mallet; but this method is imperfect, especially because of the inequality of the washing. In some establishments machines are employed, which accomplish this object better. We are acquainted with none preferable to that of the celebrated manufacture of Oberkampf, of which he has had the kindness to impart the knowledge to several bleachers. It consists of a strong beetle or mallet, which strikes the pieces arranged on a circular table, moveable round a pivot. A description, detailed enough to guide to its construction, would require too much room for us to give it a place here.

We may, however, obtain a pretty complete washing, sufficient for the most part of goods, by making use of two wooden rollers, placed one above another on frames, set in the direction of the breadth of a river. Their length is 0.4 of a metre, the under one is 0.48 in diameter, while the upper is only 0.40 of a metre. The latter is fluted parallel to its axis, the depth of each furrow being nearly equal to one-half of the ridge. At each extremity it has a pivot, fitted to a groove cut in the frame (support). These pivots are not fixed, hence this cylinder can rise freely above the other. The surface of the under roller is smooth; and it carries a handle at one of its pivots. When we wish to wash goods by its means, we throw the piece into the water, laying hold on one of its ends, and putting it between the two cylinders. On turning the winch, the cloth passes between them, pressed by the upper one, which, at every groove, receives a small stroke, and communicates it to the cloth in its tumbling round. Pieces passed in this way five or six times successively, are very well washed.

To moisten goods, or to wash them slightly, we may also employ a species of reel (winch), with four leaves, placed on a river, like the rollers. The piece whose end is laid on the reel is thrown into the water, and, turning on the reel, the piece passes over it, and falls on the other side into the water. If it be rapidly enough turned, and if the pieces be thus passed several times, they will be tolerably well washed by this simple means.

What has now been stated shews the advantages of arranging the workshops as near as possible to the water placed at our disposal. (NOTE P.)

CHAPTER VI.

Of the other Operations of Bleaching.

The bleaching of goods commences by leaving them for some time in tubs full of water. In a few days a fermentation commences, which promotes the separation of the colouring matter, and particularly of the paste with which weavers imbue the webs. This operation, which is called *ungumming*, may, without injury, last for eight or nine days, at mean temperatures. It may be longer when the air is cold, and ought to be shorter in summer, because it is to be feared that fermentation, pushed too far, would affect the texture of the goods. Old leys are also used for this purpose ; but the experiments of Home prove, that it is more advantageous to employ only pure water.

As to yarns, it is sufficient for them to be steeped for two or three days.

If the moist grey yarn, on coming out of the ley, be piled up, it gradually heats, and eventually takes fire ; but if it reaches only the animal temperature, it is not perceptibly weakened ; the slight combustion which it thereby experiences even contributing to the effect of the leys. If it be shut up in the dark, however, when ill-dried, it is speedily destroyed.

When no more greyness remains in linen yarn, or linen cloth, which commonly occurs after the fourth immersion, it is passed into water acidulated with sulphuric acid. For this purpose, into a small tub containing water sulphuric acid is poured, till the mixture has assumed a degree of sourness, approaching to that of lemon juice. Into this the yarn is dipped, handful after handful, so as thoroughly to imbue it. It is then thrown into another tub large enough to hold 1200 pounds of it, in which it is left for about 15 or 20 hours before being removed. A longer continuance, of two or three days, for example, can do no harm, provided care be taken that no portion of the yarn rises out of the acid. As to piece goods, they are attached end to end, and passed by means of a reel through large tubs full of acidulous water. Linen yarns and cloth are passed three or four times through the acidulous water, making it progressively weaker. It is sufficient for cotton goods and yarn to be passed once. The quantity of acid employed in the first liquor is 8½ kilogrammes, for 600 kilogrammes by weight; and this proportion is diminished at each subsequent operation.

Great pains must be taken to wash perfectly before and after the acidulous water, otherwise a fine white can never be obtained. It is no less important to prevent the yarns or cloth impregnated with acidulous water from remaining long exposed to the air; for as the water evaporates, the acid becomes concentrated, acts on the fibre, and destroys it.

The acid dissolves the iron which in the course of the operations had been deposited on the stuffs, communicating to them a faint yellowish tint. In proof of this, the prussiate of potash occasions, after some time in the sour, a blue precipitate. But is the action of the acid confined to the above use? If it be, why repeat this operation four times, and apply a ley between each of them, while for cotton, equally exposed to be stained by the ferruginous deposite, a single sour is sufficient?

In Flanders, Holland, and Ireland, the bleaching of cloth by the ancient methods is accelerated, by letting them stand for several days in the acidulous liquors. Sour milk is commonly employed for this purpose; sometimes, also, bran or rye-meal is mixed with the cloths, and the liquor of the tubs becomes sour from fermentation. It was long believed that the fermentation itself promoted the bleaching; but it is now well proved, that it is the acid alone which acts. Home has satisfied himself, that the vegetable and mineral acids may be substituted for milk and rye-meal; that sulphuric acid, however, combines most advantages; that muriatic and nitric acid produce the next greatest effect, which effect is aided by a gentle heat. He assures us, that sulphuric acid does, in five hours and less, what could be obtained only in five days with bran or milk. To these substances he also makes the serious objection, that they frequently run into putrefaction, and thus affect the fabric. We may hesitate the less to substitute water acidulated with sulphuric acid for milk or rye-meal, as this change has been long adopted in England, and in several French bleach-works.

Notwithstanding all these operations, the thread has not yet got all the whiteness of which it is susceptible. There remains a matter insoluble in acids and alkalies, which is removed by powerful washings in water frequently repeated, and by some days' exposure on the grass. There is a certain yellowish tint, which is more effectually destroyed by the action of air and light, than by that of the oxygenated muriatic acid. In general, yarns of a yellow colour bleach with more difficulty than those of a grey hue bordering on brown. For those, it is right to lengthen somewhat the exposure on the ground.

For giving softness to yarns, some pounds of soap are added to the last leys. Immediately afterwards they are laid out on the green, on being lifted from which they are washed with great care; for if they retain any soap, their white might change. In linen webs, the selvages being of a denser texture than the rest, preserve for a longer time a tint, which can be completely removed only by reiterated washings and soft soap. It is the same with all the places on the body of the cloth where there are broken threads repaired during the manufacture. These constantly preserve a black hue, which yields only to rubbing with a hot solution of soap, of greater or less strength. Some persons are in the practice of treading the cloths in tubs, along with this solution, one or two times, towards the end of the bleaching. This operation is performed with the feet, tramping more or less, according to the hardness of the web. To cleanse the cloth completely, it is soaped by hand in tubs, whose edges, instead of being perpendicular to the bottom, are turned considerably outwards, forming an inclined plane, on which the workmen rest their webs, so as to rub them more conveniently. If the goods are almost quite cleared by the two treadings, a single rubbing is sufficient to bring the selvages to the same tone of white as the rest of the piece; most frequently two are given, especially to webs of a dense texture, or of a coarser yarn. Occasionally they are obliged to rub, even separately, the spots where the black threads are observed. All these manipulations, by cleansing thoroughly the goods, give them, moreover, a certain pliancy, and that marrowy feel which is in request. The whole of the soap that may possibly remain is removed, by exposing them on the field, and washing them several times in limpid water. The soaping does not begin till the webs have passed once through the acid, care being had to lay them down on the grass on their quitting each operation, and to water them on it. They are next washed and lixiviated. The acid and soap are alternated, till a perfect white be formed.

Cotton stuffs do not present the same difficulties. The black threads are easily cleared towards the end of the bleaching, by soaping the places where they are observed; but the selvages whiten as rapidly as the body of the web; and exposure on the green may be dispensed with.

When a perfect white is attained, the blueing is given in the following way:—

The most beautiful azure-blue (*smalt*) is selected, the colour of which proceeds from oxide of cobalt reduced to very subtile powder. It is diffused through a little clear water. Some of the water thus charged is drawn off, and passed through a silk searce, into a small tub filled with the most limpid water; and when the workman judges, by a trial made on a handful of thread, that the water is sufficiently charged, he passes through it all the thread in succession, squeezing it, and taking care to add blue from time to time, to keep the shade uniform. The yarn is now carried to the wringing frame, and then dried in the open air.

The preparation is the same for piece goods. They are wrung at the peg, and dried. As to gauzes, *linons,* and some other cotton stuffs, a little starch is added to the water containing the azure-blue. Cambrics are usually passed twice through the blue, letting them dry between each operation.

CHAPTER VII.

Number and Order of the Operations.

Suppose there is a solution of potash made in the proportion of 40 measures of water, each weighing 16 pounds, for a quintal of potash, and 1250 pounds of thread.

The linen or hempen yarns having been steeped in water for three days, are to be well-washed, and arranged in the ley-tub.

First ley; 20 measures of solution of potash, three hours of boiling. The ley, on cooling, becomes thick like a jelly.

Second ley, for completing the removal of as many of the colouring particles as possible. This ley contains 10 measures of solution; and the boiling lasts for two hours.

Washing, to carry off the ley and the colouring particles which it has dissolved.

First immersion. Liquor at 2°; that is, of such strength that one measure of liquor discolours two measures of solution of indigo. The immersion is continued till the yarn no longer weakens the liquid, after it is restored to its standard strength.

Washing.

Third ley. 12 measures of solution; three hours of ebullition.

Second immersion. Liquor of the same strength as the first.

Fourth ley. 8 measures of solution ; two hours of ebullition.

Third immersion.

Washing.

Fifth ley. 5½ measures of solution ; two hours of boiling.

Fourth immersion. Departing from this point, the liquor is brought down to 1°.

Washing. At this period the white is usually manifest.

Acidulated water.

Washing.

Sixth ley. 5½ measures ; two hours of ebullition.

Exposure on the green for six days.

Washing.

Fifth immersion.

Washing.

Acidulous water.

Washing.

Seventh ley. 4½ or 5 measures ; one hour of ebullition at least.

Sixth immersion.

Washing.

Acidulous water.

Washing.

Ley and soap. 3 measures of solution. To this, 8 pounds of black soap are added ; and the solution is heated till the hand cannot be tolerated in it. When the soap has penetrated thoroughly, the process is stopped.

Exposure on the grass, three days.

Washing.

Blueing.

After this operation the bleaching is finished, the thread is wrung out, and is set to dry.

The operations are the same for linen cloth, only they must be preceded by the ungumming. There may also be run upon them, before the first ley, hot water, to which no alkali is added; an affair which lasts three hours. If the goods be not sufficiently whitened, the bleaching must be continued in the order indicated, setting out from the last ley.

The cotton cloths are ungummed (freed from the dressing), then receive the hot water, and the operations prescribed for yarns down to the last immersion. At this time they are white. They are passed into blued acidulous water, and next dried. In the first immersion, the liquor should be of only 1°, and somewhat weaker for the subsequent ones. A few measures less should likewise be put in each lixivium. The black threads are soaped after the third immersion. For cotton in hanks, the same mode of operating is proper.

CHAPTER VIII.

Of the Different Preparations of the Oxygenated Liquor.

In the first experiments which were attempted on bleaching, though it was proposed merely to employ the property which the oxygenated muriatic acid possesses of destroying colours, yet potash was mixed with it, which seemed to accelerate its effect. It was soon perceived, that in order to obtain a uniform white, without weakening the cloth, the operations of ordinary bleaching must be imitated; the oxygenation of the colouring particles by a liquor weak enough to do no injury to the fabric, being followed up by the action of leys which serve to dissolve them.

Soon after the practice of the new bleaching had begun to be established, a liquor mysteriously talked of was prepared at Javelle, which is still employed under the name of the lixivium of Javelle.* It is a combination of oxygenated muriatic acid with a certain proportion of fixed alkali. This liquor can be imitated, by employing the following proportions for the distillation and the alkaline solution:—Muriate of soda 77 grammes; sulphuric acid 61 gr.; oxide of manganese 30 gr. The gas disengaged from these materials is received in a litre of water, in which 120 gr. of common potash or soda have been dissolved. This liquor is to be diluted for use with 10 or 12 parts of water.

To diminish the offensive odour of the oxygenated muriatic acid, Descroizilles mixed with it carbonate of lime or chalk.

A short time since, Tennant made a preparation for which he obtained a patent in England:

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* Annales de Chimie, tom. ii.

it is a combination of oxygenated muriatic acid and lime, or oxygenated muriate of lime. This substance has the property of absorbing readily a great quantity of oxygenated muriatic acid. To obtain this combination, it is requisite merely to pass the gas, as it is disengaged, through slaked lime till it be saturated. This lime is afterwards dissolved in a certain proportion of water; which solution is employed in bleaching. Its effect may be augmented by the addition of a little sulphuric acid.

To judge of the effect obtained from these different preparations, and of their relative utility, we must call to mind, first of all, the results of observations collected from the theory.

Oxygenated muriatic acid is composed of two elements, which are feebly united, and which are disposed to enter into other combinations; whence the easy oxygenation of substances exposed to its action. But this action is exerted with greater facility and energy when not impaired by any combination which the oxygenated muriatic acid may have previously made. Thus, in the gaseous state, it acts with more energy than when it has been combined with water beforehand; and in that case its activity may be too great for the object proposed in bleaching. The action of the water, however, being very feeble, the liquid retains a lively odour, and there may be obtained from it its whole sensible effect, only retarded and modified at will, according to the concentration which is given it.

The alkalies exercise a much more powerful action on the oxygenated muriatic acid than water does, and thereby can give it a much greater condensation, repressing almost entirely its smell, which requires freedom of expansion, and solution in air. The above (alkaline) liquor is dissolved in a sufficient quantity of water to accomplish the intended object of obviating the inconveniencies of too brisk an action. It produces its effect more quickly, probably because the potash tends to form a more intimate and more energetic combination with the muriatic acid, while the colouring matter exerts its action on the oxygen.

The advantages presented by the lixivium of Javelle,—the oxygenated muriate of potash or soda, are therefore, 1. To require a less complex apparatus, for it is sufficient to employ a receiver containing the alkaline solution, in order to condense the oxygenated muriatic gas, with the single precaution of plunging the conductor-tube to the bottom of the receiver, and receiving the gas under a tub; 2. To repress almost entirely the suffocating odour of the oxygenated muriatic acid; 3. To furnish the agent of oxygenation, much more condensed, under the same volume, and consequently to render it of easier and less expensive carriage; 4. lastly, To produce its effect somewhat more speedily.—Let us next examine the disadvantages of this preparation.

When a fixed alkali acts on the oxygenated muriatic acid, the effect is not simple; a portion of the oxygenated muriatic acid is merely condensed, retaining the proportion of its elements, and the properties dependent on the tendency which they preserve to enter into other combinations.

Another portion is decomposed ; and the result of the two new combinations which are established in its stead, gives from five to six parts of muriate of potash for one of superoxygenated muriate of potash, a salt which contains nearly 0.38 of its weight of oxygen, to which it owes its characteristic properties. Now, the oxygen present in this last combination, in which it is accumulated, is so fixed down, that it can no longer attack the colouring particles, nor resume the elastic state by the action of light. The whole of the oxygenated muriatic acid which suffers this transmutation of combination, is therefore lost for bleaching. Its quantity varies according to the condensation of the alkaline liquor which receives the gas, and it appears to increase when the liquor is kept ; probably temperature causes the results to vary.*

We thus perceive, that liquors, analogous to the lixivium of Javelle, ought not to produce in their agency on the colouring particles so much effect as a simple aqueous solution, which contains, under the same liquid volume, a quantity of oxygenated muriatic gas equal to what has been condensed by the alkali.

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* Essai de Statique Chimique, tom. ii.

It has even been found, that by adding simply an alkaline solution to the oxygenated muriatic acid, its discolouring effect was diminished. Rupp has made decisive experiments on this subject. He employed a solution of indigo for comparing, by the quantities of which the colour was destroyed, the oxygenated muriatic acid without mixture, with the same after adding to it different proportions of potash; but to avoid the uncertainty which might have proceeded from the action of the sulphuric acid on the potash combination, he decomposed the solution of sulphate of indigo by acetate of lead, thus rendering what he used, a solution of indigo in acetic acid. He made similar trials with an infusion of cochineal, which is still less liable to objections. It results equally from both, that the more potash he put into a like quantity of oxygenated muriatic acid, the less liquor he could blanch. The difference between the simple oxygenated muriatic acid, and that with which he had mixed most potash, was nearly one-fourth in favour of the first.

It is therefore proved, by theoretical considerations and direct experiments, that the addition of an alkali, when even it is not employed to condense the oxygenated muriatic gas, impairs the effect which this ought to produce. But in the lixivium of Javelle, it raises the price of the liquor nearly three times higher. It is obvious, that these disadvantages ought to make the use of it be rejected in a manufacture, where economy is an indispensable condition.

The oxygenated muriate of lime has one advantage over the lixivium of Javelle, from the great difference of price between lime and potash or soda; and its state of condensation, and desiccation, renders its carriage less expensive. But it has also the inconvenience of transforming a portion of the oxygenated muriatic acid, and of containing superoxygenated muriate, which cannot be indicated in this combination by nomenclature, which is precise only with regard to very uniform combinations: it appears even that the proportion of superoxygenated muriate is considerable; for if, after expelling by a slight degree of heat the oxygenated muriatic acid which had retained its properties, the remaining substance be examined, it is found no longer to produce discoloration; and if it be urged with a stronger heat in this state, much oxygen gas is disengaged. Welter tells us, that in his comparative experiments he had observed, that the gas condensed by lime produced only one-tenth of the effect which may be obtained when it is received in water. The use of the oxygenated muriate of lime must therefore be disadvantageous; but it may be convenient for certain purposes, from the facility of carriage and preservation, where the economy of the process is of secondary consequence. Under this point of view, it merits the commendation which it has received. (NOTE Q.)

The addition of sulphuric acid to the solution of the oxygenated muriate of lime, increases the effect, by the decomposition of the superoxygenated muriate; but to produce this effect fully, a quantity of acid is required, which might become dangerous.

These objections do not apply to the addition of chalk, which has been recommended by Descroizilles, of which he makes use in his elegant manufactory. Its value is very trifling; and although our experiments appear to prove, that it somewhat lessened the total effect of the oxygenated muriatic acid, yet this diminution is so small that it may be neglected. Hence, though the process with the simple oxygenated muriatic acid may be executed without inconvenience, there is no harm in employing the addition of chalk, so as to repress the greater part of the odour. We even recommend not to omit its use, whenever persons are not very well instructed in conducting the operations with the customary attentions which are required.

CHAPTER IX.

Of the other Uses of the Oxygenated Muriatic Acid.

The property of discolouring and whitening which the oxygenated muriatic acid possesses, has met with several applications, which their analogy to bleaching, and their relation to the art of dyeing, induce us to enumerate.

When cloths have been printed with different mordants, they are passed into the madder, where the designs assume different hues, according to the nature of the mordants; but the (vacant) ground of these cloths also receives the madder colour. This colour is much less fast than that which has been fixed by the mordants; and it must be destroyed by means of cow dung and bran, and long exposure on the grass. Nearly the same process is employed to destroy the yellow ground of printed goods, which have been passed through weld to give the figures those hues which belong to yellow. At Manchester, the properties of oxygenated muriatic acid, modified by certain operations, which have not been made public, were speedily applied to that purpose.

Widmer and Haussman made some trials, each in his own way, from which it was ascertained, that a liquor, composed in the proportions which we have pointed out for the lixivium of Javelle, might be employed with success, but with the precaution of diluting it for use with a larger quantity of water. We shall state the result which Widmer has given of his experiments.

" When the cloth comes out of the madder, it is exposed for four or five days on the grass; it is then passed through a bath of cow dung, after which it is laid down four days longer on the grass, as at first. It is now submitted to an immersion of about half an hour in the bleaching liquor, previously diluted with about 35 parts of water. After this operation, the cloth must be exposed for two days on the grass. It is then subjected to a new immersion, and exposed for other two days on the field. Betwixt each operation the cloth must be well washed and beetled. The exposure on the field, here prescribed, is understood to be during fine weather; for in bad weather it must be exposed some days longer. In general, the ground of a cloth which has been well maddered, in order to have fast thorough-proof colours, should be perfectly white after this manipulation.

"It appears from this detail, that we no longer employ bran at all for the whitening of maddered goods. It is also obvious, that we have infinitely reduced the heating operations, since formerly, a piece of goods, after the maddering, received at least from three to six boils, whilst at the present day it gets one or two at most, and it is an infinitely less time on the grass.

"I have often bleached maddered goods without giving them any boil, submitting them merely to immersions every twenty-four hours, and exposing them alternately on the field. But this has several inconveniencies. In the first place, the goods are liable to have spots of a brick-red colour, which the workmen call *madder stains;* they proceed frequently from adulterated madders; an inconvenience felt only with the madders of Alsace. At other times, fat or oily matters, which are present in the goods, are the cause of them. These stains oblige us pretty often to subject the cloth to two boils, because the action of the acid, and the exposure on the grass, are insufficient.

"The goods, on coming out of the madder, are laid on the field, because the large quantity of colouring matter deposited on their ground, destroys too great a quantity of the acid, and the colours are thus much impaired, which has led me to believe that they need the contact of air to be rendered fast, if it be permitted me to make use of this expression.

"The cloth, after the first exposure on the grass, is subjected to a boil with cow dung. This operation has the advantage of predisposing the cloth to become white, to heighten by its heat the colours fixed by the mordants, and to render them more durable under the action of the air, and of the oxygenated muriatic acid holding potash in solution. I have diluted the liquor very much, because I do not then fear injury to any colour. I also pass through a colour that has a black ground, or its derivative hues, with as much confidence as those which have a mordant of alumina. The cloth, on coming out of these immersions, sometimes appears not to be sufficiently bleached, but they are wonderfully disposed to receive the action of the atmospheric oxygen. I have found several times, that on a piece of cloth being cut in two, when one-half of it had an immersion, and the other none, the former bleached more in two days on the field, than the latter in fifteen.

"When we are obliged to make the cloth undergo a second boil, it is given on its return from the grass, immediately after the first immersion in the liquor. By this second boil, we succeed in reducing entirely into a species of soap, and removing, those spots of grease which I have mentioned above. This likewise dissolves the colouring matters which have begun to oxygenate.

"The cloths which come out of the weld, whether with a yellow ground or a white, are first exposed for four or five days on the grass, and are then, in like manner, subjected to an immersion in the same liquor. The ground of the goods does not appear at all bleached; but as I have already stated, they are disposed to receive the action of the oxygen, and at the end of two or three days' exposure on the grass, they are of a superb white. When these cloths return for the last time from the field, the yellow has a deep cast, which renders it somewhat dead. This probably depends on the action of the oxygen of the liquor, and of the atmosphere, which seems to have effected a commencement of combustion. Its vivacity is easily restored, by passing the cloths through a water very slightly acidulated with muriatic acid; but the water must be no sourer than weak lemonade. This operation has moreover the advantage of carrying off the last portions of the yellow, which may have remained on the ground, or on the red; and which, consequently, would dull the lustre of both. This little manipulation, which lasts at farthest five minutes, has also the advantage of rendering the olive colours more of a greenish cast, tints which the dyer has usually much difficulty to obtain.

"I forgot to mention, that it is the strength of the colours which directs me as to the strength of the liquor. When the colours are powerful, I contrive it so, that the oxygenated muriatic acid may predominate in the liquor; on the contrary, if the colours be weak, it is the alkali which ought to predominate. But if a saturated oxygenated muriate (chlorate) of potash were made, it would no longer have the property of bleaching. I suspected, that by passing cloths merely into an alkaline water, it would dispose them equally to whiten on the grass; but experience has not realized this expectation.

"I was a long while of obtaining complete success with the oxygenated muriatic acid holding potash in solution, because I employed it in too strong a dose, and, of consequence, I injured the colours. But at present M. Oberkampf becomes every day more attached to this new method, which is infinitely less costly than the old one, and by which we obtain a more beautiful white, and far livelier colours."

Widmer has however been obliged to abandon this process, because it required to be conducted by himself, and because the accidents, from inattention of workmen, rendered this method too uncertain and too expensive. We know not whether a like cause has made it be equally given up in the other manufactories, or if they have found out some modifications which render the process less uncertain; but it should be retained for bleaching cloths in the texture of which there is linen or cotton dyed with some colour, which could not resist the too lively action of the oxygenated muriatic acid, or even exposure on the grass. (See Note G.)

When we wish to deprive of colour a piece of cloth which has some defect of dyeing or design, or whose colours have been rendered dull by use, a ley should first be given to it, and then one immersion, which is commonly sufficient. It is now submitted to a second ley, and passed through water acidulated with sulphuric acid. Without this last operation it would preserve a great part of its mordant, and could not, for this reason, receive a new impression or another design.

Chaptal made, at an early period, a happy application of the properties of the oxygenated muriatic acid to the bleaching of paper, and the restoration of engravings and books. We shall insert here the description which he gave of his processes.

" Blotting paper put into oxygenated muriatic acid becomes white in it, without being altered in its texture. The rags of coarse and bad cloth, made use of in paper mills to form this paper, are bleached in this acid, and then afford a paper of superior quality. I have whitened by this process a quintal of paste intended to furnish blotting paper, and the increase of value in the product was estimated at 25 per cent, while the cost of the operation, rigorously calculated, did not raise the expense above 7 per cent.

"The property which this acid possesses, of bleaching paper, without affecting the texture, renders it valuable for repairing old books, and smoked engravings. Engravings injured to such a degree as to render the design difficult to be distinguished, have been repaired and refreshed in so astonishing a manner as to appear new. Old books, soiled with that yellow tint which time leaves on them, may be so restored as to make us think they had just issued from the press.

"Simple immersion in the oxygenated muriatic acid, and a longer or shorter continuance in it, according to the strength of the liquor, are sufficient to bleach a print; but when a book is the object, other precautions are necessary. As it is requisite that the acid should moisten all the leaves, care must be taken to open the book well up, and to make its boards rest on the edge of the vessel, so that the paper alone dips into the liquor. Such leaves as are sticking together, must be adroitly separated, that they may be all equally impregnated. The liquor assumes a yellowish tint, the paper becomes white, and after two or three hours the book is withdrawn, in order to be plunged into pure water, which is to be renewed from time to time to carry off any remaining oxygenated muriatic acid, along with its disagreeable smell.

"This process has succeeded with me pretty well. It was the first which I employed. But too frequently the colour of the leaves was variegated; sometimes several pages have not been at all bleached; and I was forced to adopt a surer process. We begin by unstitching the books, and reducing them to leaves. These leaves are set in squares contrived in a shallow leaden tub, with very thin plates, so that the leaves, laid flat, are separated from one another by hardly perceptible intervals. The acid is then poured gently in, making it fall on the sides of the tub; and to prevent the leaves from being deranged after the operation is finished, the acid is drawn off by a stop-cock placed in the bottom of the tub. This liquid is replaced by fresh water, which washes the paper, and deprives it of the odour of the oxygenated acid. It is now hung up to dry, smoothed and bound. I have restored by this means several precious works, which were of no value from their bad condition. The leaves may be set also upright in the tub, a position which offers some advantages, as they are less readily torn. For this purpose I constructed a wooden frame, which I fixed down at the height which I thought suitable, conformably to the height of the leaves that I wished to bleach. This frame supported very thin slips of wood, leaving between them intervals of half a line. I placed two leaves in each of these intervals, and fastened them with two small wedges of wood, which I pushed between the slips so as to press the leaves against them. I give the more preference to this process, because, when the operation is done, I lift out the frame with the leaves, and plunge the whole into fresh water. By this operation, not only books are restored, but the paper receives a degree of whiteness which it never had. This acid has also the advantage of effacing spots of ink which frequently depreciate books and prints. This liquor does not attack the stains of grease or oil; but it has been long known, that a weak solution of potash (caustic alkali) is a sure means of removing these marks.

"When I have had to repair engravings in such bad condition that they exhibited merely fragments pasted down on paper, I was afraid of spoiling these fragments in the liquor, from the loosening of the paste. In this case, I took the precaution of enclosing the print in a large cylindrical jar, which I inverted over a glass, into which I put the proper mixture for disengaging oxygenated muriatic gas. This aeriform substance filled the interior of the jar, and acted on the print, consuming the filth, destroying the spots of ink, while the fragments remained glued, and thus preserved their relative position."

Loysel has prosecuted particularly the application of oxygenated muriatic acid to the bleaching of the paste of paper, because he was charged, as member of the committee of assignats and coins, to inspect this process, which was used for the assignat paper. We shall present a summary of the observations which he published.*

By the ordinary processes, only a small portion of the rag can furnish fine white paper; all the rest being appropriated to papers of inferior quality.

The bleaching of the paste of paper, even when derived from the most ordinary rags, can give it the quality of that of the finest rags.

The sinew of the paper depends on that of the fibres of which it is fabricated. The rags of new cloth and cordage afford a more sinewy paper than old rags. In the first rank are put rags of fine new webs, either green, or bleached by the oxygenated muriatic acid; after these come cordage and old rags.

The paper intended for bank-notes, or bills of commerce and service, should be sinewy, to render it less apt to be torn than its thinness would otherwise occasion. For this, it is right to employ in whole, or in a great measure, materials of the first class.

The processes prescribed for the bleaching of threads and cloths must be employed here, that is to say, the substance must be subjected to lixivia and immersions in the oxygenated liquor, when it is green (unbleached); but in operating upon rags, it is sufficient to give them an immer-

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* Annales de Chimie, tom. xxxix.

sion, and to pass them afterwards into acidulated water.

An inconvenience has been experienced in operating upon the paste of paper. It appeared very white, and yet it furnished an unequal paper. It was because this paste subsided, so that the leys and the liquors could hardly penetrate it. This inconvenience was remedied by taking the matter in a medium state, between that of a paste and of rags. This was secured by tearing it asunder under a first cylinder, thus destroying the texture of the rags, and separating the fibres that composed the thread.

When a very tough paper is wanted, the green rags must be submitted to the successive operations of bleaching. But when whiteness is the principal object, the cost of the operation may be considerably diminished, by leaving the rags for some time in the fermenting tub, and washing them with care. After this, one lixivium, two oxygenated liquors, and acidulated water, will be sufficient.

In this operation, the combination of oxygenated muriatic acid with potash, dissolved in twenty times its weight of water, has been employed. Undoubtedly, with a suitable apparatus, there might be used without inconvenience simple oxygenated muriatic acid, or this mingled with chalk.

Notwithstanding the increase of expense caused by this addition of alkali, Loysel shews, that the value added to the paper by the process affords a considerable profit.

In treating of hemp and flax, we have described the processes by which it has been attempted to give them the appearance of cotton; but the oxygenated muriatic acid may be beneficially employed for this purpose.

Pajot des Charmes seems to have been the first who made this application. We shall recite the passage where he points it out.*

After having announced that the loose fibres bleach very quickly, that is to say, at one or two immersions less than average yarns, he adds: "It is to be remarked, that the tow of flax or hemp proceeding from the fibres thus bleached, or bleached separately, cut, if it be too long, and then carded, singularly resembles the cotton of Siam, which is known to be the shortest and the most common of the cottons of commerce. When it is well carded, their difference cannot be discerned; nor is it possible to distinguish between them in spinning. I took occasion to make some of it be woven at the end of a web: it would have been taken for real cotton. I took occasion, in like manner, to employ some of it for candle-wicks, without any perceptible difference being found by the quantity of light or the brightness. It would be very interesting, without doubt, to know all the benefits which could be derived from this application of the oxygenated muriatic acid to the arts of life."

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* L'Art de Blanchiment, page 106.

Some time thereafter, but without knowing what has been now detailed, a description of operations made in the laboratory of the Polytechnic school, to accomplish the above object, was published in its Journal. But Giobert has given us more extended and more exact observations, capable of directing this new branch of art, which may probably acquire some importance.*

“ The process which I have followed,” says he, “ is in general the same as what Berthollet has just proposed, but with this difference, that in the trials made at the Polytechnic school, long fibres cut in fragments about six centimetres in length were employed; whereas, in all my attempts, and in my operations on the large scale, I employed merely hemp tow of the worst quality, at three sous the pound.

“ The process which Berthollet describes is the same, and consists of the following operations.

“ The fibres are covered with water, and left in it for three or four days; after which they are boiled in simple water.

“ 2. They are treated with a ley, and then assed into the oxygenated muriatic acid; operations which should be repeated alternately four times.

“ 3. The fibres are now transferred into a bath of water, charged with one-hundredth of sulphuric acid, and left in it for half an hour.

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* Bibliot. Ital. vol. ii.

"4. The fibres, when taken out of this bath, are washed very carefully, and plunged in soap water. They are then stretched out without wringing, on hurdles, and left to dry.

"On this process Berthollet has remarked, 1. That it requires only from five to six hours when small quantities are operated on; 2. That the loose fibres thus prepared, were capable of being spun into very fine yarn of sufficient strength, although the filaments had been cut very short in his trials; 3. That the leys should not be too strong, but that they should be boiling hot; 4. That whether the finest flax, or the coarsest hemp tow be employed, we obtain filaments equal in their fineness and whiteness; finally, he adds, that by preventing too strong desiccation, the last immersion in soap water might be suppressed.

"The different observations which we are going to make on this process, are the result of operations on a large scale, which have brought into the market *cottony* cloth, and *bales* of this hemp-cotton, which were not distinguishable from ordinary cotton. From these results, various ameliorations have suggested themselves. We shall follow in our operations the same order as ought to be pursued in the practice of the above process.

"1. *Preliminary maceration of the fibres, (filasse.)*

"This operation is not absolutely necessary, and it may be supplied by a good ley. But a previous maceration is more economical. Instead of pure water, old ley should be used in preference; but if there be none of this, plants, especially mucilaginous ones, boiled in water with the addition of a little potash, afford a better solvent. The steeping may also be continued longer, even for five or six days without risk in the hottest season, along with the employment of alkalies that seem to favour the putrid fermentation. In spring, autumn, and winter, it may be prolonged with advantage from seven to nine days. By this longer maceration, the fibres become finer, that is to say, the filaments come asunder, and the operations to which they are subjected in the sequel have a greater effect.

"When the fibres are well steeped, it is absolutely useless to wash them with hot water, which only augments the cost. Cold water is sufficient; but it must be in a stream, treading the fibres with the feet till the water issues very clear.

"2. *Of the leys and immersions in oxygenated muriatic acid.*

"The leys might be dispensed with, by abandoning the fibres to fermentation, in the manner above stated, after having passed them through the oxygenated muriatic acid; but this practice is too tedious. Nothing however occasions more inconvenience here than the lixiviation. Every filament of hemp or flax which has been lixiviated thence derives stiffness, especially in its extremities, which are to be joined continuously in the formation of yarn. Hence its spinning becomes difficult, disagreeable, and unequal. The spinster loses patience; while the ends of the fibres do not twist well together, their adhesion is imperfect, and by sliding on each other, when the thread is slightly pulled, render it feebly tenacious. This may be regarded as a general fact. Yet leys can hardly be dispensed with in a great manufacturing establishment of hemp-cotton. For this reason, we must try to remedy these inconveniencies, which cannot be economically avoided. We shall point out by and by two methods which succeed pretty well. As to the leys, they ought not to be strong, as Berthollet rightly says; but they should be very caustic, carefully preventing an excess of lime or of lime water in the liquor; for, in this case, the fibres are too much weakened on one hand, and grow stiff on the other. A ley is not too caustic, when on evaporating a portion of the liquor, it is not disturbed, nor lets fall lime. The ley-boil ought not to exceed three hours; but after this the greatest part of the liquor must be drawn off, and the fibres must be allowed to cool in a heap in the tub before washing them. It is useful to place on the cloth which covers the fibres, large compressing weights. This repose of the fibres, with little liquor, has a more decided effect than the lixiviation; and the larger the quantity operated upon, the better does it answer.

"It is useful to arrange the apparatus, so that the fibres can be thereafter washed by a stream of water in the very tub in which the lixiviation has taken place; and it is in this same tub that it is afterwards subjected to the oxygenated muriatic acid, which ought to be very weak.

" 3. *Bath of sulphuric acid.*

" An acid bath is indispensable to give a shining whiteness to the fibres. But these when bleached contain lime, which, forming an insoluble salt with sulphuric acid, causes this to be ill adapted for the purpose. The resulting sulphate of lime adheres to the fibres, making them rigid; nor is it possible to carry it entirely away by washing. I have found, that by substituting muriatic acid for the sulphuric, the fibres have more pliancy. Muriatic acid has a somewhat higher price in commerce; but by making it within the manufactory, the expense incurred by this substitution is not very considerable, and it ought to be preferred.

" 4. *Soaping.*

" The last operation is the soaping. This is indispensable; nor ought any person to imagine he can do without it, for it is only by the soaping that we succeed in thoroughly separating the filaments. Besides, it is only by the soaping that we begin to correct the rigidity which the ley gave to the fibres, and to give them the pliancy of ordinary cotton. But to attain this end, we must proceed in a different manner from that described by Berthollet.

" The fibres, on coming out of the preceding bath of muriatic acid, instead of being washed with much care, as is stated in Berthollet's process, ought not to be washed at all. They should be plunged, while still wet with the acid liquor, into the hot soap water, without fearing in the least the action of the acid. The soap is decomposed by the acid, the resulting muriate of soda is carried off by successive washings, and the oil of the soap being absorbed by the fibres, gives them pliancy and softness. The filaments remain more delicate, and the successive operations of carding and spinning become consequently easier. This is the first of the two methods which we announced for removing from the fibres the stiffness which the alkalies of the lixivia gave them.

" 5. *To give pliancy to hemp-cotton.*

" Notwithstanding the preceding processes, the cotton has not yet got all the pliancy which is required. This will be completely given by the following operation. The dried fibres are formed into large bales, and kept well packed up in a somewhat damp place for two or three months. A species of fermentation is by this means excited in the fibres, which gives them the desired fineness.

" 6. *To give the appearances of ordinary cotton to hemp-cotton.*

" The cotton procured from hemp by the preceding operations, whatever care may have been bestowed, is always different from ordinary cotton, and it is easy to distinguish it. The fibres preserve a peculiar glitter, very different from the dead white of cotton. This lustre is sufficiently agreeable, and may possibly be sought after for several objects of manufacture; but it is not a property of cotton, and must therefore be regarded as a defect in our attempts to imitate ordinary cotton. I have discovered only one method of remedying it, which consists in mixing by the cards from 10 to 15 per cent of ordinary cotton with that of hemp. The cotton yarn made by this means is no longer distinguishable from ordinary cotton yarn."

SECTION IV.

OF DYEING OPERATIONS IN GENERAL.

CHAPTER I.

Of Dyehouses and the Manipulations of the Art of Dyeing.

If it may be regarded as a general principle, that processes performed in a great manufactory are more advantageous than those which are insulated *(isolés)*, since from the subdivision of labour each workman, occupied with a single object, acquires celerity and perfection in his employment, and since every thing being concatenated, each portion of the work is carried forward without loss of time; this principle should be applied to dyeing for a peculiar reason, because the residuum of one process can frequently serve for another. A bath which is found to be too much exhausted for one colour, or even for what is called the *suites* (gradations) of a colour, may either give a ground *(footing)* to other dye stuffs, or form a new bath, by mixing other ingredients with it. Gall-nuts which have been employed for galling silk, may still be useful for other operations on wool and cotton. A great number of similar examples might be adduced.

By such considerations, it would be easy to prove how adverse to the advances of the art were that division into the *great and little dye*, that classification of silk, wool, and linen dyers, and those regulations which prohibited a dyer of one class to keep by him the ingredients assigned to another class. On the contrary, it seems proper to encourage large undertakings in dyeing; and those who are to direct them ought to lay down a plan of the operations, so that there may be a relation between them all, and that there may be no waste of ingredients, time, fuel, or manual exertion. This arrangement should be made subservient to the probable demands of commerce.

A dyehouse ought to be spacious, well lighted, and as near as possible to a stream of water. It should be floored with lime and cement; it should be provided with ready outlets for the water and the spent dye-baths; and the whole so ordered as to secure the utmost cleanliness.

The boilers, whose arrangement and size depend on the operations for which they are intended, should be made of copper or brass; except for dyeing scarlet, for which it is better to employ boilers of tin, as well as for other delicate colours, where a solution of tin is made use of. Brass is less liable to be attacked by saline substances, and to stain the goods, than copper. We shall see, however, that in many cases vessels of wood may be substituted for metal boilers. It is of consequence to cleanse the boilers well after every operation; and such as are of great capacity ought to have in their bottom a copper pipe, with a stopcock at its outer end, which is opened when the baths are to be emptied.

Above each boiler, holes are pierced in the chimney-piece or wall, for resting the ends of poles, which serve to sustain the hanks of wool or silk while draining, or stuffs of which only small portions are to be dyed. Thus also the bath-liquor falls back into the boiler.

For piece-goods, a winch or reel is employed, the two ends of which rest in two forks of iron, placed, at pleasure, in holes bored in the curb that supports the edges of the coppers.

Several silk and cotton dyes, for which ebullition ought not to be employed, are performed in long vessels of copper or wood, called troughs or backs, *(barques ou baquets)*.

As the most part of colours applied on silk are very delicate, they require to be speedily dried, to prevent their changing. For this purpose a drying room is provided, which is heated by means of a stove. The silk is stretched on a moveable pole, called a shaker *(branloire)*, which is hung up and agitated to accelerate the desiccation. A drying room is also used for cotton cloths which have been impregnated with a mordant.

Long details must be entered into, were we to describe every thing which constitutes a dye-house. Inspection will instruct much more speedily and exactly than a minute description of these objects could do. The distribution of a dyehouse ought also to be subservient to the operations for which it is destined. It should be so regulated, that these operations may follow one another with most advantage.

But it is desirable for the advancement of the art, as well as that of the science itself, that a small place may be reserved, in which the apparatus necessary for the common experiments of chemistry and the trial of dyes may be collected.

The manipulations of dyeing are neither difficult nor complex. Their object is, to impregnate the substance which we wish to dye with the colouring particles held in solution in a bath; to make the agency of the air co-operate in the fixation of the colouring particles, or in giving them lustre; and to discharge with care such as have not been fixed in the dyed stuff. We shall content ourselves with giving an account of the most common manipulations, and of the denominations.

When one or more pieces of goods are to be dyed, the winch (reel) is employed, as above described. One end of the cloth is wrapped round this reel, which being turned quickly, carries round the whole piece in succession. The winch is next turned in the opposite direction, in order that the part of the web which was first plunged the former time, may be last at the second immersion, whereby the dyeing is rendered as equable as possible. If the piece of goods be long enough, or if several are to be dyed of the same colour, their two extremities are stitched together, the winch is passed within, and then set on its forks.

When a solution of iron is employed, especially to give different shades to cotton goods, which are, for example, to be afterwards passed through madder, we must prevent with great care the progressive and unequal oxidation of the metal, according to the directions of Chaptal on this subject,* which we shall take occasion to recite.

If wool in the fleece is to be dyed, there is set over the boiler a very broad kind of ladder, (called by English dyers, a *scraw* or *scray*), the bars of which are very close together. On this the wool is laid to be drained and aired, as well as during the changing of the bath.

When the wool is in skeins, a rod is passed through each of them, and the manipulation is the same as for silk and thread. This manipulation consists in turning round in the bath the hanks of silk, and the skeins of thread or woollen yarn on the rods. This is called *liser* (shaking over), and to the rod the name *lisoir* (skein stick) is given.

After silks and yarns have been dyed, it is necessary to wring them, in order to squeeze out the excess of the colouring particles. This operation is performed on a cylindrical piece of wood, which is fixed at one end in a wall or to a

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* Memoires de l'Instit. tom. iii.

post. It is called *espart.* When this operation is repeated several times in succession, in order to dry and give lustre, it is called *cheviller,* (wringing by the jack and pin).

When a certain quantity of ingredients is added to a bath, it is said that a *brevet* is given it; and it is pallied *(on le pallie)* by stirring it about and mixing it with a rake.

Sometimes a first colour is given in order to apply another one above it, thus forming a compound colour. This is what is called *giving a ground, (donner un pied).*

Disbroder (rinse) is to wash silk from its dye, or its soap water, in a small quantity of water, to which the name of *disbrodure (rinsing)* is given.

When a stuff must be passed several times through the same bath, the name *passe (dip)* is given to each particular operation.

A colour is *rosed,* when the yellow tone of a red colour is changed into a shade which borders more on the crimson, or on the colour of roses; and a colour of a red-yellow is *veered (virée),* when it is made to turn to a more decided red.

Although the manipulations of dyeing may not be very various, and may appear very simple, they require peculiar care, as well as a skilful eye, to judge of the qualities of the bath, to raise and support the heat at the degree suited to each operation, to remove all the circumstances which might produce inequality in the colour, to judge with precision of the shades as they come out of the bath, to match those which serve for patterns, and to establish the desired relation between a succession of hues.

CHAPTER II.

Of Fuel.

As fuel is one of the chief articles of expense in dyeing, it is of great consequence to diminish its consumption as much as possible, and to select the kind which may afford the desired effect with the least cost. It is proper, therefore, to be acquainted with the philosophical principles of the production of heat by combustion, the theory of which we owe chiefly to Lavoisier, as well as with the laws of its communication, in order to be able to guide ourselves afterwards in their application to the various circumstances that may occur.

When a body is burned, none of its ponderable principles are destroyed. They previously formed a mere combination with each other, and they are separated at the high temperature to which they are exposed; thus forming other combinations with the oxygen with which they come into contact. Such of these principles as cannot combine with it, that is to say, earth, certain salts, and metallic ingredients, constitute the ashes.

The combinations formed, when the reciprocal action of the oxygen gas and of the inflammable principles present in the combustible becomes complete, are carbonic acid and water. The proportion of these new products varies, according to that of the carbonaceous particles, and of the hydrogen or base of inflammable air which exists in the combustible. Let us take common charcoal for an example:—

If 100 parts of charcoal be burned in a glass bell, whose orifice is plunged under mercury, there is found, after the combustion, a weight of carbonic acid, equal to that of the charcoal burned, and of the oxygen, which has now lost its properties. This acid so formed is composed, in 100 parts, of about 72 of oxygen and 28 of charcoal. A little water is however generated, which is taken up by the carbonic acid, or remains in the liquid state. The unknown quantity of water prevents us from regarding the determination now given as rigidly exact.

If alcohol or spirit of wine be burned, the result is different. A weight of water is obtained exceeding that of the alcohol, because the combustible principle of alcohol is chiefly hydrogen, which forms water by combining with oxygen. Oil also affords much water, for the same reason. Charcoal and alcohol, or rather ether, may be regarded as the two extremes, of which one yields most carbonic acid, and the other most water; and the other combustibles may be viewed as mean terms, which approach more or less to one of the two extremes, according to their composition.

While the hydrogen and the carbon combine with the oxygen, which forms a little less than the fourth part of the atmospheric air, the caloric or principle of heat, which was combined with the oxygen gas, giving it the elastic state, is in a great measure disengaged. A portion of it is also probably disengaged from the charcoal, and especially from the hydrogen; but as the heat produced when oxygen passes from one combination into another, appears nearly proportional to the quantity retained, we depart very little from the truth, in ascribing to it the whole heat disengaged in combustion. Hence the heat produced in combustion, must be regarded as proportional to the quantity of water and carbonic acid formed. We must however remark, that the same quantity of oxygen which enters into combination with hydrogen to form water, gives more heat than when it produces carbonic acid with charcoal. Hence combustibles which contain much hydrogen, such as the oils, the resins, and pit coal, produce in equal weight, and in circumstances equally favourable, more effect than those which owe their inflammability to charcoal.

If the proportion of oxygen gas which combines be insufficient (for saturation), water and carbonic acid are not the sole products. A gaseous substance is formed, which may be regarded as intermediate, being convertible into water and carbonic acid, by means of a new proportion of oxygen. It has been named *oxycarburetted hydrogen,* in order to denote its composition.*

Oxycarburetted hydrogen gas produces the blue flame over furnaces, when its temperature is great enough to burn on passing into the atmosphere, where it finds the oxygen which was deficient in the furnace.

The conditions necessary to obtain the greatest effect of combustion may be established on the foregoing considerations: 1. The quantity of oxygen ought to be sufficiently great for the whole charcoal and hydrogen to enter into complete combination, without producing oxycarburetted hydrogen gas, and without the combustibles escaping under the form of soot or smoke.

2. On the other hand, too great a proportion of air must be avoided, for whatever is useless to the combustion, by abstracting the heat disengaged from the fuel entering into combination, would obstruct the elevation of temperature which is the object of the combination.

3. The current should be rapid, that the heat may become intense, and the temperature be sufficiently elevated for every thing combustible to undergo the oxygenous combination.

In order to obtain the greatest effect of a combustible, none of its particles capable of combining with oxygen should escape the operation; there should be neither soot nor smoke; a result obtained chiefly by the just proportion between

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* Statique Chim. tom. ii.

the lower opening of a furnace, its grate and chimney.

The current of air which maintains combustion should be easy; but if the chimney is too large, the carbonic acid formed is carried off with difficulty; it remains too long in contact with the combustible body, thereby opposing its combustion, while an interior circulation is established, which brings back the cold air towards the boiler, and pushes down the smoke. If the chimney is not high enough, a portion of the inflammable gas escapes without burning, as well as the carbonaceous particles that form the soot; whence the effect of the combustible is diminished. A higher column of air, rarefied, and rendered lighter by heat, and next its condensation, as well as that of the steam and carbonic acid, towards the top of the chimney, would have contributed to establish a more rapid aërial current. These effects are peculiarly observed in reverberatory furnaces, in which it is easy to verify the benefit of a chimney whose opening is in due proportion to the size of the furnace, and whose activity is increased by adding to the upper orifice a certain extent of pipe. But too lofty a chimney is another inconvenience to be avoided; because the combustible parts which rise have time to cool below the degree at which their combustion takes place, forming merely a mass, which, with the carbonic acid, opposes the circulation of air.

When a furnace is intended for a boiler or a series of boilers, it must be so managed that the combustion is completely executed in front of the space in which the heat should be concentrated. In order to obtain this effect, it is proper that the grate (hearth) in which the combustion takes place be in front of the boiler, as Curadau recommends,* to whom we owe several interesting observations on the regulation of furnaces. Since the current of air is greatly more rapid when the furnace has a high temperature, it is proper to diminish its column by means of a register (damper) placed in the chimney. This register serves likewise to intercept the current when the combustion is finished, and when we wish to turn the remaining heat to account by preventing it from being hurried off by the air.

The form of boilers is not unimportant towards obtaining the greatest effect of fuel with the least cost and loss of time. It should be subordinate, however, to the kind of operation that is intended. We shall restrict ourselves to a few observations on this subject.

The boilers should present the utmost possible surface to the fire, and the heat should be applied to the greater part of their outer surface by making the flame circulate round them. Consequently, when they are intended for evaporation, distillation, or the heating of liquids, as leys for example, their width should be greater than their height. Chaptal recommends, moreover,† to con-

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* Ann. de Chimie, tom. xlvi.

† Elemens de Chimie, tom. i.

struct them so that the bottom shall be convex within. By this construction, the insoluble parts thrown off upon the sides obstruct less the communication of the heat, while the copper at the bottom is longer preserved.

It is not enough to pay attention to the combustion, but the resulting heat must be distributed also, so as to produce most advantageously the desired effects.

There are bodies which afford a ready passage to heat; such, in particular, are metallic substances. There are others, on the contrary, which conduct it slowly and with difficulty; such are glass, pottery, bricks, woollen tissues, ashes, and especially charcoal. The latter substances ought therefore to be made use of, either directly or as envelopes, when it is desired to maintain the temperature; but metallic substances, when the heat is to be diffused. The colours of the surfaces which disseminate or receive heat, may also possess an influence, according to the recent ingenious observations of Count Rumford; but we are not yet acquainted with their applications to the arts.

When the object is to form a solution, attention ought to be paid to the effect that specific gravity may produce on the solution, or on the communication of the heat.

Every chemical combination, and that of caloric, which follows its laws, are more speedily effected the more distant the point of saturation. Hence, when a salt is dissolved at the bottom of a liquid, which thus acquires a greater specific gravity by its saturation, the successive layers of liquid are kept in their respective position, and the most saturated remain at the bottom. There is but a slight difference in saturation between each of the layers, and thus the equilibrium of the whole is long of being acquired. But if the salt is placed at the surface, the portion of the liquid which becomes saturated falls to the bottom in consequence of the specific gravity which it has acquired. A current is established which continually brings the least saturated liquid in contact with the salt, whence the solution is more quickly made, even without employing manual agitation, which also acts by approximating the less saturated portions to those which are completely so.

On these grounds we have recommended, after Welter, to operate at the surface of the water the solution of potash intended for leys. If a gaseous substance is to be dissolved, the solution should, on the contrary, be effected in the lower portion, in order to keep at a distance, by a less specific gravity, the liquid which may be already saturated.

When water is converted into vapour by ebullition, it contains a great deal of caloric in a latent state, which it gives up when restored to the liquid condition. It results from the experiments of the celebrated Watt, that this quantity would be sufficient to raise the thermometer of Fahrenheit 900°, or the centigrade thermometer 500°;

whence it follows, that one part of steam at the temperature of ebullition can raise, by losing itself the vaporous state, five parts of water from the temperature of zero to the boiling point.

We thus perceive what advantages might be derived from the steam that issues from boilers; but the requisite manipulations would seldom permit us to take the full benefit of it.

The celebrated Rumford, to whom we owe a great many ingenious observations on heat, its distribution, and the economical use of fuel, has pointed out modes of employing the vapour of water for the communication of heat, which may be peculiarly advantageous in the art of dyeing. We shall give some account of them.

The purpose of the apparatus is to generate steam, to be carried into a vessel filled with any liquor which we may wish to heat by its agency. A boiler must therefore be procured for keeping up the ebullition of water. It ought to be spacious enough to form a sufficient quantity of vapour; and agreeably to what has been described, it ought to have greater length than height, and be so placed in the furnace as that most part of the circumference shall be exposed to the current of flame.

This boiler must give origin to a large pipe, which serves as a reservoir of steam. From this reservoir the conductor tubes branch out, which are to transmit the vapour into the receivers to be heated. These tubes should have a slight inclination, that whatever vapour has resumed the liquid state may flow back into the boiler. Into the end of each a vertical tube enters, which carries the steam into the lower part of the receiver, and which may be placed even in the inside of the receiver, or on its outside surface. Above the level of the liquid the latter tube should have an accurate stopcock, to prevent the liquid from rushing back into the boiler when its steam is condensed by cold, or has lost some of its elastic force. To prevent the accidents, however, which might be occasioned, either by negligence in shutting the stopcock, or, on the other hand, from so rapid a formation of steam as might burst the apparatus, the boiler ought to be provided with two valves, one intended to permit the introduction of air when a vacuum is formed interiorly, the other to give an outlet to the steam when its force becomes too considerable.

To supply the steam-boiler with water, a reservoir is needed, which communicates with it by means of a tube. This ought to have a stopcock opening by means of a floater, when the water of the boiler is diminished to a certain point. This tube should be more or less elevated, according to the degree of temperature which the steam is to possess; for without sufficient pressure, the vapour of water could not raise the water which condenses it to the degree of ebullition. This circumstance obliges us to give the boiler sufficient thickness to support the expansive action of the steam at a temperature above the boiling point. The water contained in the reservoir may be prepared to produce its effect, by previous heating through the prolongation and distribution of the chimney of the furnace.

The whole outside of the apparatus must be preserved from the loss of heat, by surrounding it with non-conducting substances. The author recommends to apply, by means of paste, to the surface of the tubes, two or three coats of paper; and still better, hemp wrapped round in the direction of its filaments. He has made curious experiments on the power which this envelope gives. They are next surrounded with a wooden case filled with charcoal dust, or pounded bricks.

In this way dye-baths may be heated, substituting wood for metals, and heating several by means of a single furnace, which may be at the same time portable. Different degrees of heat are given, according to the dimensions of the tubes which conduct the vapour into each bath; and an uniform temperature is obtained. Lastly, the same method may be applied to the construction of drying rooms and stoves, the condensed water being reconducted into the boiler.

This method, which may be varied and multiplied in its applications, deserves peculiar attention, since English industry has already turned it to several purposes. (NOTE R.)

Having thus given an idea of the phenomena of combustion, and pointed out the means of profiting by the heat, it remains to consider the different kinds of fuel, in reference to their peculiar advantages.

To compare the effect of different combustibles, the process described by Lavoisier may be employed.* It consists in burning each species of combustible in the same furnace, over which a boiler is placed. Into this boiler an equal quantity of boiling water is poured, and what has been evaporated is replaced by letting in an equal weight of water at each operation. The quantities of fuel required to evaporate the same quantity of water are afterwards compared. It is obvious, that the qualities of the combustibles are proportional to the quantities necessary to produce the same effect. We have to compare, then, merely the quantities of each combustible employed in the evaporation, with its respective price, in order to determine what are the most advantageous, and ought to be preferred. For this calculation, the weight or volume of each combustible may be made use of indifferently, provided the price of the measure be known.

Instead of evaporating the same quantity of water, the desired result may be equally attained, by burning either the same weight or the same measure of each kind of fuel, and comparing thereafter the quantities of water evaporated.

As the bulks and weights of fuel should be compared with the price, and as this price varies considerably in each country, nothing of an abso-

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* Mem. de l'Academie, 1781.

lute nature can be established concerning the combustibles whose employment is the most profitable. In one place it will be pit-coal; in another, it will be wood or turf; the ratio of the prices may vary even in a short time, either by opening a canal, by working a mine of pit-coal, or by the destruction of a forest. Several operators retain a prejudice against the use of pit-coal; but it is enough to observe, that it is at present employed in so great a number of dyehouses, without any inconvenience being experienced, that there can be no doubt of its answering as a substitute for other fuel; but as in equal weight it yields much more heat, a little practice is required in its management.

Pit-coal requires in the furnaces a construction somewhat different from that of the furnaces in which wood is used. As it kindles with difficulty, it must be burned on a grate, which affords passage to a current of air. Its qualities are moreover very variable; and the kind useful for one purpose is not fit for another. Even should experience prove, that there is no advantage in our country in preferring pit-coal to wood, the use of it should be begun; because it is very probable, that the price of wood will progressively increase, while, on the contrary, that of pit-coal will fall, because its mining will be promoted by being made with more intelligence than it has hitherto been in France, and because it is to be hoped that canals for facilitating its carriage will be multiplied.

Coal & wood

Pit-coal is reduced into a true charcoal, by an operation analogous to that by which wood is carbonized; an operation to which the name of *dessoufrage* (cokeing) is given. This charred coal affords a real advantage in the great furnaces, which serve to smelt ores of iron, because pit-coal swells and agglutinates when it is highly heated, thereby choking the furnaces; inconveniencies which it no longer possesses after being coked. But for other uses, it is preferable in its natural state; because all the bituminous oil, burned off when it is reduced into charcoal, is wasted, without producing any effect; and this operation requires labour, which must be paid for.

Turf (peat) is also reduced to charcoal; but this operation presents a difficulty not easily overcome. When the recent charcoal of turf is exposed to the air, it takes fire of itself, like a pyrophorus; an inconvenience which has, however, been eventually obviated.

What has been said of pit-coal is applicable to turf. When it can be employed in its natural state, it is more profitable to do so than to incur the necessary expense of converting it into charcoal, with the loss at the same time of the whole portion which is consumed in this operation, and which could have served to produce heat.

CHAPTER III.

Of the Means of ascertaining the Goodness of a Colour (Dye.)

As colours differ greatly from one another, in their manner of resisting the action of air, light, and other agents to which they may be exposed; and as in this circumstance an important quality consists, of which the eye is no competent judge, methods have been sought after for verifying their goodness by easy and ready tests.

The purpose of these tests was to condemn the dyes which could not resist them. It is truly important to protect commerce from the frauds which may impair the confidence of which it stands in need; and its interests would be promoted, were we able to assign the standard of manufactured productions like that of gold and silver. But is it possible to find means sufficiently certain, and at the same time expeditious, capable of determining the solidity (durability) of a colour, as well as its lustre, and the other qualities which it is desired to possess? Were these means found out, could they be applied with equal success to the processes which an active industry discovers and introduces every day?

Much importance has been assigned to those tests formerly called *debouillis*, at a time when the processes of the arts were subjected to regulations which sometimes directly counteracted their advancement. By these, the workman in the fugitive *dye* was punishable for employing certain ingredients, capable of giving fast colours.

These shackles were perhaps necessary to the establishment and the early progress of industry; but at the present day, they are irreconcileable with its interests. With regard to goods which are to be exported, it is possibly wrong to depend upon such indications of manufactures as are exacted from the *chefs des pieces*, (inspectors of dyes). It is well known how much our commerce has lost in the Levant by fraudulent fabrications and dyes, under known appellations.

We shall not examine this question; but we shall recapitulate what experience has taught concerning the methods which may be employed, among which a dyer may select some profitable even for his own use. We are peculiarly induced to do this, because the tests at first prescribed have been rectified by the experiments of Dufay, a philosopher possessed of much sagacity. We shall now, before transcribing the instruction founded on his trials, present the history which Hellot has given of them, with his judicious reflections.

"Since it cannot be exactly ascertained, either by informations taken from different dyers, or by the perusal of ancient regulations, what are the precise characteristics of the colours of the good dye (fast), or those of the small dye (fugitive), it became necessary, in order to acquire this knowledge, to take the longest, the most difficult, but, at the same time, the most secure, or to speak more properly, the only method on which it was possible to depend with certainty. The late M. Dufay, of the Royal Academy of Sciences, whom the government appointed to labour towards the perfection of this art, caused woollens to be dyed, under his eye, of all colours, and with all the ingredients which are used in dyeing both in the *great* and little *dye*, (in fast and fugitive colours). He even brought from different provinces articles not employed at Paris. Lastly, he collected most of the materials which he suspected to be made use of in dyeing, and he tried a very great number of them, without attending to the prejudices of dyers relative to their good or bad qualities.

" He began his trials on woollen yarns; but he found in the sequel, that pieces of white cloth were more convenient for the experiments which he had the intention of making.

" In order to ascertain among the different colours, those which were solid, and those which were not so, and consequently distinguish the fast from the fugitive dyes, he exposed to the sun and the air, during twelve days, patterns dyed by himself of all these colours, with whose composition he was acquainted. This period seemed sufficient to prove them; for good colours are either not at all damaged, or very little, while the spurious are in a great measure effaced. Hence, after twelve days' exposure to the sun in summer, and to the moisture of the air during the night, no doubt could remain about the class to which each colour ought to be assigned, when it was tried in this manner.

"Nevertheless, one difficulty still remained; for, not having exposed all these colours to the air precisely at the same time, or in the same season, some of them must have had more sun than others, and must, of consequence, have lost more in the same space of twelve days than those which had been exposed in gloomy weather, or when the days were shorter. But he obviated this inconvenience, so as to leave no more difficulty or doubt of the correctness of the test; for he selected one of the worst colours, that is to say, one of those on which the sun had taken the most sensible effect during the space of twelve days. This colour served him as a comparison piece for the whole course of his experiments, and every time that he exposed the patterns to the air, he annexed to them a piece of this same stuff. It was now no longer the number of days to which he had respect, but the colour which his comparison specimen assumed, and he kept this exposed till it had lost as much as the piece which had been exposed during twelve days of summer. As he always noted the day on which he exposed his specimens, he had occasion to observe, that in winter it was sufficient to leave them in the open air four or five days longer, for them to lose as much colour as they had done in summer. By pursuing this method, no scruples remained in his mind about the accuracy of his experiments.

"In this proof, by exposure to air and the rays of the sun, he had still another object; it was to find the *debouillis* suitable to each colour. The term *debouilli*, or *debout*, denotes the test which is applied in order to learn if a stuff has a fast dye or otherwise. A pattern is boiled with alum, tartar, soap, vinegar, lemon juice, &c.; and from the effect of these drugs on the colour, its quality may be judged of. The *debouillis* practised up to the year 1733 were so insufficient, that they could not serve to M. Dufay as indications for finding out surer ones. Indeed some good colours were thus carried off, while the bad ones were very little damaged. Hence he was obliged to fix on several tests, each of which serves for a great number of colours. The following is in a few words the path which he pursued in order to find them.

"After having observed the effect of the air on each colour, whether good or bad, he tried on the same stuff different species of *debouillis*, and he kept by that which had the same effect on this colour as the air had produced. Noting afterwards the weight of the drugs, the quantity of water, the duration of the trial, he was sure to produce on that colour an effect equal to what the air ought to make on it, supposing that it had been dyed in the same manner as his own had been, viz. according to the method either of the fast or fancy dyers. Making thus a survey of all the colours, and of all the ingredients used in dyeing, he discovered a method which may be regarded as accurate, of knowing the good or bad quality of each colour, making by the *debouilli* a kind of analysis of its composition. We cannot without injustice fail to acknowledge, that the means which led M. Dufay to the discovery of these *debouillis,* or tests of colours, are very ingeniously imagined; because the trial by the air and sun cannot be put in practice in cases where it must be decided on the spot, whether a stuff, exposed to sale, in a fair or elsewhere, is of good dye, should its price correspond to this quality.

" The *debouillis* of the new instruction, founded on the memoirs of M. Dufay, cause the dye to lose in a few instants, if it be spurious, all that it would lose on being exposed during 12 or 15 days to the air. But as general rules for similar trials must be subject to many exceptions, which are either not foreseen, or, being foreseen, cannot be detailed, without running the risk of causing confusion, or numberless subjects of controversy, it follows that these rules, advanced perhaps as too general, are also too severe in several cases, where light colours admit of salts, or doses of salts, which will be less active than deeply charged dyes, which may lose a considerable quantity of their colouring ingredients in the active liquor of a particular *debouilli,* without exhibiting any very sensible change. It would have been requisite, therefore, to have prescribed a *debouilli* for almost every shade; which was impossible, considering their infinite varieties. Hence the air and the sun will be always the true tests; and whatever colour shall not suffer alteration during a certain time, or shall thus acquire what the dyers call a body *(fond)*, must be reputed of good dye, even though it should change considerably in the *debouillis* prescribed by the new instruction. Scarlet is an example of this. As soap carries off this colour almost entirely, it was subjected to the proof of alum; and when it is made with cochineal alone, without a mixture of other ingredients, it should assume, in a boiling-hot solution of alum, a purple colour. If scarlet be exposed to the sun, however, it loses a part of its vivacity, and becomes deeper; but this shade is not the one which alum gives it. Hence the *debouillis*, in certain cases, cannot be substituted for the action of the air and sun, at least with regard to parity of effect.

"I have made with brazil wood, which, like all the other woods charged with colour, is a false dye, a much more beautiful red than the madder reds, and as lively as the reds made with the grain of kermes. This red, from its peculiar preparation, of which we shall speak in its place, remained exposed to the air during the last two months of 1740, which were very rainy, and during the first two of 1741. Notwithstanding the rain and the bad weather, it stood; and far from losing, it gained body *(fond)*. Yet this same red, so solid in the air, does not resist the proof of tartar. Would it be right to proscribe it, because this salt destroys it; or are the stuffs which we employ for our clothing intended to be boiled with tartar, alum, or soap? I do not presume, however, to disapprove of the trials by the *debouillis.* They are useful, because they are speedy. But there are cases where they ought not to serve as rules for pronouncing a sentence of confiscation, especially when they do not demonstrate that a colour, which ought to have been made with drugs of the *good dye,* has been made with the ingredients of the spurious *dye.*"

Instructions *concerning the Debouilli (chemical trials) of Wool and Woollen Cloths.*

" Since it has been admitted, that the method prescribed for the *debouillis* of dyes, by Article XXXVII. of the regulations for dyers in the great and good tint, of cloths, serges, and other woollen stuffs, of the month of August 1669,—by the Articles CCXX. and following, of the general instruction for dyeing of wool of all colours, and for the culture of drugs and ingredients used in it, of March 1671,—is not sufficient for judging exactly of the goodness or spuriousness of several colours; and since this method may even sometimes lead into error, and give rise to disputes, there have been made, by order of his Majesty, different experiments on the wools destined for the fabrication of tapestry, in order to learn the goodness of each colour, and its appropriate *debouillis.*

"To attain this object, fine wools have been dyed with all kinds of colours, both in the good and little tint, and they have been exposed to the air and the sun during a suitable period. The good colours stood perfectly well, and the spurious were more or less discharged, according to the badness of their quality. Since a colour should not be reputed good, unless inasmuch as it resists the action of the air and the sun, this is a test which has served as a rule for deciding on the goodness of the different colours.

"Different proofs by *debouilli* have afterwards been made on the same woollens, of which patterns had been exposed to the sun and air. It has been observed at first, that the same ingredients could not be employed indifferently in the *debouillis* of all colours, because sometimes a colour found good by exposure to air, was considerably altered by the *debouilli,* while a spurious colour resisted the same *debouilli.*

"These different experiments have shewn the inutility of lemons, vinegar, soured waters, and strong waters (aquafortis), from the impossibility of ascertaining the degree of acidity of these liquors. It has therefore appeared, that the surest method is to make use of ingredients, whose effect is always equal, along with common water.

"In pursuing this object, it has been judged necessary to separate into three classes all the colours of which woollens can be dyed, both in the fast and fading tint, and to define the ingredients that should be employed in the *debouillis* of the colours comprised in each of the three classes.

" The colours comprehended in the first class should be tested with Roman alum; those of the second, with white soap; and those of the third with red tartar (argal.)

" It is not enough for ascertaining the goodness of a colour by the trial of the *debouilli,* to employ ingredients whose effect may always be equal; it is requisite, moreover, not only that the duration of this operation be exactly determined, but even that the quantity of the liquid be fixed; because more or less water diminishes or increases considerably the activity of the ingredients which enter into it: hence the manner of proceeding with the different *debouillis* will be prescribed in the following articles.

" Article I.

" The *debouilli* with Roman alum shall be made in the following manner.

" Into an earthen or stoneware vessel, one pound of water and half an ounce of alum shall be put: the vessel is to be set on the fire, and when the water boils with large bubbles, there shall be put into it the wool whose trial is to be made, and it shall be allowed to boil there for five minutes, after which it is to be withdrawn and washed in cold water. The weight of the pattern ought to be about one gros, (nearly 60 grains troy).

" Article II.

" When there are several samples of wool to be tested together, it will be necessary to double the quantity of water and alum, or even to treble it, which will in no respect change the force and effect of the *debouilli*, if the proportion of water and alum be observed.

" Article III.

" In order to make the effect of the *debouilli* more certain, care must be taken not to test together wools of different colours.

" Article IV.

" The *debouilli* with white soap shall be made in the following manner.

" Into a pound of water there shall be put only two gros of white soap, cut into small bits. The vessel being then set upon the fire, care shall be had to stir the water with a rod, so as to cause the soap to melt properly. When it is melted, and the water is boiling briskly, the sample of wool shall be introduced, and it shall in like manner be made to boil for five minutes, counting from the instant of its being put in, which shall be only when the water boils with large bubbles.

" Article V.

" When several samples of wool are to be tested together, the method prescribed in Article II. shall be observed; that is to say, for every pound of water, two gros of soap shall be taken.

" Article VI.

" The *debouilli* with red tartar shall be made precisely in the same way, with the same doses, and in the same proportions, as the *debouilli* with alum, observing to pulverize the tartar well before putting it in the water, that it be entirely dissolved before the samples of wool shall be put into it.

" Article VII.

" The following colours shall be tested with Roman alum; namely, crimson of every shade, scarlet of Venice, scarlet of a fire colour, scarlet of a cherry colour, and its other shades; violets and gridelins of every shade, purples, *langoustes* (pinks), *jujubes*, pomegranate flowers, blues, slate-greys, lavender-greys, violet-greys, wine-greys, and all other similar shades.

" Article VIII.

" If, contrary to the articles of regulation concerning dyes, there has been employed, in the dyeing of fine wools crimson, ingredients of the spurious tint, the infringement will be easily recognized by the *debouilli* with alum, because it renders fine crimson only a little deeper, that is to say, makes it verge a little towards the gridelin hue; but it destroys the lightest shades of false crimson, rendering them of a very pale flesh colour, and even blanching almost entirely the deep shades of false crimson. Hence this *debouilli* is a certain means of distinguishing the spurious crimson from the true.

" ARTICLE IX.

" The scarlet of kermes or grain, commonly called scarlet of Venice, is in no respect injured by this *debouilli.* It causes scarlet of a flame colour, or of cochineal, to pass to a purple hue, and strengthens the low shades, so that they get a gridelin tinge; but it carries off almost the whole false colour of brazil, and reduces it to an onion-skin hue. It has a still more sensible effect on the deep shades of this false colour.

" The same *debouilli* also carries off almost entirely the scarlet dyed with *bourre,* and all its shades.

" ARTICLE X.

" Although violet is not a simple colour, but is formed of blue and red hues, it is, nevertheless, so important as to merit a particular examination. The same *debouilli* with Roman alum has almost no effect on the fine violet, whereas it greatly injures the spurious; but it will be observed, that its effect is not always to carry off equally a large portion of the false violet hue, because this has sometimes a ground (*pied*) of pastel or indigo. This ground being of good tint, is not carried off by the *debouilli ;* but the redness is effaced, the brown shades becoming almost blue, and the pale ones of a disagreeable wine-lees colour.

" Article XI.

" With regard to half-fine violets, prohibited by the present regulation, they shall be put in the class of spurious violets; nor do they stand the *debouilli* any better.

" Article XII.

" The fine gridelins will be distinguished in the same manner from the spurious, but the difference is slight. Gridelin of good tint loses only a little less than that of spurious tint.

" Article XIII.

" Fine purples resist the *debouilli* with alum perfectly; whereas the spurious lose the greatest part of their colour.

" Article XIV.

" The colours of *langouste* (pinks), *jujubes,* pomegranate flower, will incline towards purple after the *debouilli,* if they have been made with cochineal; whereas they will become considerably paler if fustet has been employed, the use of which is prohibited.

"ARTICLE XV.

"The blues of good tint will lose nothing in the *debouilli,* whether the colour be pastel or indigo; but those of spurious tint will lose the greatest part of their colour.

"ARTICLE XVI.

"Slate-greys, lavender-greys, violet-greys (reddish greys ?), wine-greys, lose almost their whole colour if they are of spurious tint, whereas they will stand perfectly if they are of good tint.

"ARTICLE XVII.

"The following colours are to be tested with white soap: namely, yellows, jonquilles, lemons, oranges, and all the shades which are derived from yellow; all the shades of green, from yellow-green, or nascent-green (pomona-green), to cabbage or parrot-green; madder-reds, cinnamon, snuff colour, and other similar hues.

"ARTICLE XVIII.

"This *debouilli* shews perfectly if the yellows and their derivative shades are of good or spurious tint; for it carries off the greatest part of their colour, if they are made with Avignon berries, annotto, turmeric, fustet, or saffron, the use of which is prohibited for the fine dyes; but it does not affect the yellow made with *sarrette* (saw-wort), *genestrolle* (dyer's broom), fustic (yellow-wood), weld and fenugreek.*

" ARTICLE XIX.

" The same *debouilli* will also shew perfectly well the goodness of greens, for those of spurious tint lose almost all their colour, or become blue, if they have a ground of pastel or indigo; but those of good tint lose scarcely any of their hue, and continue green.

" ARTICLE XX.

" The reds of pure madder lose nothing in the soap *debouilli*, becoming, in consequence, only more beautiful; but if brazil-wood is mixed with it, they lose some of their colour in proportion to the quantity of the latter which has been introduced.

" ARTICLE XXI.

" Cinnamon, snuff, and other similar colours, are scarcely affected in the *debouilli* if they are of good tint; but they lose a great deal if annotto, fustet, or *fonte de bourre* have been employed in it.

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* The botanical names of the above vegetable substances are as follows: *Rhamnus infectorius*, (French or Avignon berries); *bixa orellana*, from which annotto *(rocou)* is made; *curcuma longa*, turmeric *(terra merita)*; *rhus cotinus*, fustet; *crocus sativus*, saffron; *serratula tinctoria*, saw-wort; *(genet) genista tinctoria*, dyer's broom; *morus tinctoria*, fustic; *reseda luteola*, weld; *trigonella fœnugræcum*, fenugreek.—T.

" Article XXII.

" The *debouilli* made with alum would be of no utility, and might lead even into error, with regard to several colours of this second class; for it does not injure fustet or annotto, which do not however withstand the action of the air; and it carries off a portion of saw-wort, and dyer's broom, which give, however, very good yellows and very good greens.

" Article XXIII.

" All the fawns (duns) or root colours shall be tested with red tartar. Thus, all those colours are termed which are not derived from the five primitive colours: such colours are made with walnut peel, the root of the walnut tree, alder tree bark, sumach or *roudoul*, sanders, and soot. Each of these ingredients affords a great number of different shades, which are all comprised under the general name, dun, or root colour.

Article XXIV.

" The ingredients enumerated in the preceding article are good, with the exception of sanders-wood, and soot, which are a little less so, and which make woollens harsh when too large a quantity is taken. Hence, all that the *debouilli* can teach concerning these kinds of colours is, whether they have been surcharged with sanders-wood or soot, in which case they lose considerably by the *debouilli* of tartar; and if they are made with other ingredients, or if there be but a moderate quantity of sanders-wood or soot, they stand much better.

" ARTICLE XXV.

" As black is the only colour which cannot be comprehended in any of the three classes above stated, and since it is necessary to make use of a *debouilli* much more active, in order to learn whether wool has had the deep blue ground conformably to regulation, the *debouilli* shall be made in the following manner :—

" One pound or one pint of water shall be taken : into this shall be put one ounce of Roman alum, and as much pulverized red tartar ; the whole shall be made to boil, and a sample of wool shall be introduced, which ought to be kept boiling briskly during a quarter of an hour. It is to be thereafter washed in fresh water, when it will be readily seen whether it has had the proper blue ground; for in this case the wool will remain of a blue, nearly black ; if that be wanting, it will become considerably grey.

" ARTICLE XXVI.

" As it is the practice to brown colours sometimes with nut-galls and copperas, and as this operation, called browning *(bruniture)*, which should be permitted in the good tint, may have a peculiar effect on the *debouilli* of these colours, it will be observed, that although after the *debouilli* the bath appears charged with the dye, because the browning has been carried off, the wool will be not the less reputed of good tint, if it has preserved its body. If on the contrary it loses this, it will be declared of spurious tint.

" Article XXVII.

" Although the browning given with copperas and nut-galls be of good tint, as it usually renders wool harsh, it will be proper, as far as possible, to employ the indigo or pastel vat in preference.

" Article XXVIII.

" The ordinary greys made with gall-nuts and copperas should not be subjected to any trial of *debouilli*, because these colours are of good tint, and are not made otherwise. But it must be observed to gall them first, and to put the copperas into a second bath, not nearly so hot as the first, because in this way they are finer and more fixed."

From the remarks of Hellot, it appears, that there has been heretofore only one certain manner of ascertaining the permanence of colours, namely exposing them to the air, the sun, and moisture, for an adequate length of time. The *debouillis*, whatever care be taken to make a good choice of them, can be applied only to determinate processes, such as those prescribed by the regulations to which they were to be subjected. One of these *debouillis* might, however, be excepted, that which is applied to black, with the view of determining whether a blue ground has been given, and whether it be strong enough to inspire confidence in the goodness of the dye.

"The oxygenated muriatic acid affords a ready and easy means of determining the degree of solidity (durability) of a colour. Hence, when a colour is wished to be examined, a pattern of the stuff has only to be put into the oxygenated muriatic acid, along with a pattern of a like colour which had been dyed by a good process. The degree of resistance which the colours of the two patterns oppose, becomes the measure of their goodness; but as this liquor has a very lively action on the colouring particles, it must be employed in a very dilute state. This proof has the further advantage of making known, pretty nearly, the shades and degradations through which the stuff is to pass, when it shall be altered by the air;—were it required, however, to examine a stuff juridically, the action of the oxygenated muriatic acid could not be entirely trusted to; nor would it be possible to pronounce with certainty, unless from the results afforded by exposure to the air."

We extract this passage from the first edition of the Elements of Dyeing, because Bancroft has objected to the testing of colours by the oxygenated muriatic acid, as being entirely illusory and deceitful. We persist in the opinion, that this easy test may be useful, especially in experiments on dyeing; and that it rarely affords unfaithful indications, when the precaution is taken which has been prescribed, of comparing two patterns of the same colour, one of which has a known durability; but we might be led into error, if we wished to make the comparison of different colours with one another. We should run the risk, for example, of ascribing to yellow and fawns a greater comparative solidity than they really possess in the air; because the oxygenated muriatic acid giving this hue to substances of an animal nature, this effect might be easily confounded with the preservation of these colours.

For trying colours on silk, it is usually held satisfactory to expose them to heat in acetic acid, or in lemon juice. They are regarded as permanent and fine if they resist this trial; and in fact, when woods or archil are simply made use of, the colour passes to red by the action of the vegetable acid; but if the solution of tin has been used in dyeing with these substances, the colour which had been prepared in an acid liquid is not affected by the vegetable acids; and in this case a colour might be regarded as fine, which had cost much less for its preparation, and which is easily altered. Hence, with regard to silk, the oxygenated muriatic acid must be had recourse to, or above all, exposure to the air.

As to cotton and linen goods which are intended to be submitted to soap and leys, they must be tried by the action of soap and alkalies.

There is another species of test which ought not to be neglected; the purpose of which is to determine the goodness of colouring substances of the same nature. The look, and some other criteria, are generally trusted to; but they afford only uncertain estimates, and can furnish no scale of comparative value. The oxygenated muriatic acid possesses this property in a degree which leaves nothing to be desired; because, whenever indigo is compared with indigo, the nature of the colouring particles is the same, or nearly the same, and no foreign affinity prevents the action of the oxygenated muriatic acid from determining the proportional quantity of colouring matter.

If an inconsiderable difference existed between the nature of the colouring particles that were assumed as the same, it is very probable that the action of the oxygenated muriatic acid would be, moreover, a measure of their respective goodness.

Whenever, therefore, it is wished to compare two or several substances which have the same colour, and to determine their quality or value in reference to the purpose for which they are intended, it is necessary merely to compare the quantities of the same oxygenated muriatic acid requisite to reduce an equal weight of each of these substances to the same degree of destruction; then the qualities of these substances, or the quantity of colouring particles which they contain, are in direct proportion to the measures of liquid which have been necessary to produce the same effect upon each. For making this valuation, the colouring particles of each substance ought to have been dissolved in a proper liquid, and every circumstance of the comparative operation should be equal.

If it is desired to compare several species of indigo, for example, an equal weight of each is taken, and pulverized with care; they are then put into separate matrasses, with eight times their weight of concentrated sulphuric acid. The matrasses are kept in a heat of from 30° to 40° R. for a few hours. Each solution is afterwards diluted with the same quantity of water. The liquids are filtered; and the *residua* collected on the filters being bruised in a glass mortar, with the addition of a little sulphuric acid, they are left again to digest. These last solutions are diluted with an equal quantity of water, then filtered, and added each to its correspondent liquor. Lastly, into each solution there is poured the quantity of liquid oxygenated muriatic acid which is requisite to destroy its colour, or rather to bring it to the same shade of yellow. The qualities of the different species of indigo are proportional to the measures of oxygenated muriatic acid which was needed to destroy their colour.

The tests for colouring particles soluble in water are much more simple. After exhausting them, equal volumes of the decoctions of the same weight of these substances are taken; and then the quantities of oxygenated muriatic acid necessary to bring them to the same tint, are compared.

SECTION V.

OF THE CHEMICAL AGENTS EMPLOYED IN DYEING.

In order to form an exact idea of the effects produced by the substances employed in dyeing, their chemical properties must be known, for these effects are merely consequences in particular cases.

We shall here present a summary view of the history and properties of the substances most commonly used in dyeing, and in the arts immediately related to it, stating, at the same time, the general principles which may serve to explain their action. We shall so order it, that those persons who have but a limited acquaintance with chemistry, may find in this summary the most useful notions, and that those who are further advanced in the speculations of the science, may perceive the relations connecting the particular phenomena to the general laws of combination.

CHAPTER I.

Of the Acids.

The acids are recognized by their taste, their property of reddening the blue colour of several vegetables, such as that of litmus, flowers of mallow, and violets, and by the effervescence which they produce when mixed with mild calcareous earth and alkalies. But these characters being merely a consequence of their action, afford no idea of the properties by which they act in the production of these very effects.

All the chemical properties of a substance depend on its affinities to other substances; but the effects of an affinity differ according to the physical dispositions of the substance which exercises it, and of that on which it exerts its action. The latter acts reciprocally on the former by its affinity, and according to its physical dispositions.

The affinity by which two substances form a combination, in which their properties have become more or less latent, produces an effect dependent not only on its energy, but also on the quantity of the substance exercising it.

In proportion as an affinity is satisfied, or as it experiences saturation, its energy diminishes; and when it is exactly counterbalanced by the action of the substance that produces saturation, the combination is neutral, or affords no farther indication of the action peculiar to each of the elements which compose it.

The substances which produce in the highest degree the saturation of the characteristic properties of the acids, and which make them entirely disappear, are the alkalies, whose properties experience, on their part, a like saturation. The reciprocal action of these substances is thereby capable of even disclosing the laws of chemical action, or of the tendency to combination.

The acidity, or the power of combination of the different acids with the alkalies, should therefore be proportional to the quantity of the same alkali which they can saturate, or to their capacity of saturation; and reciprocally.

The physical qualities of the substances diversify the effects of affinity. We understand here by physical qualities, all such as do not depend on the tendency of a substance to form with another a combination whose weight results from the two, although some of these qualities be still derived from affinity; for example, solidity, which is a result of the reciprocal action of the molecules of any one substance, whether simple or compound.

Those physical qualities which change the results of affinity are principally solidity, liquidity, expansibility, or the disposition to assume or retain these different states. They do not disappear by the action of affinity; they thence experience no saturation; but they receive modifications from it, while they themselves act as forces which contribute to the immediate effect of affinity, or which are opposed to it.

The disposition to solidity determines the combinations which precipitate when an acid is mixed with an alkaline solution, and similarly when several acids and several alkalies exercise a reciprocal action; whence proceed the precipitates or the salts which separate by crystallization. This disposition is increased by the approximation or condensation which affinity produces; and the compound which separates in consequence, readily acquires an excess of the element in which this quality predominates. Hence two substances, possessing liquidity, may form an insoluble combination, or a salt less soluble; and the compound which separates may preserve an excess of acid or of alkali, according as one or other of these has a greater disposition to solidity. Thus may be explained the precipitations produced by the acids or the alkalies, and the formation of *acidulous* or *alkalinulous* salts.

Heat, whose function it is to dilate bodies, and separate their particles, diminishes insolubility, and increases the tendency to the liquid state. It augments especially the disposition to elasticity; and as the latter exercises a force contrary to the tendency to combination of a fixed substance, with a substance possessing the elastic condition, it is obvious, that by increasing it to a sufficient degree, the whole effect of the tendency to combination may be destroyed. If several acids and several bases exert a reciprocal action, by the same means, the most volatile elements will be determined to form a compound, which will separate by volatilization from that contracted by the more fixed elements.

The acids act, therefore, by their affinity or tendency to combination, in the ratio of their capacity of saturation; and the physical qualities of their compounds depend on those of the elements composing them, and of the modifications produced on them by the condensation due to the combination, or the expansion which is the effect of heat.

When an acid acts on a neutral combination, the base divides its action in the ratio of the quantity of the two acids, and of the energy of their affinity ; but the result depends principally on the dispositions to the solid, liquid, or elastic state of the elements which are in action. The capacity of saturation of two acids usually differs too little to produce an effect capable of counterbalancing one of the causes just designated.

Hence, when an acid which has a certain fixity (sulphuric acid for instance) acts on a muriate whose acid is volatile, the latter ought to be expelled, especially by increasing its elasticity with heat, although it has a greater capacity of saturation for soda.

From the physical qualities of two substances which enter into combination, may therefore be inferred those which subsequently exist in the compound itself ; and as the same causes act when there is a rivalship of different acids for one base, or of different bases for one acid, or of several acids for several alkalies, there will be found, in considering the qualities of each of these substances, the reason of the peculiar compounds which separate by precipitation or volatilization, or which remain liquid, and of the changes that different temperatures may produce on these combinations.

The acids and alkalies exercise a pretty powerful action on most of the colouring substances. We have shewn that the results of this action are, more soluble compounds with such of these substances as have in themselves greater disposition to solubility. Thus the acids act in general. But we have remarked, that the crystals of tartar retain the colouring matter of cochineal. Potash, soda, and ammonia, act also as solvents; while the slightly soluble alkalies, lime, barytes, and strontites, form insoluble compounds. Few experiments have hitherto been made in this point of view.

Some acids act on colouring substances by the oxygen which enters into combination with them, or with their elements. This subject has been already sufficiently discussed.

Neutral salts possess but a feeble action on colouring particles; they change their solubility little; and they produce but a moderate effect on their shades. Sometimes, however, this effect is taken advantage of when they are employed as alterants.

Article I.

Of Sulphuric Acid.

Pure sulphuric acid is without smell or colour, transparent as water; and when concentrated it is of an unctuosity approaching to that of oil. To denote this unctuosity, it was called *oil of* *vitriol*, a designation which may lead to dangerous mistakes concerning its nature.

This acid was at first extracted from the sulphate of iron or vitriol of iron, whence its old name of vitriolic acid. At the present day, nearly the whole that is employed in the arts is obtained from sulphur, by a much less expensive process. It is the result of the combustion of sulphur, which, by burning, combines with the oxygen present in the atmospheric air, and in the nitre which is added to a certain quantity of the sulphur before setting it on fire. The latter, however, seems to be especially useful for exciting the high temperature necessary to the formation of sulphuric acid; for it has to enter into the composition of the sulphate of potash produced. The mixture of sulphur and nitre is kindled, and its vapours are received in a leaden chamber, whose bottom is covered with a stratum of water. The vapours which collect and unite to the water, form the sulphuric acid, which should be considered as sulphur completely burned. (Note S).

The sulphuric acid, as it comes out of the leaden chamber, is not in a concentrated state, but is mixed with a certain quantity of redundant water. It retains the odour of sulphurous acid, which differs from sulphuric acid in its composition; as the former is not sufficiently saturated with oxygen, while this element is less condensed in it. It retains also a little nitrous acid, proceeding from the nitre mixed with the sulphur. If it be left for some time exposed to the air, the smell of sulphurous acid is dissipated. But another method is employed to deprive it of odour, and at the same time of a portion of its redundant water. It is evaporated with heat.

Only a very small quantity of vegetable or animal substance is required to give this acid a brown colour; and the acid of commerce has rarely a very clear colour. But this limpidity may be obtained by boiling it for some time in a retort. By this operation it is deprived at once of a portion of nitric acid usually present, and of a portion of water which it had retained. It becomes white and transparent; the concentration being the greater the more water has been driven over by the distillation. To procure it of thorough purity, we must, after having separated the first portion, which is impure and feebly acid, continue the distillation till no more liquid remains in the retort. The residuum consists of a little alkali derived from the nitre, which remains combined with an excess of sulphuric acid; a combination named acidulous sulphate of potash; sometimes a little sulphate of lead is also left.

For this rectification, there must be selected a retort not very lofty, which is to be well secured in an open furnace, or placed in a sand bath, so that the movements occasioned by the ebullition of the acid may not break it.

Sulphuric acid powerfully attracts the humidity of the air. To preserve it concentrated, it must therefore be kept in glass vessels carefully corked.

When it is mixed with water, a great heat is produced. Hence this mixture should be gradually made to prevent the fracture of the vessel, an accident which is avoided by making the mixture in a leaden vessel. In order to effect a complete mixture, the liquid must be long stirred with a glass rod; for notwithstanding the great affinity of this acid for water, the difference of their specific gravities opposes their combination.

The difference of volatility, and the mutual action of the sulphuric acid and water, explain the effects which arise from this action in different circumstances. It attracts water, causing the moisture which is held dissolved in the atmospheric air to lose its elasticity; and it is only by increasing the elastic disposition of the latter by heat, that it can be again separated. But to reduce the water into vapour, a greater heat is required than if it were not retained by the affinity of the acid; a heat which must be augmented according as the proportion of water diminishes. Lastly, the acid passes over itself in the distillation along with a decreasing proportion of water, which must in its turn promote this effect by reason of its volatility.

The fixity of this acid, its concentration, the property it has of freezing, shew that it must carry into its combinations a great disposition to insolubility, when the base has the same disposition. Hence it produces slightly soluble combinations with lime, barytes, strontites, and several metallic oxides.

The condensation of sulphuric acid proves that the combination of oxygen with sulphur is here very intimate, and consequently it should not easily part with its oxygen. For this reason, it produces no decomposition of the colouring substances which it dissolves, unless this solution be exposed to a strong heat. Then the hydrogen and the carbon of these substances may combine, particularly with a portion of the oxygen of the acid, which is thereby brought to the state of sulphurous acid, which, being volatile, escapes in the progress of the decomposition. As the oxygen is endowed with greater elasticity in the latter acid, it abandons the sulphur more easily, although this substance be in larger proportion than in sulphuric acid.

Sulphurous acid, therefore, acts on colouring substances, by giving up oxygen to them less easily and less efficaciously than the nitric or oxygenated muriatic acids; but in other circumstances, it may carry off even oxygen, as it does from oxygenated muriatic acid on being mixed with it.

Highly concentrated sulphuric acid has a specific gravity, nearly double of that of distilled water. When it is weak, that is, diluted with a great deal of water, the fallacious name of *spirit of vitriol* has been given to it.

In order to obtain uniform effects, it is right to employ for the same operations a sulphuric acid which has always the same degree of concentration. Its specific gravity must be therefore ascertained, which is commonly done by means of the areometer of Baumé. For this purpose, the acid is put into a glass cylinder, and the areometer for salts is plunged into it. The denser the liquid, the less the areometer sinks, and the degree on that part of its scale which rests at the surface of the liquid, indicates its concentration. Sulphuric acid is regarded as highly concentrated when it is at 66° of this areometer.

Hitherto sulphuric acid has been used in dyeing, principally for making solutions of indigo; for which purpose it must be strongly concentrated, and very pure. But a great deal of it is employed for preparing cotton goods intended to be printed, as well as for the bleaching of cloths and yarns, whether by oxygenated muriatic acid, or by exposure on the grass.

These latter purposes do not require a concentrated sulphuric acid. If therefore a manufacture of sulphuric acid exist in the neighbourhood, it is more advantageous to purchase it before being concentrated, and thus avoid the cost of this operation. But if such an establishment be at a distance, the diminution of the expense of carriage may render it more profitable to purchase it in a state of concentration, than if it were diluted with a certain quantity of water.

Article II.

Of Nitric or Nitrous Acid.

Chemists have given different names to this acid, according to the processes by which it is extracted from nitre. What is obtained from a mixture of nitre and clay is called *aquafortis;* that procured from nitre distilled with sulphate of iron, *spirit of nitre;* and the *fuming nitrous acid* is derived from a mixture of nitre and sulphuric acid. These distinctions are not made in commerce, but the name *aquafortis* is usually given to this acid, whatever process may have been employed. In fact, it is always the same acid, differing only in the degree of concentration, and in colour. It is sometimes white, sometimes red and fuming. The colour and property of fuming, are owing to the nitrous gas which it holds in solution, as we shall explain hereafter.

If the reddest acid be exposed to a sufficient heat, the nitrous gas is disengaged, and the acid remains white. In this state it is called *nitric acid,* while the name *nitrous* is given to the red acid.

As there is no great consumption of this acid in dyehouses, and as these are often at a great distance from the places where the acid is manufactured, it may often be useful and economical to prepare it one's self. This motive induces us to describe here the process by which it is extracted from nitre by means of sulphuric acid.

Pure nitre, called nitre of the third boiling, being the result of a third crystallization, is pulverized, and put into a retort with half its weight of concentrated sulphuric acid, or a little more, in such a manner that one-half of the capacity of the retort remains empty, in order that the materials in boiling up shall not pass over into the receiver. To the neck of the retort a bent tube is adapted, whose orifice must be sufficiently large to embrace and receive it. The other end of this tube, which ought to have a much smaller diameter, is introduced, through a cork, into a receiver with a double neck. To the other opening of this receiver a tube is also adapted, which terminates in a little water contained in a matrass. The communication of the retort with the first tube, and the openings of the first receiver, must be carefully coated and covered with fat lute, consisting of pulverized white clay, boiled linseed oil, and a little litharge. This lute must be beaten for a long time in a mortar, to render it smooth and ductile. The lutings must be wrapped round with strips of linen cloth soaked with white of egg, and bedusted with powdered quicklime. It is of advantage to have a tubulated retort to prepare the whole apparatus, before introducing the sulphuric acid into it by the tubulure, and even to dilute the sulphuric acid previously with a certain quantity of water.

The second matrass should maintain a free communication with the air, that the vapours incondensable in water may escape. The quantity of water put into the second vessel must bear a proportion to the quantities of materials operated upon. The fire must be nicely tempered at the beginning, and be gradually augmented up to the end of the operation. The acid which is obtained in the first receiver is highly concentrated ; that which is in the second is weakened by the water put into it for condensing the vapours. The colour of the latter acid is blue or green ; colours owing to the nitrous gas ; their diversity depending on the proportion of water. Thus, if a little water be added to that which is green, it becomes blue ; and when the gas is expelled by heat, the liquor remains limpid. The acid of the second matrass is always pure, but that of the first contains sometimes a little sulphuric acid, arising from the heat not being rightly regulated at the commencement of the operation. For, when tempered with discretion, a perfectly pure acid may be obtained, if the sulphuric acid does not exceed the half of the weight of the nitre.

It is of importance to test the nitric acid of commerce, because a considerable quantity of sulphuric acid is frequently present in it, whether it may have come over in a distillation negligently conducted, or have been added to the nitric acid in order to augment its specific gravity. For testing it, we dilute it with an equal weight of distilled water, and then drop in a little of the solution of nitrate of barytes. If the acid which we try contain sulphuric acid, a precipitate takes place, because this acid forms an insoluble salt with barytes. Nitric acid may likewise contain some muriatic acid, proceeding from the sea-salt which might exist in the nitre employed. This mixture cannot be prejudicial to the operations of dyeing. If, however, we desire to discover it, the acid must in like manner be mixed with distilled water, and a nitric solution of silver is to be then poured into it. A precipitate occurs if muriatic acid be present.

To deprive the nitric acid of the sulphuric, it must be redistilled from a little nitre, or solution of lead may be added to it, which produces a precipitate that is to be separated. After this, the acid is submitted to a new distillation. By this operation the nitric acid is separated, not only from the sulphuric acid, but also from the muriatic which it may contain. To accomplish the latter object entirely, the first portion of liquid that comes over must be removed, because it may contain some oxygenated muriatic acid.

Nitric acid may serve for several metallic solutions, whose use as mordants may be various, but its principal employment is for aqua regia, or nitro-muriatic acid, which shall be treated of in a particular article. It appears that sulphuric acid is injurious to it, when it is to serve for the solution of tin; and the acid prepared in manufactories, by means of the sulphuric, usually contains some; whence dyers often prefer that extracted by the agency of clay.

For understanding a great number of phenomena, it is essential to have an exact idea of the nature of the nitric acid, and of the action which it exercises on other substances.

Nitric acid is composed of two substances, which, when they are insulated, assume the elastic, aeriform, or gaseous state. These substances are oxygen and azote, which also compose our atmosphere. The different action (of these two compounds) depends on the state in which they exist. In the atmosphere they are endowed with elasticity, which is an obstacle to their combination with other substances; but this obstacle, and the intensity of their action, vary, by reason of their state of expansion and their condensation.

The elastic force of oxygen gas, and azotic gas, like that of other gaseous substances, being diminished by the affinity which produces their combination, and which reduces their volume, they can act in a greater mass on the other substances, and the energy which they thereby acquire may exceed by much the diminution which results from their reciprocal saturation.

But these two gases may contract an union, which differs according to their proportions, according to the condensation derived from it, and according to the concurrence of other substances, and particularly of water, which may augment their condensation without acting on them by a great saturation.

These circumstances determine the different states of combination of these two elements, and the properties of these compounds.

Nitrous gas must be regarded as the first state of combination. It dissolves in only a small quantity in water; it does not combine with alkalies; it is easily decomposed by substances which tend to unite with oxygen; but it unites by mere contact with a greater proportion of oxygen. It thereby passes to another state; and as its two elements are little condensed, the action of heat alone, or the dilatation which it produces, has but little efficacy to separate them. The proportions that constitute it are nearly 44 parts by weight of azote to 56 of oxygen, (47 to 53.)

When an oxygenable substance deprives the nitrous gas of a portion of its oxygen, such as a sulphite, which thereby passes to the state of a sulphate, another combination is established, in which the elements, by reason of the proportions in which they exist, exert more powerfully their reciprocal action, so that their condensation is greater. This is the gaseous oxide of azote, whose specific gravity, according to Davy, is to that of oxygen gas in the ratio of 147 to 100; and which contains, by the determinations of the same chemist, 63 parts by weight of azote to 37 of oxygen.

This greater condensation, which proves a stronger reciprocal action, and the composition, explain the properties which characterize this gas. It dissolves more copiously in water than the nitrous gas, and yet it has no acid taste, but on the contrary a saccharine one. The oxygen present in it, is too strongly saturated by the azote, to produce the acidity which depends on its combinations. It no longer acts on oxygen gas, and is not decomposed at an ordinary temperature, by the substances which operate the decomposition of nitrous gas; but if the temperature be elevated, the expansive action of the heat, which tends to separate its two condensed elements, determines its decomposition, and the oxygen produces a vivid combustion.

When nitrous gas acts on pure oxygen gas, or on that present in the atmosphere, it becomes ruddy, and the new substance designed by the name *nitrous vapour*, which condenses very little, and preserves a livelier ruddiness, as the temperature is higher, forms another combination when it is placed in contact with water. This decides the formation of nitric acid, of which it is itself an essential part; for nitric acid resumes the state of nitrous vapour when it is deprived of water, unless it be retained in a state of condensation by another base, as in the nitrates.

If nitrous vapour contain too great a proportion of nitrous gas, this excess remains in the gaseous state; if the oxygen gas be in excess, a portion of it remains gaseous.

A portion of the nitrous gas may, however, be held in solution by the nitric acid; but this quantity varies according to the proportion of water, giving the acid an orange, green, or blue colour. This excess of nitrous gas attracts oxygen by degrees from the atmospheric air, passing itself to the state of nitric acid.

In nitric acid, the proportion of oxygen is to that of azote nearly in the ratio of 3 to 1 by weight. It is not surprising, therefore, that this compound, containing oxygen in so large a proportion, should have the qualities of an energetic acid, whilst the gaseous oxide of azote, where the azote predominates, has perceptibly none. But the nitric acid owes its liquid state only to the action which water exerts upon it.

When it is combined with an alkaline base, and when a more fixed acid, as the sulphuric, divides its action on this base, heat augments its elastic disposition, so as to volatilize it with the water which the sulphuric acid contained. This water is inadequate to make the whole of it preserve the acid condition; a portion is therefore disengaged in the state of nitrous vapour, and by the condensation of this in the water presented to it, some nitric acid is reproduced. But the acid which has assumed the liquid state, retains nitrous gas, and is more or less ruddy. The corresponding portion of the oxygen gas is disengaged in the elastic state.

If nitre, or nitrate of potash, be decomposed by means of clay, this seems to retain the water with sufficient strength, so that a quantity of it, capable of maintaining the nitric acid in the liquid condition, may come over even to the end of the operation. Hence, in this case, the acid is not fuming, or is very slightly so.

The substances which have a great action on oxygen, may decompose nitric acid, according to the energy of this action. Thus the very oxidable metals especially, produce gaseous oxide of azote; while the oxide thereby formed dissolves in a portion of the undecomposed acid. But the less oxidable metals give rise only to nitrous gas, which retains a greater proportion of oxygen.

The facility with which nitric acid is decomposed, when it is not condensed by a base which gives it stability, renders it little fit for being employed with the colouring particles, which separate the oxygen from it more or less speedily, and thereby suffer destruction. In destroying these particles, it causes them to undergo the changes due to an imperfect combustion, in which the hydrogen enters into combination with the oxygen, in larger proportion than the carbon, making the latter principle predominate in the residuum.

In purchasing this acid, we must not let ourselves be imposed upon by its more or less ruddy colour. It is easy to give it this appearance, by a small quantity of iron, or other substance, which generates nitrous gas. It must, indeed, have a certain degree of concentration to be fuming; but it may be highly concentrated without possessing this appearance.

The specific gravity may likewise lead to fallacies, because it can be increased by the addition of sulphuric acid. It is only after ascertaining that this cause of error does not exist, that we can repose confidence in that criterion.

Article III.

Of Muriatic Acid.

Muriatic acid is particularly distinguished by being more volatile, or more disposed to preserve the gaseous state, than the preceding acids, and by having much less affinity for water. Hence, when combined with it, its elastic action needs only be increased by heat for it to quit it, and to resume the state of gas, till little enough remains to make the attraction of the water be equivalent to the elasticity of the acid.

Although muriatic acid has a greater capacity of saturation for the alkaline bases than sulphuric acid, it is however expelled from its combinations by this acid, especially when its elasticity is augmented by heat. Hence the effect of its elasticity overcomes the excess of affinity, which tends to maintain its combination with the base.

Muriatic acid gas, combined with water, forms muriatic acid, which was known under the name of *marine acid*, or *spirit of salt.* It has a peculiar odour, analogous to that of saffron. When concentrated it gives white vapours to the air, which are produced by the combination of this acid with the water present in the atmosphere. It ceases to afford these vapours at the point in which it is saturated with the whole water which it can take from the atmosphere. It has usually a yellow colour, derived from a little iron or oxymuriatic acid; for, when very pure, it is as limpid as water.

This acid is extracted on the great scale from sea salt, or muriate of soda, distilled along with clay. But by this process it is always weak. It is disengaged from the same salt by means of sulphuric acid.

This process has much resemblance to that described under nitric acid; but there are some differences which depend on the greater volatility of the acid.

A tubulated retort is made use of, or which is preferable, a large matrass, to whose orifice there is adapted a tube bent in its middle, with an enlargement in the lower part of its curvature. By this tube the sulphuric acid is introduced, a portion of which being retained in the curvature and the swelling, serves to stop the issue of the gas, whose pressure disturbs only the level at which it stands in the two branches of the curvature. The obstacle resulting from the elevation of the column of sulphuric acid, determines the gas, therefore, to pass off by a conductor tube, where it finds less resistance.

The salt is first introduced into the matrass; after which there is poured in three-fourths ($\frac{4}{5}$) of its weight of sulphuric acid, which should be previously diluted. The rest of the apparatus should have been also arranged beforehand. It consists of two bottles, into which is distributed a weight of water equal to that of the salt employed. But as the vapour which is disengaged unites speedily with the water, a vacuum is readily formed, which makes the liquid of the second bottle pass back into the first, and from the first into the retort. To prevent these reabsorptions, the first bottle ought to be furnished with the tube of safety contrived by Welter. This tube is introduced into a particular tubulure, or still better through one of the corks which give passage to a tube of communication. If a vacuum be formed, the atmospheric air returns into the bottle; but while the issuing vapour presses on the liquid, this rises in the tube, till its column counterbalances the pressure of the vapour. It is requisite to lute with much care, because the vapours of muriatic acid are very penetrating; and when they have once forced a passage through the lute, it is very difficult to repair it. Should this accident, however, happen, the best means of remedying it is, to rub the outlet with some alkali, so as to saturate the acid, and immediately after to stop it with the lute. It is necessary to wait till the effervescence produced by the affusion of the sulphuric acid be assuaged, before putting fire under the retort, which should be placed on a sand bath, and the fire should be nicely tempered, especially at the beginning of the operation.

The acid obtained in the first bottle is highly concentrated and smoking, especially if it had been plunged in cold water or pounded ice; but it may contain sulphuric acid, which is discovered by diluting it with distilled water, and pouring into it a little solution of barytes, which produces a precipitate. It may be rectified by distilling it from a little sea salt.

The acid of the second bottle is much less concentrated. If too weak for the purposes for which it is intended, it may be used instead of water in a second operation. It has, however, the advantage of being pure.

Muriatic acid is hardly ever employed directly in the processes of dyeing; but it serves to form metallic solutions fit for making mordants, alone, or in conjunction with nitric acid. Muriate of tin is the combination which deserves most attention. We owe to Pelletier and Proust very interesting observations on this muriate.* We shall detail such of them as relate to our subject.

To prepare the solution of tin by muriatic acid, Pelletier directs to put one part of tin, and four parts of concentrated muriatic acid in a matrass, placed in a sand bath, which is gradually heated to ebullition. The heat of ebullition cannot be favourable to the combination of the muriatic acid, on account of the elastic force which it gives it. It seems therefore that a more moderate degree of heat is suitable; but ebullition may be afterwards produced, in order to expel the excess

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* Mem. et Observat. de Chimie de Pelletier, tom. i. Proust, Journal de Physique, tom. li.

of acid, which may be condensed in a second matrass. We then proceed to crystallize.

The muriate produced by this process contains the tin in the lowest degree of oxidation requisite for its combination with an acid. In this state it carries off the oxygen, not only from the oxygenated muriatic acid and sulphurous acid, but also from the atmospheric air, and from all bodies which do not retain this element with force. Hence, it may obviously be a very proper guide in researches on the properties of colouring substances; and since the oxide of tin combines easily with stuffs and colouring particles, this muriate may be very useful in the processes of dyeing.

Its effects must vary according to its state or actual oxidation. Pelletier concludes from some trials, that in its most oxidized state it is most advantageous in dyeing. This conclusion is perhaps too general, and we believe that experiments must decide what is proper in this respect for each species of dyeing.

To obtain muriate of tin in the most oxygenated state, Pelletier prescribes the transmission of oxygenated muriatic gas into a solution of tin in muriatic acid, till this retains the odour of it; after which the excess of acid must be volatilized by heat. The muriate of tin may be oxygenated by leaving its solution simply exposed to the atmospheric air. But the operation is slow.

It is particularly for cotton and linen that the muriate of tin may be advantageously employed in dyeing, or at least it cannot be used in quantity for substances of an animal nature, because muriatic acid exercises too keen an action on them. This fact is applicable to the other metallic muriates.

The alkaline muriates are used only as alteratives. In general they give a deeper shade to colours.

We have discussed at sufficient length the preparation and properties of oxygenated muriatic acid, in treating of bleaching. We shall confine ourselves here to some considerations on the properties which distinguish it from the preceding acids, and on the differences thence resulting as to their preparations.

Muriatic acid naturally possesses considerable elasticity; yet the action of water can condense a very large quantity, and give it the liquid state, although it is much less powerful than on nitric and sulphuric acids. It combines with oxygen to form oxygenated muriatic acid. But this combination is feeble, so that it produces but a slight change on the natural qualities of the oxygen and muriatic gases. The oxygenated muriatic acid is, therefore, much less soluble in water; hence the apparatus for the preparation of liquid oxygenated muriatic acid ought to be so contrived, that the gas may be disengaged in the lower part of the receiver, so as to be retained in contact with the water under a first tub, that that which arrives next may flow out under a second, and lastly under a third tub. Thus, by the length of the contact, the solution requiring longer time as it is effected by a feeble affinity, may have leisure to take place. (Note T.)

The apparatus which we have described, and which may be modified in different manners, is adapted to maintain the contact of the gas with the water; but it would be too troublesome and expensive, when oxygenated muriatic acid is wanted only for some tests or experiments. In this case, an apparatus similar to what we have pointed out for the preparation of muriatic acid may be substituted. It is necessary to employ merely three successive receivers, or three bottles furnished with their tubes of safety. The conductor tubes, intended to transmit the gas from one bottle into another, must issue from the upper part of the one bottle, and dip into the lower part of the next. If the gas be received into an alkaline solution, two receivers, or even one, may suffice.

Instead of the mixture of muriate of soda and sulphuric acid which we have prescribed, muriatic acid may be directly employed. One part of manganese is then necessary for four parts of concentrated muriatic acid, or for an equivalent quantity of weak muriatic acid; and the latter is preferable on account of the too tumultuous disengagement of gas, produced by the concentrated acid. The heat can hardly be too slowly conducted. The operation should cease whenever the first tube becomes hot. Oxygenated muriatic acid acts differently, according to the affinity which the other substances have for the two elements that compose it. If these bodies tend to combine particularly with oxygen, they carry off this element from the muriatic acid, which is retained by the water. Thus light disengages the oxygen, restoring it entirely to its elastic state, while the water retains the plain muriatic acid. Thus, also, the colouring substances take possession of the oxygen, which thereafter exerts its action on such of their elements as have most affinity for it.

The alkalies tend to combine with the two elements of the oxygenated muriatic acid, although, in some circumstances, the action which they exercise on the muriatic acid determines, by the formation of a muriate, the separation of a portion of the oxygen, which resumes the gaseous state. But, excepting this effect, the action of the alkalies condenses the oxygenated muriatic acid, and, by a necessary consequence, lessens or represses its odour.

When the condensation arrives at a certain degree, the action of the alkalies, becoming proportionally more energetic, decides the formation of two new combinations, one of which is a simple muriate, and the other a superoxygenated muriate. The oxygen accumulated in the latter undergoes on the part of the alkalies so strong an action, that light and colouring substances can no longer disengage it. The whole oxygenated muriatic acid, which contributes to the formation of a superoxygenated muriate when we receive the oxygenated muriatic gas into an alkaline solution, is therefore lost as to the power of discoloration.

The difference of action between nitric acid and the oxygenated muriatic acid, on colouring substances, and in general on vegetable and animal bodies, depends on the affinity of the oxygen for azote, and for muriatic acid. The first is by much the stronger. Hence, nitric acid gives up its oxygen with far greater difficulty; but when the resistance of this affinity is overcome, the results of the action of both are similar.

The same difference is observed in the action of the two acids on the metals. Nitric acid is decomposed only in part by the action of the metals; and while one portion gives up its oxygen, another usually combines with the metallic oxide without changing its nature. But the oxygenated muriatic acid is entirely destroyed by the action of the metals. From the metals, merely superoxidized muriates are obtained; and only alkaline muriates in the precipitation by the alkalies. Hence, the denomination of oxygenated muriate of mercury, for example, might give a false idea of this combination, which is merely a highly oxidized muriate of mercury. Oxygenated muriates of the metals may, however, be formed, by combining the oxygenated muriatic acid with a metal already saturated with oxygen, as Chenevix has shewn. (Note U.)

Article IV.

Of Aqua Regia, or Nitro-muriatic Acid.

To this compound acid, the name *aqua regia* has been given, because it has the property of dissolving gold, which was called the king of metals. But it should be regarded as a mixture of muriatic acid and nitric acid, which combine their forces to effect solutions which they could not separately do.

By the reciprocal action of these two acids, a portion of the nitric acid is decomposed. Hence results a production of oxygenated muriatic acid which exhales, diffusing its odour; and nitrous gas is proportionally formed, which remains dissolved in the compound acid, and which colours it progressively, till an equilibrium of combination be effected. But neither the oxygenated muriatic acid, which is volatilized as it forms, nor the nitrous gas, which is also expelled whenever the acid exerts its action on another substance, contribute to its action on the metals. As its operation only is considered, the name *nitro-muriatic acid* is retained for it, whatever be its composition.

Nitro-muriatic acid may be prepared, either by simple mixture of the nitric and muriatic acids, or by dissolving muriate of ammonia or of soda in nitric acid. Other salts might be made use of, for example nitre (nitrate of potash), which might be dissolved in muriatic acid. Several other processes might be employed, which it is needless to describe.

It is especially for the solution of tin that nitro-muriatic acid is to be examined, because it is the principal use which is made of it in dyeing.

Dyers do not prepare in an uniform manner the solution of tin, to which they give the name of *composition* (spirit). Every one has his recipe. This solution, however, produces different effects, according to the process made use of. It is essential that the same artisan should prepare it always in the same manner, in order to obtain uniform effects, and to guide himself by the observations which he may have made in the preceding operations.

Several dyers make use merely of the aquafortis of commerce; and it seems, that when they began to employ the solution of tin, they used no other solvent. This aquafortis is a species of nitro-muriatic acid, because there has been employed for its preparation an impure nitre, which is mixed with a greater or less quantity of marine salt. But this quantity varies; and the concentration of the aquafortis is likewise subject to many variations. Hence this acid must produce uncertain effects.

Pure nitric acid dissolves tin only when it is very much weakened, and when care is taken to keep the vessel with the materials in cold water. The metal is, in this case, at the lowest degree of oxidation, according to Proust's observation. But it speedily falls down, even at an ordinary temperature.

Vogler employed a similar solution in dyeing. He prevented the precipitation of the oxide, by adding muriate of soda or ammonia: but it is better to employ immediately the nitro-muriatic acid, which requires less attention.

When a more concentrated nitric acid is used, or when heat is applied, the tin passes to the maximum of oxidation, and is entirely precipitated. This process is had recourse to for ascertaining the weight of tin which exists in an alloy; the tin having thus taken 40 parts of oxygen for 100 of metal.

Hellot took 32 parts of nitric acid, which he mixed with an equal quantity of filtered water (distilled water?); he dissolved in it, by little at a time, two parts of very white muriate of ammonia, and one part of nitrate of potash; and lastly, two parts of granulated tin. Scheffer dissolved one part of tin in four parts of nitro-muriatic acid.* Macquer dissolved three parts of tin in eight parts of nitric acid, with which he mixed one part of muriate of ammonia, and six parts of water. Pœrner employed other proportions, &c.

These solutions, so very various, possess undoubtedly different properties. In them all, one essential object is wanting, which is a preparation constantly uniform. For this purpose, it is indispensable to make use of a pure nitric acid, and to

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* Essai sur l'Art de la Teinture.

determine its specific gravity by means of the hydrometer. The process which was resolved upon, after several trials, in the first edition of these Elements, consists in taking nitric acid at 30° B. (1.26. sp. grav.); to dissolve in it one-eighth of its weight of muriate of ammonia, to add by small portions at a time one-eighth of its weight of tin, and afterwards to dilute this solution with a fourth of its weight of water.

A pure tin, such as the Malacca tin, or good English tin, must be selected; because the common tin (of France) contains copper and lead, metals which would be injurious to the beauty of the colours. Even in the fine tin of England some copper is found; but common tin contains occasionally nearly one-half its weight of lead, and antimony and bismuth besides.* The tin must be reduced into granulations, by melting it and pouring it into water, which is agitated with a bundle of small rods; an operation which ought to be cautiously made, to avoid explosions.

In the solution of tin, there is usually formed a small blackish deposite, from which the liquid should be decanted.

The solutions which contain a great proportion of tin are brown, and afford deeper and duller colours; yet occasions may be found where they can be useful. One may be obtained highly charged with tin, which may be advantageous in

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* Recherches sur l'Etain; par MM. Bayen et Charlard. By common tin, the Author must mean what we call Pewter. —T.

certain cases, by decomposing in a retort, at a very moderate heat, muriate of ammonia, mixed with an equal weight of oxide of tin. The residuum is dissolved, filtered, and evaporated so as to crystallize. By this means crystals are procured of a triple salt, composed of muriatic acid, ammonia, and oxide of tin. To make use of this salt, a little muriatic acid must be added to its solution, which prevents the precipitation of the oxide of tin.

The solution of tin in nitric acid is accompanied by a production of ammonia. We have ascertained that the same production took place, when the solution was effected with the simple mixture of muriatic acid and nitric acid, although it be made with great slowness and precaution, and although the oxide of tin be only in the lowest state of oxidation. It thence appears, that there must be less difference than might be thought between the action of simple nitro-muriatic acid, and that of the preparation into which muriate of ammonia is put.

It is probable that a new quantity of ammonia is produced in the very process of scarlet dyeing, which is performed at a degree of heat approaching to ebullition.

It has been attempted to explain, by the action of this ammonia, which saturates the muriatic acid, and whose formation contributes at the same time to the destruction of the nitric acid, why the nitric acid does not attack (corrode) wool in dyeing scarlet, which is done at so high a degree of heat, although this acid be very destructive to it when it is insulated.

In this saturating action, has been also seen the explanation of an observation of Bancroft. In dyeing scarlet, he wished to substitute muriate of tin* for the nitro-muriate; but a larger proportion of it was required, and the wool was found to be deteriorated. In this operation no ammonia could be formed, and the muriatic acid, which weakens the woollen fibre, exerts all its action on it.

Muriate of tin may be more useful for cotton and linen, on which substances muriatic acid has much less action.

No consideration ought to be neglected for varying the mordant best fitted to procure fine colours in dyeing.

The solution of tin assumes more or less quickly the consistence of a jelly. When this occurs, the dyers say that the composition has turned. For avoiding this, it is proper to make the preparation only a short while before it is to be used. When the jelly is merely beginning to form, the solution may be restored, by adding a certain quantity of muriate of soda. This inconvenience proceeds from the tin continuing to get more oxidized by means of the oxygen which it attracts from the atmosphere, or receives from the nitric acid; and from a greater quantity of ammonia being formed, which, rendering the tin insoluble

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* He prescribed also murio-sulphate.—T.

in the acid, causes it to precipitate. Heat promotes this effect; hence the solution of tin does not keep so long in summer as in winter.

Uniform observation has taught, that when the solution of tin is briskly made with the copious evolution of vapours, the colours obtained from its employment are less lively and less agreeable, than when the solution is made slowly and without effervescence. Hence, at least for the dyeing of wool, tin should be at the lowest stage of oxidation. It does not remain in this state; and it seems to pass to a more advanced degree of oxidation in the very operation of dyeing. It would not otherwise afford a white basis to the colour. But this circumstance is undoubtedly advantageous. It is a reason for preferring solutions which are recent, and made with slowness, to those which are old, with whatever care they may have been prepared.

Haussman has recommended, for some purposes, the acetate of tin obtained by means of a solution of tin (muriate) and acetate of lead.

Other (metallic) solutions are made with nitro-muriatic acid, which may be useful in dyeing. De la Folie has proposed that of bismuth; and although he begins to dissolve the metal in the nitric acid, it is however a combination with the nitro-muriatic acid, which is formed in this process by means of the muriate of soda which he adds. The solution in nitric acid alone would not answer, because, whenever it is mixed with water, the metallic oxide falls down, forming an insoluble salt, and thereby separates without being able to unite to the colouring particles.

According to the description of this process given by Dambournay, of which he himself made much use,* one part of bismuth is to be dissolved in four parts of nitric acid. This solution is to be poured into a bath which contains tartar, along with a solution of muriate of soda.

It has been found, that whether the solution of bismuth had been made directly with nitro-muriatic acid, or whether the solution in nitric acid was mixed with a solution of sea salt and tartar, a considerable precipitate was always formed on contact with water, although less copiously than when the simple solution in nitric acid was mixed with water. It has been remarked, moreover, that the precipitates which this solution occasioned with the decoctions of colouring substances, had an unequal colour, and speedily became brown.

Article V.

Of the Acidulous Tartrate of Potash, and of some other Acids.

The tartaric acid, which predominates in the acidulous tartrate of potash, owes the properties which distinguish it from other acids, the features of which are traceable in its combinations, to its

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* Recueil de procédés et d'expériences sur les Teintures solides.

fixity and disposition to take the solid state, which is so great, that notwithstanding its affinity for water, it separates from it, and crystallizes at ordinary temperatures.

The effects of this tendency are increased by the condensation which affinity produces; while, at the same time, the action which it exerts on water, as well as that of its base, is diminished by their mutual saturation.

These considerations shew, that the tartaric acid might produce, with alkaline bases in themselves very soluble, combinations of little solubility, when circumstances permit them to retain an excess of the least soluble element, which is the acid. Thence arise the acidulous tartrates, or salts with excess of tartaric acid, as also the oxalates, the acidulous sulphates, which equally proceed from acids having more disposition to the solid state than their bases.

For the same reason, this acid produces with the bases that have little solubility insoluble salts, which have no need of an excess of acid to acquire this quality. This same insoluble combination is formed every time that combinations of acid and of bases are brought together, some of which may be sparingly soluble, provided there be no excess of acid to oppose this effect by its solvent power. This disposition determines therefore the precipitates, and the exchanges of base which take place, by means of the tartaric acid, in the reciprocal action of the acids and alkalies, or of their combinations.

If in an acidulous and slightly soluble tartrate the proportion of base, which has of itself much solubility, be increased, proportions are attained which yield a neutral salt. Such are the tartrates of potash, soda, or ammonia, which, by this increase of base, have acquired a greater solubility than in the acidulous state, although they still possess the property of crystallizing. Should an insoluble base abstract their acid, the alkali does not part with it entirely. Thus Vauquelin observed, that on decomposing the acidulous tartrate of potash by quicklime, which forms an insoluble tartrate of lime, the remaining alkali retained a portion of tartaric acid.

If instead of lime we make use of the carbonate of lime, it is only the excess of acid which, by its action on the lime, produces a disengagement of carbonic acid, and forms a proportional quantity of tartrate of lime. When the tartrate of potash has thereby attained the neutral state, the tartaric acid has no longer a strong enough action on the lime to separate its carbonic acid.

Hitherto tartaric acid has not been employed in the art of dyeing. It is the acidulous tartrate of potash which is used. (See NOTE H.)

This salt, usually called *tartar*, is deposited on the sides of casks, from which it is afterwards detached. In its natural state it is mingled with impurities deposited at the same time. When it is separated from red wine, it retains a great deal of the colouring matter of the wine, whence it is called *red tartar*.

Tartar is purified by different processes at Montpellier and Venice. At Montpellier the tartar is dissolved in hot water, and crystallized by cooling. The crystals are boiled in another copper, and there is added five or six kilogrammes of the white clay of Murviel for every myriograme of the salt, (five or six parts for ten). This earth is boiled with it, and by evaporation we obtain the purified tartar, *cream of tartar, the acidulous tartrate of potash.*

The process practised at Venice consists, according to the description given of it by Desmarets,* 1. In drying the tartar in iron boilers; 2. In bruising and dissolving it in hot water, by the cooling of which purer crystals are obtained; 3. In redissolving these crystals, and clarifying the solution with whites of eggs and wood-ashes.

In the latter process the alkali of the ashes must saturate a portion of the acidulous tartrate; the calcareous earth must also effect a decomposition; and, towards the end of the evaporation, tartrate of potash should be obtained.

The acidulous tartrate of potash, or cream of tartar, retains always a little calcareous tartrate.

Water dissolves less than one-hundredth of this salt at 10° Reaumur (about 55° Fahr.); but boiling water dissolves much more of it.

Much use is made of acidulous tartrate of potash, or tartar, in dyeing. For delicate colours it is indispensable to employ the purified salt, and

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* Journ. de Physique, 1771.

it is preferable in every case. In some processes red tartar is recommended as proper to contribute by its colour to the colour that is wanted. But the red particles separate from the tartar when the salt is dissolved, and they should be regarded merely as hurtful impurities.

Of the effects produced by tartar in dyeing, a clear explanation cannot yet be given. Experience teaches merely, that it moderates the action of alum on woollens, the fibres of which are easily degraded. It is probable that the colouring particles, in fixing themselves on the stuffs, either alone or with a base, carry a small portion of it into their combination, thereby modifying the colour.

There is another salt, which has some analogy with tartar, and which may perhaps produce good effects on several occasions. This is the acidulous oxalate of potash, or salt of sorrel, extracted from wood-sorrel in several parts of Switzerland and Germany. Scheele has shewn, that the acid of this salt is the same as that obtained from sugar, and from several animal and vegetable substances, on treating them with nitric acid, whose oxygen enters into combination with a due proportion of hydrogen and carbon. But it exists native, combined in excess with potash, in wood-sorrel and some other plants. Oxalate of lime, which is insoluble, is found in several roots.

The properties which oxalic acid communicates to the different bases, and the effects which it produces on the other combinations, are to be explained, like those of the preceding acid, from its insolubility, which causes it in like manner to crystallize. Hence it is made use of in chemistry to discover the existence and the quantity of calcareous earth held in solution. But for the complete production of this effect an excess of acid must be avoided, and all its combinations must be nearly in the neutral state. The acidulous oxalate of potash, or salt of sorrel, produces analogous effects.

This oxalate readily dissolves iron, forming a soluble salt, which renders it useful for removing spots caused by that metal. Oxalic acid produces also an oxalate of iron, which dissolves easily in an excess of acid. This property makes it be employed at present, in some manufactures, for destroying the colours whose basis is oxide of iron.

Acetous acid, or the acid of vinegar, was distinguished from acetic acid, or radical vinegar, on a supposition that the latter contained a larger proportion of oxygen, and had thereby a greater acidity. But Adet and Darracq have shewn, that between these acids there is no difference which can authorize their being distinguished. Acetic acid is merely more concentrated, and the processes by which it is prepared serve only to exclude its water. We shall therefore designate them by the common appellation of *acetic acid.*

Acetic acid has qualities opposed, as it were, to those of the preceding acids. It is volatile, but it has a great affinity for water. It ought therefore to form combinations which have in general much solubility. It seems to have a small capacity of saturation; hence its combination must produce but a feeble condensation. From these causes it retains its bases but weakly, and is easily expelled from them by the action of other substances, as well as by heat. As it is volatile, and can assume the gaseous state, according to the experiments of Priestley, the action of the air promotes its separation.

This acid is formed, not only by the fermentation which is termed acid (acetous), but also by putrefaction, as Fourcroy and Vauquelin have proved. It would appear that the substances which contain no azote are not capable of yielding this acid; for they receive no azote from the atmosphere during fermentation; and the experiments of Proust shew that this acid contains a certain portion of it. (Note V.)

Acetic acid is also formed in the distillation of several substances, and particularly of wood. To acid thus formed the name *pyrolignous* was given; but Fourcroy and Vauquelin have proved that it did not differ essentially from the acetic acid, and that it is merely this very acid holding in solution a bituminous oil, which is produced in the same operation, a part of which separates by keeping. It gives up the greater part of it when rectified by a second distillation. It may, however, be distinguished by the name of *pyrolignous acid,* not in order to indicate any difference of acidity, but its bituminous condition and uses.

Bosc has shewn[*] that this acid possessed peculiar properties for black dyes on cotton, which it derived from its carbonized oil. We shall, elsewhere, point out the interesting process, which we owe to him.

This acid merits much attention, not only for this purpose, but for several others, because it can be obtained at little expense, and its carbonized oil may be useful, or is at least not injurious. Guyton,[†] by distilling in an iron retort chips of very dry beech-wood, and rectifying the first product by a second distillation, extracted a quantity of acid, which exceeded in weight one-third of the wood employed, and the charcoal remained.

CHAPTER II.

Of Alum, or the Sulphate of Alumina.

Alum is designated in chemistry by the name of *sulphate of alumina;* and although this denomination does not indicate rigorously the elements of which it is composed, it is however useful, and fulfils the usual purpose of nomenclature, because it denotes the ingredients which should

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[*] Annales des Arts et Manufactures, tom. v.

[†] Encyclop. Méthod. au mot *Lignique*.

fix attention in the greater number of the phenomena that are investigated.

This combination is of very frequent use in the art of dyeing; it is also employed in several other arts. Hence, for directing its application, we must be well acquainted with its properties and diversities; and its preparation becomes an object of considerable importance.

Alum is found in some mineral springs. It effloresces on the surface of schists in coal mines, or on the lavas in the neighbourhood of volcanoes, and on several rocks. But the greatest part of the alum employed is extracted from peculiar ores, or is fabricated by an artificial combination of alumina and sulphuric acid.

Alum is mentioned in the works of the ancients, and that from Melos in particular was esteemed among the Greeks;* but Bergman† thinks that the alum of the ancients was a substance which is found native, and which differs greatly from the salt to which this name is now given; that the species of alum of which Dioscorides speaks, was rather a stalactite which might contain alum, but only in small quantity, and blended with other sulphates. In the time of Pliny,‡ the best alum came from Cyprus; and its species was selected according to the colours for which it was

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* Voyage de Jeune Anacharsis, tom. iv.

† Bergman, de Confect. Alum. Opusc. vol. i. This dissertation is of date 1767. Beckman established the same opinion in the Mem. de Gottingen, 1778.

‡ Amailhon, Mem. de l'Instit. Beaux Arts, tom. iii.

intended. But it appears that the kind appropriated to brown colours was very impure, and contained much sulphate of iron, since Pliny distinguished it by the name *nigrum*, stating that it afforded a black colour with gall-nuts, which circumstance cannot apply to any factitious alum.

It was in the East that factitious alum began to be known. It is not ascertained at what place, or at what period it was at first fabricated. One of the most ancient manufactories was that of Rhodes, a city of Syria, called at the present day Edessa. Thence comes the name of *roche alum*, which, by a confusion of words, is still given to the crystallized masses of alum. This art was carried in the 15th century into Italy, from which it was spread into Germany and the rest of Europe.

At Solfatara, near Naples, an aluminous ore is found, under the form of a white earth. The alum is formed in this ore by the action exercised on the argillaceous lavas by the sulphurous acid disengaged from the volcano by heat.

The purest alum ore is that of Tolfa, near Cevita-Vecchia. It is composed, according to Monnet, who first made its analysis, of 40 parts of sulphur and 50 of clay, consisting of a mixture of argillaceous and siliceous earths; and besides these, a small quantity of carbonate of potash, and a very little iron. Bergman also analyzed it, and gave nearly the same proportions. Vauquelin has still further confirmed this analysis, bestowing on it very great precision.

The other ores from which alum is extracted, are schists more or less pyritous and bituminous. Those which are too pyritous ought to be rejected, because they yield an alum which contains much sulphate or vitriol of iron, of which it would be difficult to get rid.

The operations by which alum is extracted from its ores, when it is not found ready formed in them, as at Solfatara, have for their objects the alumation, the extraction of the alum, and its crystallization.

These ores, exposed to the air and the rain, may be alumed, for the most part, without being prepared; but those which contain either too much bitumen or too much sulphur, require to be roasted before being exposed to the action of the air and humidity; and in all, the torrefaction accelerates the formation of alum.

The *alumation* consists in the combination of oxygen, which uniting to the sulphur changes it into sulphuric acid, as Lavoisier has shewn. But usually it is the sulphate of iron which is formed, and the iron oxidizing to a *maximum* by exposure to the air, is decomposed by the alumina. There is only the mine of Tolfa, among those which are known, where the acid appears to combine immediately with the alumina. (Note X.)

When the alum is formed, the ore must be lixiviated, and the liquid be afterwards evaporated till it be in a condition to yield crystals. The first crystals are to be washed, redissolved in a small quantity of boiling water, and the solution poured into peculiar casks, whose staves are then unhooped and separated, in order to get at the mass of alum which is formed.

The residuum of the crystallizations, mixed with more or less of the lixivium of the mineral, is evaporated till it be in a state to crystallize; and the process is carried on by adding the residuums of the preceding crystallizations to the new solutions.

This mixture is the principal cause of the impurity of alum, and of the differences which exist among its species.

In the progress of the chemical arts, the fabrication of alum by the direct combination of sulphuric acid and alumina has been discovered. For this purpose, a clay should be selected as free as may be from iron and calcareous earth; it must be roasted to prepare it for combining with the sulphuric acid. This combination is either made immediately with the acid, or by exposing balls of baked clay to the vapour of the sulphuric acid, in the leaden chamber in which this acid is itself manufactured. Chaptal has published the details of this process, which he established at Montpellier.*

This mode of forming alum requires, as we shall see, an addition of potash, or sulphate of potash; and the salt obtained by this process appears to be peculiarly liable to have an excess of acid.

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* Mém. de l'Academie, 1788.

Before prosecuting the examination of the preparation of alum, it is proper to determine the nature of this combination.

It was at first imagined, that alum was a salt formed simply by the combination of sulphuric acid and alumina; whence Bergman recommended to saturate the excess of sulphuric acid which is usually found in the lixivium of alumed earth with a pure clay, instead of the potash or putrefied urine (naturally charged with ammonia), which is commonly added. But Chaptal observed,* that *if the acid lixivium be boiled with baked or raw clay, the solution is but slowly made, and after a long ebullition. If the lixivium be filtered, when it appears to be saturated, it lets fall, on cooling, a large proportion of the clay which it had dissolved; and if in this state the solution be concentrated, the clay separates, forming a precipitate which prevents all crystallization.* From this observation we may conclude, that potash or ammonia must enter into the composition of alum. Descroizilles asserted, that the potash did not contribute to the crystallization of alum by the saturation of the acid, but by its combination; and he found, on trial, that sulphate of potash could produce the same effect. Chaptal had come to the same result, and established this practice in his factory. Lastly, Vauquelin made an exact analysis of alum, and discovered that it contained, necessarily for its crystallizing, sulphate of potash or

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* Mém. de l'Academie, 1788.

ammonia, or both at the same time. He estimated the amount of sulphate (of potash) present in alum, drawing from his observations this inference, that whenever crystals of alum are obtained from an earthy or stony substance, by means of sulphuric acid, that substance contains potash. It has been seen, that the ore of Tolfa naturally contains carbonate of potash. Some other ores may be in the same condition. The wood-ashes formed in their roasting, supply them likewise with potash and sulphate of potash. Hence it is not surprising that alum may be obtained without the addition of potash, or putrefied urine, to furnish the ammonia. Bergman remarks, that the latter addition gives rise to an alum which alters the colours. It is not known whether it be by too large a proportion of sulphate of ammonia, or by the mixture of some other hurtful substance, that alum may acquire this bad quality.

It may be remarked, that Bergman had himself discovered,* after his first work, not only that it was not for the absorption of the excess of acid that potash or ammonia was necessary to the formation of alum, but that they were still efficacious when in the state of sulphate.

It ought not, however, to be thence concluded, that the effect is entirely the same, whether potash be employed, or sulphate of potash. By the first, the requisite saturation of the acid, when it

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* De Platina, § Opusc. vol. ii.

is in excess, is greater, and consequently the production of alum ought to be more considerable, if enough of alumina be present. Whenever, therefore, there is an excess of acid, but a defect of potash or alumina, the advice of Bergman may probably be followed with advantage, namely, to add alumina, and at the same time a sufficient quantity of potash. To accomplish this twofold object we may employ, as Vauquelin points out, the residuum of the distillation of nitrate of potash by clay, which may be particularly adapted to the fabrication of alum by means of sulphuric acid.

In the prices of the alums of commerce there is a considerable difference, and that of Rome is generally preferred for colours that are to be lively and clear. By analysis, therefore, must be discovered what are the differences which distinguish alums from one another.

Vauquelin has brought to the analysis of alum the precision and accuracy which characterize his researches.[*] On decomposing alum by potash, its ammonia is disengaged. On the other hand, by decomposition with ammonia, evaporation of the liquid, and drying the residuum strongly, the sulphate of potash is obtained by itself. By this means Vauquelin has ascertained, that alum contains nearly 7 per cent of the sulphate of potash or of ammonia; and this quantity is usually divided between both of these sulphates. (Note Y.)

† Annal. de Chim. tom. xxii.

He has recently examined five kinds of alum, taken from different factories. He determined the proportion of acid which each contained, by precipitating the sulphuric acid with barytes, and comparing the weights of the precipitates. He had previously precipitated the alumina by ammonia, and subjected it to a strong desiccation.

It results from his experiments, that these five kinds of alum, among which was the alum of Rome, afforded proportions almost rigorously the same; and that the quantity of iron which is found, for example, in that of Liege, of good quality, is nearly the same as what he obtained from Roman alum. Hence he is led to believe, that it is only from a prejudice that the last continues to be preferred; and if a proportion of iron which can do harm be present, he recommends to get rid of it by prussiate of potash.

We shall deviate a little from the consequences to which the experiments of this great analyst seem to lead. 1. We have examined alums, particularly factitious ones, *(ceux de fabrique)*, which contained undoubtedly a pretty considerable excess of acid, for they left, after their crystallization, a very acid liquor. What Vauquelin has found in the five specimens, four of which had been sent by the manufacturers themselves, and were consequently choice samples, does not authorize the conclusion, that all the alums in the market have a like proportion of acid.

2. We have mixed with a solution of the alum of Liège, which appeared to be very pure, a little

gallic acid; and a similar test was applied to the Roman alum. The first assumed a black hue, and the second did not change. Analysis would probably have pointed out but a slight difference; but this slight difference is sufficient to produce an alteration on lively colours, for which, especially, a severe choice is requisite.

After submitting this alum to crystallization, in which the first formed crystals were taken, the solution of these crystals was no longer affected by the gallic acid, so that it then presented properties completely analogous to those of Roman alum. Bergman had already observed this effect of a careful crystallization which he recommended.

With regard to the iron present in alum, and which may exist in considerable proportion when it is crystallized with little care, Monnet had formerly observed, that the sulphate of iron could be entirely separated by crystallization; on the other hand, Leblanc has made mixed crystals of sulphate of iron and sulphate of alumina (*sulfate d'alun*). These facts would seem to be reconcileable, by the consideration of the state in which the iron exists. When highly oxidized, as it undoubtedly is in the lixivia of alum ore, it requires a great excess of acid to be susceptible of solution, and the oxide must precipitate, as we shall afterwards see, during the evaporation and crystallization, or be retained in the uncrystallizable residuum. But if a little oxidized sulphate be mixed with the sulphate of alumina, and if crystallization take place immediately, the iron no longer requires in this case an excess of acid. It may thus be placed in circumstances which allow it to form a combination.

To recapitulate: We conceive that, in the manufacture of alum, matters should be so managed as to leave no excess of acid, and to avoid those additions of uncrystallizable residuums, which it is proper to treat separately, according to Bergman's advice, whether it be for extracting their salts, or for making an alum out of them, which afterwards requires more care for its purification, or an alum intended for purposes where it is not needed to be pure. In the second place, The crystallization should be so conducted that the purity of the salt shall not be affected. Consequently, it should not be suffered to condense in great masses, but have a residuary liquid that may retain what would affect the qualities required in the combination. To accomplish this object, the crystallizations might be reiterated, and all the residua treated separately.

It appears to us that this art is improving progressively, as the manufacturers are becoming more enlightened in the conduct of their operations, and that there will soon be no need of having recourse to Roman alum.

Those who require alum need not make a selection in employing it for sombre hues; but they should be very nice with regard to lively and clear colours. Instead of analysis, which requires time and practised skill, we propose to them, 1. To crystallize a portion of the alum which they are to use; if the residuum be perceptibly more acid, this alum might modify the colours by its excess of acid: 2. To mix a little of the infusion of gall-nuts with the solution of alum; although, by its own colour, this infusion may be less proper for this trial than pure gallic acid, it will point out sufficiently well if the alum contains an injurious quantity of iron. In this case, the alum may be purified by one crystallization, leaving a sufficient (liquid) residuum.

When an exact analysis of alum is wished to be made, we must not lose sight of the difference which, according to the means employed, exists in the insoluble precipitate, from which the proportion of alumina is to be determined.

If the precipitate be made by means of a carbonate, it retains a considerable proportion of the acid, and even of the alkaline base; for on dissolving it in nitric or muriatic acid, alum is obtained by crystallization. The best agent is ammonia; but it is difficult to deprive this precipitate sufficiently of sulphuric acid, so as not to produce a precipitate of sulphate of barytes, when its solution in nitric or muriatic acid is mixed with a solution of a barytic salt.

Another circumstance impairs the precision of these comparative determinations. When the solution of alum is very dilute, the alumina retains water, which it does not give entirely up at a very strong heat; but when it is concentrated, the precipitate which it affords abandons the water much more easily, according to the observation of T. de Saussure.[*] Hence, from the circumstances of the precipitation, and the degree of heat at which the precipitate is dried, there may exist great differences in its valuation.

According to Bergman, 100 parts of sulphate of alumina (alum) contain 18 parts of alumina. T. de Saussure reduces this quantity to 0.09, and Vauquelin, in his last analysis, to 0.085.

Lime and the alkalies, mixed in certain proportions with the solution of alum, cause this salt to take a cubical form. Sieffert appears to have first described this variety of alum.[†] Leblanc has made interesting observations on the crystallization of this salt, not yet analyzed by chemists. It must have the acid properties in a less degree than ordinary alum, as Vauquelin thinks, and it would appear, that from the stronger action of the alkaline base on the acid, this salt would give up the alumina more readily to the colouring particles, since alkali is commonly added to the solution of alum for precipitating their lakes.

According to Bergman, 30 parts of water are required for dissolving one of alum; 3 parts of boiling water are sufficient.

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[*] Journ. de Physique, tom. liii.

[†] Sieffert's versuche mit einheimischen farbe materien, &c. 1775. Sieffert quotes a dissertation on cubical alum; which he printed in the Edinburgh Magazine. For obtaining this alum, he prescribes the mixture of 12 parts of alum with one part of quicklime slaked in the atmosphere, dissolving this mixture in boiling water, and evaporating gently.

We have remarked, that in several woollen dyes tartar was added, which had the property of moderating the action of alum on the filaments, without attempting to explain how it impaired its energy. Bancroft observes, that the dyers indeed frequently omit the tartar, diminishing at the same time the usual proportion of alum.

Linen and cotton have less disposition to combine with alumina than animal substances. Hence, a small proportion of soda or potash is commonly added, which must favour, as has been said, the decomposition of the alum.

This method is not sufficient for qualifying alum to become a mordant on printed goods. The solution which contains the alumina must be concentrated, without having crystals formed in it. The acetate of alumina has not only this advantage, but it possesses likewise another, dependent on the acetic acid, which serves as the solvent. This acid acts only by a weak affinity, and consequently retains the alumina more feebly than the sulphuric acid; and in the drying, to which goods impregnated with the mordant are subjected, its volatility makes it fly off, so that these goods do not carry into the bath an acid which might injure the colour. These advantages render the acetate of alumina a very fit substitute for the ordinary aluming in several cotton dyes, accommodated to the improved process of calico printing; but acetic acid scarcely effects the dissolution of alumina, as it exists in clays. Their force of cohesion is too great an obstacle for the weakness of the acid to overcome. It is by means of the acetate of lead that an exchange of bases is produced, which we shall have occasion to examine. Hence the preparation of acetate of alumina amounts to a price which does not permit its use in several dyes, till a mode be got of preparing this combination less expensively. The properties of acetate of alumina led us to believe, that it might be substituted with success for alum in the dyeing of wool. We have made trials with madder; but the cloth took a less intense colour, without our being able to point out the cause of this result, dependent probably on some circumstance which we overlooked. (See Note C.)

Alumina dissolves pretty copiously in potash and soda, especially by calcination. Macquer was much occupied with this solution, in order to employ it in dyeing. But as the alkalies possess the property of dissolving colouring substances, and of abstracting them from the stuffs on which they are fixed, they do not seem fit to serve as solvents of alumina. The experiments of Haussman, however, prove that this mordant may be employed in some circumstances with advantage. (Note Z.)

CHAPTER III.

Of the Sulphate, and some other Combinations of Iron.

The sulphate, or *vitriol of iron*, *martial vitriol*, *green copperas*, is not an uniform and identical combination. It varies, not only by the admixtures which may be present, but also by the state of the oxide of iron, whence very different effects may result from its action.

The sulphate of iron may be directly made from iron and sulphuric acid, diluted with a certain quantity of water; and a combination may thereby be obtained, possessing determinate qualities. But the low price of this article rarely allows of this manufacture being conjoined with that of sulphuric acid.

Sulphate of iron is found native in coal-mines, in the cavities of pyritous mines, and in schists. But the most part of what is employed comes from the martial pyrites, or natural sulphurets of iron.

These substances are composed of iron, sulphur, alumina, siliceous earth, and sometimes calcareous earth, in different proportions. The formation of the sulphate of iron in these minerals, is effected by exposing them for a long time to the action of air and moisture, or by roasting them in the open air, and leaving them afterwards exposed to its action. This operation must sometimes be reiterated. The sulphate that is formed is extracted by lixiviation and evaporation.

The iron in the native sulphurets of pyrites is oxidized, for when they are exposed to the action of fire in a retort, sulphurous acid is evolved, which does not happen with the sulphurets formed with the metal. It is disoxidized in this operation, and the residuum is a true sulphuret.

Sulphate of iron is also formed in the mineral waters which hold copper in solution, after it is precipitated by iron. This solution, which retains a little copper, is thereafter crystallized.

The sulphate of iron of Goslar contains commonly a little zinc, and that of Hungary and Saxony a little copper.* The sulphates of England and France are purer. They contain, however, sometimes alum, especially those of France.

Sulphates free from copper or alum would be formed, if the precaution were taken of keeping fragments of iron in the boiler, which serves for evaporation, as Monnet recommends;† for iron slightly oxidized has the property of precipitating copper and the base of alum. The superiority of English vitriol seems to be owing to this precaution. The same practice is also observed in two manufactories in the neighbourhood of Alais.‡ The zinc alone would not be precipitated. But

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* Mineralogy of Kirwan.

† Traité de Vitriolisation.

‡ Elémens de Chimie de Chaptal, tom. iii.

it is rarely found, and only in small quantity, in the sulphates of iron.

The copper which exists in several kinds of sulphate of iron is not injurious to the black dyes, in which this metallic salt is principally employed; but for other purposes, it must be got rid of. This is easily effected, by keeping for some hours in a cold solution of this salt plates of iron, on which the copper precipitates. But this operation could not be performed by crystallization, because, according to the observation of Monnet, the sulphate of iron and that of copper form a compound salt that cannot be thus separated.

Alum is probably more injurious to black than copper is; for when a black stuff is boiled with alum, it destroys the colour by dissolving it.

The sulphate of iron varies in its properties according to its state of oxidation.

It is almost colourless when its metal is very slightly oxidized, or in the condition of black oxide. It assumes a red colour when the iron is much oxidized, constituting a red oxide. Proust, who directed our attention particularly to the two states of iron, and to their distinctive properties, regards them as two fixed terms of oxidation, between which there is nothing intermediate. We cannot adopt, in this respect, the opinion of this chemist, whose delicate and numerous observations have contributed so much to the advancement of the science. As the causes, however, which may produce the oxidation or disoxidation of this iron, make it usually pass from a very advanced degree of oxidation to another adjoining the lowest degree, we neglect this consideration, and conform usually in our explanations with the opinion of Proust. (Note AA.)

When the solution of slightly oxidized iron is exposed to the air, it becomes gradually turbid, and lets fall a yellow precipitate. If the effect be complete, crystals are no longer obtainable by evaporation, but an extract is got, which has a great excess of acid. Highly oxidized iron then requires an excess of acid for its solution; and when it is in this state, the sulphuric acid has much difficulty to dissolve a smaller quantity of it, than if it is in the metallic form. By the decomposition of water which occurs in the latter case, it can take only the state of black oxide. If the crystals of the sulphate of iron be left exposed to the air, they lose their green colour, becoming dull and yellowish. Their solution now yields only a salt with excess of acid, and an insoluble yellow substance remains. It is obvious, therefore, that in order to preserve the sulphate of iron or its solution in its primitive state, air must be excluded.

The precipitate now spoken of, is a salt with excess of oxide. By means of an alkali, the acid may be abstracted, when merely a red oxide remains.

If iron be put into a solution of the highly oxidized sulphate, a yellow precipitate is deposited, which is also a salt with excess of oxide, and the solution resumes the state of green sulphate. Hence appears the utility of adding iron in the preparation of the sulphate. It is thus obtained in the state for forming crystals, and those uncrystallizable residuums called *mother waters* are avoided.

The sulphate which contains the black oxide is in a much greater state of saturation, and we have seen that gallic acid could not separate and precipitate this oxide from the sulphuric acid. It is not to be doubted, then, that it exerts a far more energetic action on the acid, than when it is much oxidized.

In the precipitates produced by the alkalies, from the solutions of both sulphates, characters appear which depend on this difference of action. The little oxidized sulphate affords with the alkalies greenish precipitates, which retain a greater proportion of acid in like circumstances; and even when the sulphate is highly oxidized, its precipitates are red, and do not retain any acid. If we treat with a concentrated alkali the green precipitate obtained from the slightly oxidized sulphate, its acid is removed, and it becomes grey or black. On exposing it to the air, it continues to oxidize, passing to yellow. It then grows red, by the action of an alkali which seizes its acid.

What we have now advanced concerning the difference which distinguishes the green sulphate from the red sulphate, must be applied to all the solutions of iron in the acids. The whole of them form a more intimate combination with the black oxide than with the red. They exhibit, besides, differences dependent on the energy of the acid. Thus, muriatic acid dissolves highly oxidized iron more easily than the other acids. It is true, that if it contains an excess of oxygen, a portion of the acid forms oxygenated muriatic acid, according to the observation of Fourcroy. Iron produces also in the precipitation of highly oxidized muriate, a yellow precipitate, which owes this colour to the acid remaining combined with it. But it may be supposed, that highly oxidized muriate of iron would be less proper for black dyes than the sulphate, because it would retain with more force the oxide which must enter into the formation of the black molecules.

Acetate of iron is employed for printed calicoes, and in general for black colours in linen and cotton, for the same reasons which make acetate of alumina be preferred. But we need not have recourse to so costly a process. Acetic acid dissolves iron directly; and to have it in the most oxidized state, fragments of the metal must be kept a long time in good vinegar. The object would not, however, be accomplished, were the solution left always over the iron. For we have seen, that in the metallic state it precipitates a highly oxidized salt. The liquor, then, is to be decanted, and kept in a vessel where it may have contact of air, so as to pass to the highly oxidized state. This decantation ought to be made whenever the solution is completed.

For the ordinary black dyes, where there is no need of so concentrated a solution, vinegar is not employed, but a less expensive acid is frequently formed with different vegetable substances, for example with the bark of the birch tree. To the vessel in which this operation is executed, the name of *tonne au noir* (black cask) is given. This object would be better accomplished, if the precaution were taken to keep the solution, after it is made, out of contact of iron.

In explaining the action of astringents, we have mentioned the observation of Proust, who found, that the highly oxidized sulphate was brought back to the state of the little oxidized, by the action of astringents, and even of other colouring substances; whence he concludes, that it is right to employ in dyeing only the highly oxidized sulphate. This conclusion appears to us just, when black dyes are in question, with the exception, perhaps, of the dyeing of silk. It should even be applied to all solutions of iron used for this purpose. But the same thing does not hold true when solutions of iron are made use of for other colours. For example, in the manufacture of printed goods, in order to obtain the colour called *rust yellow*, sulphate of iron is made use of, or, still better, the little oxidized acetate, formed by the decomposition of acetate of lead with sulphate of iron. The salt with excess of oxide, which is formed in the cloth, has an agreeable yellow colour, which, by the contact of alkalies, passes to grey; after oxidizing in the air, it becomes red.

The shades of yellow which may be given to cotton by means of iron, with which we shall be elsewhere occupied, prove that it is not the oxide of iron alone which serves to give colour in this instance, but that the precipitate retains a portion of the acid; for it is always to an acid that the oxide of iron owes this colour.

The changes of colour must never be lost sight of, which result from the different oxidations of iron in the dyes, where it is used for other colours besides black, as Chaptal has shewn. Thence the precautions which must be taken, in order that this oxidation shall go on uniformly during the operation itself, and that the stuff be exposed to it in an uniform manner.

There is one operation for which the iron should be, on the contrary, at the lowest stage of oxidation: This is the solution of indigo, by means of the sulphate of iron, precipitated by an alkali. Slightly oxidized iron gives solubility to the indigo, by carrying off the oxygen, which renders it insoluble. The oxide of copper produces a contrary effect, affording oxygen to indigo deprived of it. This renders the sulphate and acetate of copper proper for the *reserves*, that is to say, for preserving the parts of the cloths to which they are applied, from the fixation of the indigo, which by resuming oxygen can no longer combine with the stuff.

The differences of oxidation of the metallic substances employed in dyeing, and the effects flowing from them, merit the greatest attention; and by observing them with more care than has hitherto been done, several operations will be rendered methodical (*regularisées*), whose results are regarded as capricious, becoming at the same time more uniform and more advantageous.

CHAPTER IV.

Of Sulphate of Copper.

The sulphate of copper, *blue vitriol, vitriol of Cyprus, blue copperas,* is not much employed in dyeing; but it is of great service for forming the colours used particularly for painted papers; and hence its fabrication, and the means of obtaining it pure, have become interesting to the arts.

Different methods are employed for making sulphate of copper. The native sulphuret; or copper *pyrites,* or *mate,* resulting from the fusion of copper ore, which is a combination of copper and sulphur, is calcined, and the product of the calcination is left to effloresce. The copper thus deprived of a portion of its sulphur oxidizes, and the sulphur is converted into sulphuric acid. The salt that forms is then extracted, and crystallized. A second process, analogous to the preceding, consists in calcining a mixture of copper and sulphur, in exposing the sulphuret in like manner to effloresce, lixiviating the salt, and crystallizing it.

Since the (modern) fabrication of sulphuric acid has allowed it to be employed for several purposes to which its former price was an obstacle, sulphate of copper has been formed, by dissolving the metal, or its oxide, in sulphuric acid. To this sulphate it is objected, that for some purposes it contains an excess of acid; but it would be difficult to avoid this inconvenience.

There are some native waters which contain sulphate of copper.

The principles to be attended to in purifying the sulphate of copper deserve to fix our attention, because they are applicable to all the metallic solutions, and may explain several phenomena observed in the chemical action of different bodies.

The insolubility of any compound that is formed, should be considered as a cause of its formation, whenever the elements that can produce it are brought together. Thence may be deduced, as we have said, the cause of the precipitations and changes of base, which occur in the reciprocal action of the acid and alkaline substances.

The same effect takes place in the reciprocal action of metallic oxides and acids. The oxides can seldom produce neutralization in combining with the acids, when their combination retains solubility; but these combinations require a greater or less excess of acid, a condition which varies according to the state of oxidation. Thus we have seen, that the highly oxidized sulphate of iron requires a considerable excess of acid, which the little oxidized sulphate does not. If the excess of acid be removed, the highly oxidized salt, which is insoluble, precipitates.

It thence results, that when a metal is in solution, and when it needs an excess of acid in order to preserve this state, the addition of another oxide, which shall require a less considerable excess of acid, will cause the first to fall down in the form of an insoluble salt; and if the second needs an excess of acid, although less considerable, it will be precipitated in its turn by an oxide which is soluble without excess of acid, or which requires less of it.

For the same reason, different effects will be obtained, by varying the oxidation of a metal, and thereby the solubility of its combinations. Thus we have seen, that iron precipitated the highly oxidized sulphate, forming a combination which preserves its solubility without excess of acid. In these circumstances two combinations are produced, one which remains in solution, and another which is insoluble. The action even of the alkalies is usually limited to the production of a similar effect on metallic solutions.

Gay Lussac, who established this point of theory,* supported it by several interesting facts.

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* Annales de Chimie, tom. xlix.

We shall confine ourselves to an account of the observations which relate to the preparation of the sulphate of copper and the sulphate of iron.

" When the iron is highly oxidized, it is precipitated by the oxide of copper; when slightly so, the reverse takes place. Here are two consequences of great importance, because they are susceptible of frequent applications to the arts: the first is, that the whole iron can be separated from a solution of copper; the second, that the whole copper in a green solution of iron may be removed.

" Several colours are prepared with the sulphate of copper, but the iron which it always contains, and which has not hitherto been completely separated, alters their shade. If, for accomplishing this object, the iron be strongly oxidized by means of nitric acid, or, still better, by oxygenated muriatic acid, it will be precipitated entirely from the sulphate of copper, by pouring into it a sufficient quantity of potash, heating and agitating the liquor very well.

" The green sulphate of iron is pretty frequently employed in the arts, and in several cases it is of consequence to free it from all the copper. Iron has indeed the property of separating it, but it appears to do so but very imperfectly, and in a long time. It will be undoubtedly more advantageous to employ potash, pouring a little of it into the green sulphate. The precipitate of black oxide of iron will soon return into solution by agitation; and it will throw down at once the oxide of copper, and the red oxide of iron, if either exist in the green sulphate."

CHAPTER V.

Of Verdigris, or the Acetate of Copper.

Formerly verdigris was prepared only in Montpellier and its neighbourhood. The process followed there consisted in causing the stalks of grapes to ferment along with the *vinasse* (wine-lees), then plates of copper were arranged *stratum super stratum* with these stalks, and the whole was left together for some time. On withdrawing them, they were set aside *(au relai)* in a corner of the cellar, where they were further sprinkled with wine-lees ; and lastly, the verdigris formed by this operation was scraped off.

This process has been improved and rendered more economical in these latter times, by substituting for the stalks the squeezed husks of grapes, previously subjected to the acetous fermentation, thus suppressing the vinous matter with which they had formerly bedewed the stalks. Chaptal has described the details of this process.*

At Grenoble, ready made vinegar is employed, with which the plates of copper are moistened. The verdigris prepared in these two methods differs in some of its properties.

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* Mémoires de l'Instit. vol. ii.

Chaptal has made a comparison of them.* The first is unctuous, pasty, little soluble in water; it is preferred for the purposes of painting. The second is drier, of a more decided greenish blue colour, and more soluble in water. It produces better effects in dyeing; giving more vivacity to the colours, and requiring a smaller quantity to compose the mordants.

This difference depends upon their composition. The first contains, in particular, uncombined oxide of copper, or carbonate of copper, and the second approaches to the state of an acetate.

In either preparation of verdigris the copper is reduced to an oxide by the concurrent actions of atmospheric air, and the acetic acid employed or formed. But as copper vessels are much used, it will be proper to dilate a little further on the manner in which the acids act on this metal.

For dissolving copper in the acids, it must, like other metals, be combined with oxygen or reduced to an oxide. Hence it must either attract oxygen from the atmosphere, or obtain it from the acids, or from the decomposition of water by the co-operation of another force; for it has not this property of itself.

The vegetable acids cannot yield oxygen to copper; but the action which they exercise upon it so favours its combination with oxygen, that it attracts it speedily from the atmospheric air, and

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* Mémoires de l'Instit. vol. i.

is reduced to an oxide so as to become soluble in the acid liquid. This must not be hot, in order that the copper may attract oxygen from the atmosphere. The vegetable acids do not attack copper while they are hot, and the same thing takes place with oils and other substances which act on this metal, unless there be a portion of copper already oxidized; for in this case it dissolves readily, whatever temperature the liquor may have. Hence we perceive the necessity of never allowing liquors that can corrode this metal to cool in copper boilers, and of taking care to keep them always very clean, so that no oxide is formed on their surface.

Nitric and nitro-muriatic acids, though diluted with water, afford oxygen to copper, especially at a boiling heat. Hence they must dissolve a portion of this metal in the baths into which, for example, solution of tin enters, unless the boiler be tinned with care. This effect may be diminished, however, in consequence of the nitric acid exerting its action on the vegetable, and more particularly the animal, substances present in the bath, and from its being saturated by the ammonia that is generated.

In verdigris, copper is reduced to the state of oxide, and is combined with a more or less considerable proportion of acetic acid. When the oxide is completely saturated with this acid, it is wholly soluble in water, and forms by evaporation rhomboidal crystals of a blue colour, which attaching themselves to little wooden rods, give origin to those groups called crystallized verdigris, or crystals of Venus. There is this difference, then, between this salt and verdigris, that in the first the oxide of copper is completely saturated with acetic acid, forming an acetate of copper; while, in verdigris, there is but a variable proportion of the oxide of copper in the condition of an acetate. This saline portion can be separated by solution in water. There remains, in this case, only an oxide of copper, or a salt with excess of oxide, which dissolves readily in acetic acid, and thus is converted to the saline state. Sometimes the verdigris contains but very little acetate; sometimes, on the contrary, it contains scarcely one-fourth of its weight of oxide of copper uncombined; in which circumstances consists, as we have said, the difference which distinguishes the verdigris manufactured at Grenoble from that of Montpellier. (Note BB.)

Clegg, in attempting to substitute for verdigris in the black dye an ingredient less expensive, says, that he observed that the copper of verdigris threw down, in the state of an oxide, the iron of the sulphate of iron held in solution along with astringent matters. Regarding verdigris, therefore, as a precipitant of iron, he sought to substitute for it other substances capable of precipitating this metal from its solvents. He first tried the alkalies; and his experiments, which on the small scale appeared to succeed, had no success on the great. In fact, the alkalies do not precipitate the combination of iron and the astringent principle; but they unite along with it, giving it a reddish hue. He next ascertained, by several trials, that the verdigris might be perfectly replaced by a mixture of sulphate of copper and potash. He prescribed the dissolving the sulphate of copper, and adding to it solution of potash, till the blue colour disappeared, that is to say, till the whole of the copper was thrown down. For this purpose a nearly equal weight of sulphate of copper and of alkali is required. He asserts, that the weight of the two together is a substitute for an equal weight of verdigris; and that this process may be put in practice, especially for hats, the dyeing of which consumes a great deal of verdigris.

We shall remark on this process, that the oxide of copper produces in reality a precipitate in a solution of iron blackened by an astringent; but this precipitate is not solely oxide of iron; it is owing to the black molecules which result from the combination of the oxide with the astringent principle. This precipitation may, indeed, be one mode in which oxide of copper contributes to dyeing of black; but it is probable that the principal way in which it is useful to this dye consists in forming a blue with logwood, which also enters into it, or a shade between green and black, which results from its combination with the astringent; for we have observed, that it was advantageous for deepening the black to derive it from different colours. It is thus obvious how a verdigris which contains much acetate of copper, may produce better effects than one which has a larger proportion of unsaturated oxide, or carbonate.

CHAPTER VI.

Of the Acetate of Lead, or Salt of Saturn.

The acetate of lead is a combination of lead reduced to oxide, and of acetic acid. It is usually crystallized in slender confused needles.

This salt has a sweet taste, mixed with a little astringency, which has caused it to get the improper name of *sugar of saturn.*

Acetic acid out of contact of air does not attack lead in the metallic state. But if the air touches its surface, the lead is gradually oxidized by means of the oxygen which it attracts, and thereby becomes soluble in the acid. As this manner of preparing the acetate of lead would be disadvantageous, both because it would take much time, and a large portion of the acid would evaporate, other processes are had recourse to.

White lead is an oxide of lead combined with carbonic acid. To form it, the metal in plates is suspended over vinegar in earthen vessels, which are covered with horse dung, to afford heat for evaporating the vinegar, which exhaling, reduces the lead to an oxide by means of the air, and then dissolves it. Carbonic acid is evolved at the same time, which precipitates the lead in a carbonate. This carbonate, pulverized with much care, constitutes white lead. But a portion of the oxide is retained by the vinegar, forming acetate of lead, which is merely to be evaporated and purified by a second crystallization.

The greater part of the acetate of lead is prepared with distilled vinegar, obtained from beer or wine, and with white lead, which being reduced to a very subtile powder, is in the most favourable state for dissolving.

If no acetate of lead be at hand, it is easy to manufacture it one's self, by dissolving an oxide of lead in distilled vinegar, and evaporating the solution to the proper point of crystallization. Different oxides of lead may be employed. White lead dissolves more easily than the others, except ceruse; but we must avoid the latter, because it is a mixture of white lead and chalk. Litharge, or semi-vitrified oxide of lead, may be substituted for white lead; minium dissolves with more difficulty.

It would probably be sufficient to dissolve the oxide of lead in white (pale) vinegar, whose extractive part, by which principally it differs from distilled vinegar, would do no harm; but it must be remarked, that the acetate of lead is a compound not uniform in its proportions. Thenard has observed, that the ordinary acetate of lead can still dissolve a quantity of oxide almost equal to what it already contains, and then it assumes a different form of crystallization. But the new crystals are decomposed by simple exposure to air, and a portion of the oxide is converted into carbonate. On being dissolved in water, they likewise abandon a portion of the oxide, forming an abundant precipitate; after which the soluble combination is restored to the ordinary state.

On repeating this experiment, we have observed that the acetate of lead which we used, reddened the vegetable colours, acting on paper stained with turmeric like feeble acids; but after being surcharged with oxide of lead, its solution reddened the tincture of turmeric like alkalies, so that there is here an indication of the alkaline properties which the oxides exercise on the acids.

The crystals of acetate of lead usually afford a slight precipitate when they are dissolved in distilled water; which precipitate is owing to carbonate of lead formed at their surface. But they produce, with the waters of rivers and wells, a much more abundant precipitate, arising from the sulphates and the muriates which are present in these waters, the quantity of which is proportional to that of these salts. The muriate of lead, however, has a certain degree of solubility.

The acetate of lead is not employed directly as a mordant in dyeing, although it produces an abundant precipitate with the greater number of the solutions of colouring matters; but its precipitates have sombre and dead hues. The chief use that is made of it, is to procure acetate of alumina. Since the force of cohesion of this earth is opposed to its direct solution in the acetic acid, a mixture of sulphate of alumina is made with acetate of lead. Thus (acetate of) alumina is procured in the liquid state. But the elements of these combinations being placed together, and the oxide of lead possessing the property of affording an insoluble combination with sulphuric acid, this compound is formed and precipitates, while the alumina remains dissolved in the acetic acid. (See Note C.)

Accident made known this combination, so important in the printing of calicoes; several useless substances indeed were added to it, till chemistry determined the essential ingredients.

Certain expert manufacturers imagined, that they should preserve among the ingredients a given proportion of chalk and potash, with the view of absorbing an excess of acid; but this addition does nothing but throw down, uselessly, a portion of the oxide of lead, and introduce into the acetate of alumina foreign salts, which may injure the effects that it ought to produce. Experience has proved, that without these mixtures a good preparation was obtained; hence the only thing to be determined is, the proportions which effect the exchange of base most completely.

Haussman employed an acetate of tin, formed by decomposing the acetate of lead by the muriate of tin; but this preparation has some disadvantages: 1. It retains a little muriate of lead; for this salt has a slight solubility; 2. A triple salt is formed, which contains a great proportion of lead, if the necessary proportion of acetate of lead be used.

CHAPTER VII.

Of the Fixed Alkalies.

Magnesia, lime, barytes, strontites, and glucina, might indeed be regarded as fixed alkalies, since the whole of them, and some more than potash or soda, possess the property of saturating the acids, and forming with them neutral combinations. They are distinguished, however, by the name of earths, or alkaline earths, in consideration of the solidity and pulverulency which give the idea of an earth ; and the name of fixed alkalies is reserved for potash and soda, which being of great use in dyeing, should be well studied.

As for ammonia, although it be the most powerful of the alkalies, since, in equal quantity, it exercises in a higher degree the alkaline properties on the acids, its volatility is an obstacle to its use in most part of the operations of dyeing.

Article I.

Of Potash.

Potash, named *vegetable alkali*, because it is derived from the combustion of vegetables, is an identical substance. But the state of saturation in which it exists, and the mixtures confounded with it, considerably diversify its effects and value.

When its whole alkaline power is to be exerted, it must be deprived of the carbonic acid, with which it is combined in greater or less proportion, and which gives it the property of effervescing with such acids as expel its carbonic acid. With this view it is dissolved and treated with quicklime, which, seizing its carbonic acid, precipitates in the form of an insoluble salt. What is called pure or caustic potash, is thus obtained. It still retains, however, a portion of carbonic acid, to free it from which it must be treated with alcohol. In this case two combinations are formed, the one an *alcohol* of potash, and the other, which remains dissolved in a portion of water, or which separates in crystals, is carbonate of potash. On expelling the alcohol from the former combination, we have pure potash. But this preparation is not wanted in dyeing, except for experiments of research.

The watery solution of ordinary potash contains also foreign salts, which it may be worth while to separate, as is done for the manufacture of fine glass. For this purpose, the potash is dissolved in as little water as possible, and the solution is allowed to settle. The salts less soluble than potash, separate in a great measure, and fall down.

Potash, not saturated with carbonic acid, attracts the humidity of the air, and thereby dissolves, forming a liquor called *oil of tartar, per deliquium.* It also attracts carbonic acid, and in a long period of time acquires the property of crystallizing. Bohn and Monnet had observed this crystallization before its cause was known.

It should be observed, that carbonate of potash has the property of crystallizing, before getting the quantity of carbonic acid which can combine with it. When this is the case, it attracts moisture from the air. In the solution, the portion which remains liquid, acts sufficiently on the water to permit the other portion to crystallize. When this water is removed, the crystals exert sufficient force on the water of the atmosphere, and attract enough to be reduced to a liquid. It would seem, that the carbonate of potash can assume variable quantities of carbonic acid, even when it has no longer the property of attracting humidity.

These different states of saturation of the carbonic acid demand attention, when potash is employed in dyes whose colours may be affected by it, or in which the texture of the stuffs can suffer alterations; for, in the caustic state, the alkali exerts a greater power of combination with other substances.

Different names have been given to potash, according to the substance from which it is extracted. It is called *salt of tartar*, when obtained from the acidulous tartrate of potash, or tartar. To make this preparation, the tartar is wrapped up in paper cones, and is thus exposed to combustion. After dissolving the residuum in water, the solution is concentrated by heat, the foreign salts are separated in proportion as they fall down, and by desiccation the potash is procured, which retains much carbonic acid, formed by the destruction of the tartaric acid, at a sufficiently moderate heat for a great deal of it to remain in combination. This potash is very rich in alkali; but it is very costly.

The *cendres gravelées*, which are the product of the combustion of wine lees and vine branches, are also rich in alkali, although the potash is here less pure than that obtained from tartar.

The potash, known by different names in commerce, comes chiefly from the North of Europe, and the United States of America. It is the product of combustion in vast forests, for the wood of which no better use can be found. But this operation not being every-where made with the same care, is the main cause of the great differences in the product. According to Linnæus, the birch or alder is burned with a slow fire; with the ashes and water a kind of paste is made; with this paste a range of billets of the pine or fir is covered; over this range another is laid transversely, covered in like manner with the same paste; and in this manner the layers of wood and paste are continued, till the pile acquires a considerable height. Fire is now put to it, and when the ashes begin to flow, the pile is overturned, and the ashes in semifusion are beat with flexible rods. They are incrusted by this operation on the logs, and become as hard as stone.

It is obvious, that by this process the potash must contain a great deal of foreign earth; but it appears that lime is sometimes mixed with it. Home found some of it, chiefly in a species of potash called *cassoude*, much used by the bleachers in Belgium, and the neighbouring departments.

So defective a process as the above is not followed every-where; but in some places the ashes are lixiviated, by covering them with water in casks. After some hours, the liquid is run off, new water is poured on, and the operation is repeated, till the water comes off nearly insipid. The last waters are employed for new leys, as in the *lixivia* of the plaster rubbish from which saltpetre is extracted. The waters are subsequently evaporated; the result is black and carbonaceous. It is called *salin*. This substance, calcined in a furnace, becomes white, and yields a good potash.

Ashes which have undergone no preparation are also made use of, and principally for leys. What has been said of potashes, may be applied to them.

The vegetables from which potash is extracted differ much from one another, both in the quantity of ashes which they yield on combustion, and in the proportion of potash found in their ashes. We shall give an outline of the observations which have been made on this subject, because they may guide us in the art of preparing potashes, and in their different applications to the arts.

It results, from the experiments of Pertuis in particular,* that the herbaceous plants furnish in equal weight, after their drying, much more ashes than ligneous (woody) plants, and that the first contain a larger proportion of alkali; that the trunks of trees yield less than the branches, and the branches less than the leaves; but on this subject, as well as on several others relating to vegetation, much more extensive and exact researches than the above are to be found in a work just published by Theodore de Saussure.†

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* Ann. de Chimie, tom. xix.

† Recherches Chim. sur la Vegetation. We find in this excellent work, observations which occasion some modifications in the explanations which we have given on the change produced by the air on the colouring particles, and the vegetable substances which suffer its action. The author has determined in a more positive manner the circumstances of this alteration.

Saussure, on exposing extracts and other vegetable substances to the action of the air in closed vessels, found that the volume of the air was not diminished, but that its oxygen was changed into carbonic acid, extracting its carbon, and combining with it. At the same time, a production of water takes place, by the more intimate combination of the hydrogen contained in this substance with the oxygen which was equally contained in it, and, of consequence, the substance contains a larger proportion of charcoal. The effect is therefore comparable, in this respect, to that of a slight combustion.

His observations, however, even prove that the fact is not general; the oils absorbed some oxygen. It would appear, that the action of oxygen does not produce uniform effects

His experiments have placed beyond doubt, that potash, and the other salts which are found in the ashes of vegetables, are not a product of vegetation, but that they proceed from the soil from which they are absorbed, and even from the atmosphere. Consequently, the same vegetables which grow in different soils yield in their combustion a different proportion of ashes, which have different proportions of saline or earthy substances, either soluble or insoluble. The parts of vegetables leave more ashes, as they are subject to a greater transpiration; because these ashes proceed from the substances which were held in solution in the vegetable juice. Thence the leaves afford more than the bark; this more than the alburnum; and the alburnum more than the timber.

For the same reason, herbaceous plants yield much more of it than the woody plants.

The proportions of the alkalies, or rather of the soluble part, vary in these ashes. The seeds contain most; the leaves come next; but when they are young they contain more. The bark has the smallest quantity of it. This quantity is seen to diminish, according as the rain water has dissolved and carried it away.

The phosphates, which the ashes of vegetables contain, form an important consideration. Saus-

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even on the substances which are not oily. But it will be necessary to distinguish, by new observations, the cases different in the mode, but uniform in the result, which is a predominance of carbon.

sure has found, that all vegetables contain the following phosphates: Phosphate of potash; phosphate of potash and lime, soluble like the preceding; and phosphate of lime, insoluble. As they usually contain carbonate of lime, changes of combination take place during incineration. The phosphate of potash is decomposed by the carbonate of lime; and there is found in the ashes only phosphate of lime, or a smaller quantity of the first two combinations, than what existed in the vegetable. If different vegetable parts be incinerated, a result will be obtained, which is not the mean that would have been got by making the incineration separately. Thus the bean contains phosphate of potash, without carbonate of lime, and no phosphate of lime is found in its ashes. But if it be burned along with the stem, which contains carbonate of lime, there is obtained, instead of phosphate of potash, a much larger portion of phosphate of lime than the incineration of the stem alone would have given.

From these observations, some results may be drawn useful to our subject, which we abridge with regret.

1. For the fabrication of potash, it is more advantageous to collect herbaceous plants, leaves, and small sprigs of trees, than to burn the trunks themselves.

2. When the ashes are boiled into a condensed ley, in order to extract their potash, the alkali must convert a part of the insoluble phosphate

of lime into phosphate of lime and potash; and the portion of the alkali which enters into this combination becomes inactive, by reason of the saturation which it experiences.

We shall not dwell on the other substances which enter into the composition of the ashes, and of ordinary potash; because the only matter which is useful and of importance to estimate is the alkaline. We have described, in treating of bleaching, the most exact means of arriving easily at this valuation. If there be an intention, however, of employing potash as an alterative or auxiliary, it may be proper to ascertain if it contains much carbonic acid, which its effervescence with acids points out. But a solution of it must be previously made to separate the effect of the potash from that of the carbonate of lime. The quantity of carbonic acid which escapes may be ascertained by verifying the loss of weight experienced by the mixture of potash and acid, whose separate weights had been determined beforehand.

Article II.

Of Soda.

Chemists have given the name *mineral* to this alkali, because it is often found at the surface of the earth, or in subterraneous cavities. Thus a great quantity of it may be gathered in Egypt in the neighbourhood of lakes, called *natron;* a name also given to the soda obtained from them. In several parts of Barbary, Syria, Persia, in the West Indies, China, and even in our climates, it is likewise found.

The conditions which determine this production, are, judging from the observations made near the natron lakes,* a mixture of muriate of soda and carbonate of lime, in a moist ground, not too clayey, and a pretty hot temperature. In this case, a slight solution of carbonate of lime is effected, and the causes which favour the efflorescence peculiar to carbonate of soda, determine its separation, while a corresponding portion of muriate of lime infiltrates into the earth.

The soda thus collected in Egypt is not pure, but contains variable proportions of carbonate of soda, muriate of soda, sulphate of soda, and of earth, mingled, even when different specimens are taken on the same grounds.

The greatest part of the soda, however, which is made use of, is the product of the combustion of plants which grow on the sea-shores, and particularly of the *salsola soda,* Linn.

The most esteemed comes to us from Alicant. Some is also extracted from the same plant on our maritime coasts, as well as on others. To these sodas, according to the countries and plants from which they are got, different names are given; such as, Rochette, Varech, Salicor. Julia

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* Mémoire sur l'Egypte.

has lately given an interesting description of the culture of the salsola, established in the environs of Narbonne, from which a soda comes, known under the name of Salicor.*

These sodas differ much from one another in the proportion of carbonate of soda. There are ashes of Varech which contain hardly any of it; but it is useless to dwell on these differences, because confidence can only be put in the chemical proof, which should be the same as for potash. A good soda, or a carbonate of soda, should be assumed for a term of comparison; because a larger proportion of acid is required to saturate a quantity of soda than an equal weight of potash.

Soda is in the state of a carbonate, or most part of it at least is in that state, when plants are incinerated. It crystallizes, retaining much water of crystallization; but it parts with this easily to the air, and falls thereby into efflorescence, with the loss of nearly one-half its weight.

This difference distinguishes it from potash, which naturally retains, after incineration, only a part of the carbonic acid necessary to its crystallization; and which, till it be saturated with it to this point, attracts, on the contrary, the humidity of the air; a difference apparently depending on the stronger affinity which soda exercises on the acids, and on the greater condensation which it produces, particularly on those that are naturally elastic.

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* Ann. de Chimie, tom. xlix.

Although the native carbonate of soda crystallizes and dries in the air, it retains, however, weak alkaline properties, and greens the colours that characterize them. But it may take a larger proportion of carbonic acid. The celebrated Klaproth has observed in a species of carbonate of soda, or natron, a proportion of carbonic acid, nearly double of that obtained from the ordinary carbonate. Hence its alkali is in a different state of saturation. Probably it would not afford marks of alkalinity. It might be found perhaps acidulous. It does not effloresce.

As soda contains, not only a good deal of foreign salts, but a greater or less proportion of sulphuret, it is right to employ it for certain operations of dyeing in the state of a pure carbonate. It is then called *salt of soda* (crystals of soda).

In order to free soda from the foreign substances, it is to be dissolved in water, and the different salts are to be separated as they precipitate or crystallize. The crystals of carbonate of soda form last of all.

When this salt is used, it is essential to pay attention to the state in which it exists; for when it is in crystals it contains one-half (fully 3-5ths) its weight of water of crystallization. Hence, when it has effloresced, one part produces as much effect as two parts of crystals.

Lime acts on this salt in the same manner as on carbonate of potash; that is to say, it robs it of the greater portion of its carbonic acid, rendering it caustic. In this state it is pure soda, (for the small quantity of carbonic acid which it retains may be neglected), the soda of chemists, the ley of the soap-boiler.

Sometimes the name of strong water, or strong liquor of the soap-boilers, is given to a solution of caustic soda. Such a denomination may easily lead to mistakes, making this alkaline solution be confounded with nitric acid, called also *eau forte*, (strong water, or aquafortis). Hellot tells us that he was deceived in this way, in the preparation of a vat of indigo, which had been suggested to him.

Since soda exerts on acids a stronger action than potash, it may probably produce also a greater effect on colouring substances when it is pure; but its alkaline action is much more moderate when it is in the state of carbonate, for it is then in a high degree of saturation, and possesses uniform properties. From this circumstance it should therefore be preferred to potash, which has less carbonic acid, containing variable quantities of it, in the state in which it is extracted.

CHAPTER VIII.

Of Soap.

Soap is the combination of an alkali with an oil. Alkali deprived of carbonic acid must be employed for its formation; for this acid may eliminate its oil in combining with the alkali.

We must begin, therefore, with stripping it of its combined carbonic acid. In the work-shops the name *soap-ley* is then given to it.

To make this ley, the soda which is used for hard soap is treated with a suitable proportion of lime, usually two of lime for one of soda. A succession of waters is passed through the same mixture. The last, which are least charged, are employed the first in the boiling with oil; because the coagulation which would be formed at first with too strong a ley, would obstruct the uniformity of the combination.

We have remarked, that the caustic alkali, prepared with quicklime, retained a portion of its carbonic acid; which, on treating the caustic ley with oil, converts a part of the alkali into a carbonate that cannot enter into the compound. Whenever the formation of the soap is advanced, the portion of ley converted into carbonate, which may serve anew to make a caustic ley with quicklime, is run off by a stopcock placed in the lower part of the boiler. Strong ley is then added. When it is ascertained from samples that the consistence of the soap is sufficient, it is drawn out and run into a species of wooden moulds, where it cools, and takes the form adapted to commerce. But before this last operation, a certain quantity of muriate of soda is added, which facilitates the separation of the soap from the aqueous liquid, (spent ley).

This preparation may be made in the cold, but it is longer and less easily finished.

Recent soap contains a great deal of water, which it loses by desiccation. Fraudulent dealers endeavour to sell it with all this weight; and to preserve it in this state, they keep it in a moist place, even in water saturated with sea-salt. This brine does not dissolve it, but merely confines in it the whole water that it can hold. For separating, by this property, the soap from its solution in the boiler, the muriate of soda was added towards the end, as we have stated. The redundancy of water is discovered by keeping the soap in a dry and warm place, where it soon loses what is superfluous. Starch, or other foreign substances, are sometimes mixed with soap, in order to augment its weight.

Marbled veins are given to soap by adding, before it has assumed consistency, a little sulphate or red oxide of iron, which probably forms some metallic soap, that is unequally mixed with the paste. Soap becomes harder by this means, and retains less water.

The general properties of compounds are recognized in soap. Thus soda, which produces, as we have seen, a greater effect with the acids, comports itself in the same way with the oils, thereby forming soaps, harder and less soluble than those which have potash for their base. In consequence of this greater insolubility, if muriate of soda be added to a solution of soap made with potash, the soda takes the place of the potash, and it is a soap with base of soda which coagulates and separates, as Darcet, Pelletier, and

Lelievre observed, to whom we owe a very good description of the preparation of soap.*

The oils contribute, on the other hand, to the qualities of the combination which they form with the alkalies: thus the fatty substances naturally solid, such as tallow, lard, and butter, form solid and firm compounds; olive oil, which has a tendency to become solid whenever its temperature is lowered, affords a hard soap, which makes it be preferred, for this species of soap, (to which, in other respects, it communicates no disagreeable smell or colour), to the other oils, which being less consistent, yield softer soaps, commonly coloured.

If oils be combined with bases naturally disposed to take the solid state, such as lime, magnesia, barytes, metallic oxides, insoluble soaps are formed; but this insolubility is an obstacle that prevents the combination from being directly formed with accuracy. The solution of an alkaline soap must be taken, and lime, barytes, or strontites water poured into it. These alkaline earths take a portion of the oil from the soluble alkalies to form an insoluble soap, which separates. Instead of the aqueous solution of these bases, their solution in an acid may be taken. In this case an exchange of base occurs, and the earthy combination is more completely formed. The latter method must be employed for the

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* Mémoires de Chimie, tom. xix. (Annales?)

bases insoluble in water, such as magnesia, and the metallic oxides.

The uses for which soap is employed lead sometimes to the preference of a hard, and sometimes of a soft soap. The first is prepared with soda and olive oil. It ought to be white. This soap is used in the ungumming (scouring) of silk.

To make soft soap, oil of colza, turnip seed, or fish oil, is employed. The cheapest at the place of the manufacture is generally chosen. But as softness is the quality now desired, potash is used instead of soda. Whiteness is of no consequence to this soap; and the oils made use of commonly impart a greenish or even blackish colour, whence the article is called green or black soap.

This soap is chiefly used in the bleaching of cloths and raw yarns; and in the operation of fulling woollens.

For the latter purpose, a less costly combination may be employed, possessing the detersive properties of soap; this is the solution of an animal substance in potash. Chaptal observed,* that potash which has been saturated with fragments of wool formed this species of soap, which might be advantageously substituted for ordinary soap. The odour which it communicates to cloth is dissipated by washing, and exposure to the air.

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* Mémoires de l'Instit. tom. i.

CHAPTER IX.

Of Sulphur.

Sulphur exposed to a certain heat volatilizes, and then resumes the solid state by the contact of cold bodies. Thus it is reduced to subtile molecules, called flowers of sulphur. This preparation is made in the small apparatus of the laboratory; or on the great scale, in a kind of chimnies or chambers, where it attaches itself to the cool walls.

When sulphur is exposed to a more elevated temperature, it combines with oxygen, passing thereby to the state of an acid; but this acid differs according to the elevation of the temperature, or the vivacity of the combustion. When the temperature is not sufficiently high, sulphurous acid is obtained.

Sulphurous acid differs from sulphuric, 1. From the oxygen in it being less condensed, so that the combination retains a pretty great elasticity, and dissolves in only a small quantity in water: 2. From the proportion of its oxygen being smaller than in sulphuric acid, but, at the same time, this element experiences a much weaker action on the part of the sulphur; a circumstance which has great influence on its characteristic properties.

The oxygen is retained, therefore, much more feebly in sulphurous than in sulphuric acid. Hence several substances, which do not take oxygen from sulphuric acid, decompose the sulphurous. It inclines, in this respect, to the properties of oxygenated muriatic acid, although it does not give up its oxygen so easily, but, on the contrary, carries off that of the oxygenated muriatic acid, in order to pass to the state of sulphuric acid. In like manner, it inclines to the properties of nitric acid.

Sulphurous acid, or the combination of the sulphurous gas with water, is not employed in the processes of dyeing; but the vapour formed directly by the combustion of sulphur is used. In this state of gas, it exercises a more lively action, for it whitens the flowers, which, in its liquid state, it reddens like the other acids. It would be wrong, therefore, to substitute liquid sulphurous acid for the fumes of burning sulphur, as has been proposed. There are circumstances, however, where a different or more moderate effect might be wished for, in which it would be advantageous to employ it in the liquid state. We have seen one example of this, in the process of Giobert for bleaching raw silk.

For obtaining it in this state, there is a more convenient and easier means than by the combustion of sulphur; that is, merely to mix with sulphuric acid a vegetable substance containing hydrogen, as sugar, and to distil, receiving the vapour that is disengaged into the bottom of a receiver, by means of a tube. Heat, which tends to produce elastic combinations, determines a formation of water, at the expense of the hydrogen of the sugar, and a production of sulphurous acid, which issues to combine with the cold water. But there is formed at the same time a little carbonic acid, of no importance to the operations for which the liquid acid is intended. Besides, when the sulphurous acid acquires a certain condensation, it expels the carbonic acid from the water.

Sulphuring, or exposure to the fumes of burning sulphur, is employed to give the utmost whiteness to silks and woollens intended for white stuffs.

For the sulphuring process an insulated chamber, having no chimney, is made choice of, through which, on occasion, a current of air may be sent.

For 50 kilogrammes of silks stretched on perches, placed at a height of rather more than two metres, nearly one kilogramme of sulphur, reduced to a coarse powder, is put into an earthen or iron pot, at whose bottom there is a little ashes. This powder is set fire to in several places. The chamber is well closed, to prevent the dissipation of the sulphurous fumes. Next day, the windows are thrown open to let them escape, and to dry the silk. But in winter, after the smell of the sulphur has gone away, the windows are re-shut, and burning charcoal is introduced, in chafingdishes, to make the silk dry.

This operation gives the silk not merely a great whiteness, but, at the same time, creakiness or rustling in handling, *(du cri ou du maniement)*, that is to say, a species of tremulous elasticity, which is perceived on pressing it between the fingers.

As the *maniement* gives a certain stiffness to silks, those must not be sulphured which are to be *watered*, *(destinées à faire de la moire)*, because they would give too much resistance to the impressions of the calender, under which the silks are passed to give them the undulations.

In like manner, sulphuring cannot be applied to silks intended for felt, *(bonneterie)*, because they would corrode the iron and steel of the tools with which they are to be worked, and occasion rust.

Sulphured silk takes on most colours badly; and, therefore, previously to dyeing, it must be freed from sulphur, *(desoufrée)*, by repeated soaking and shaking over in hot water.

When silk is sulphured, if it be thought not to have sufficient azure for the wished-for shade, it must be azured a second time in clear water, without addition of soap, and then again sulphured.

These properties of the sulphured silk are owing to the sulphurous acid which has combined with it, whose presence may be made perceptible by means of sulphuric acid, which immediately disengages sulphurous vapours from it.

The sulphuring of woollen cloth is executed in nearly the same manner as that of silk; but it is to be remarked, that if this operation be not performed with precaution, and that if the combustion of the sulphur takes place with too much rapidity, sulphuric acid is formed, which falling down in drops, corrodes the cloth,—an inconvenience not easily avoided.

CHAPTER X.

Of Waters.

THE qualities of waters is an essential object in dyeing; but it is perhaps less important to make known the injurious effects which they may produce, than to destroy the prejudices to which they have often given rise. Thus peculiar properties have been ascribed to the water of the Bievre, which supplies the manufactory of the Gobelins; but Guillaumot remarks, that when this little river is too low, the water is drawn from the Seine, without seeming to render the dyes less beautiful.

It is superfluous to say, that the waters used in dyeing must not be muddy, or contain putrid substances; that waters so much charged with foreign matters, as to be ranked among mineral waters, easily distinguishable by the taste, must not be employed. With these exceptions, waters act on the colouring particles principally by the earthy salts they contain, which render the colours in general deeper and more dull.

The carbonates of lime and magnesia have, moreover, the inconvenience of being thrown down during the ebullition, which expels the excess of carbonic acid that held them in solution. Thus these earths applied to the stuffs darken them, and hinder the colouring particles from penetrating.

It is of importance, therefore, to ascertain these species of waters, called hard or crude, in order to avoid them in most dyes. Chemists possess methods, not only of determining the different principles contained in waters, but even of assigning with precision the quantity of each; but the precautions requisite for this analysis, in general demand a profound knowledge and experimental dexterity, which persons engaged in dyeing cannot be presumed to possess. Happily a trivial and easy test is sufficient to shew whether a water contains an injurious quantity of these salts. This is, the solution of soap.

All the salts having an earthy base decompose soap by an exchange of bases. Their earth unites to the oil, while their acid combines with the alkali of the soap; and from the combination of the oil and the earth, a soap with earthy base results, which being insoluble in water, forms the clots, (or mottling), which are in that case observable.

Whenever, therefore, a water is limpid, when its flow is constant, when it has no sensible taste, and dissolves soap well, it may be regarded as very proper for dyeing; and all such as possess these qualities are equally suitable.

But since a choice of waters is not always equally at command, methods have been sought for correcting such as were bad, at least to a certain degree, particularly for the purpose of dyeing delicate colours. With this view, water in which bran has been fermented, called sour water, is principally used.

It appears that sour water acts by decomposing the carbonates of lime and magnesia, its acid expelling the carbonic acid. The earthy sediment which forms during ebullition is thus obviated.

Mucilaginous plants are also boiled along with the water to be corrected, when a froth forms, that is skimmed off. The mucilage coagulates, carrying with it the earths which separate on the volatilization of the carbonic acid, as well as such as are merely mixed with the water, and which render it turbid.

The salts with an earthy base, which are in general injurious to dyeing, may in certain cases be useful, serving to modify the colours when our object is to obtain deep shades.

As the water of a river may contain more or fewer salts with an earthy base, according as its bed is higher or lower, it happens sometimes that on following exactly the same process the same

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shade is obtained only at certain periods; or some modifications are required to be made in the process to obtain the same result, according to the state of the river.

The waters which decompose soap, and form a soap of lime, are disadvantageous to bleaching, not merely by the waste of the soap uselessly decomposed, but principally because the calcareous soap, which is insoluble in water, fixes on the stuff, gives it a greasy feel, renders it at the same time yellow, and shakes off in small scales. This inconvenience is obviated by decomposing the earthy salts with a little carbonate of soda or potash.

END OF THE FIRST VOLUME.

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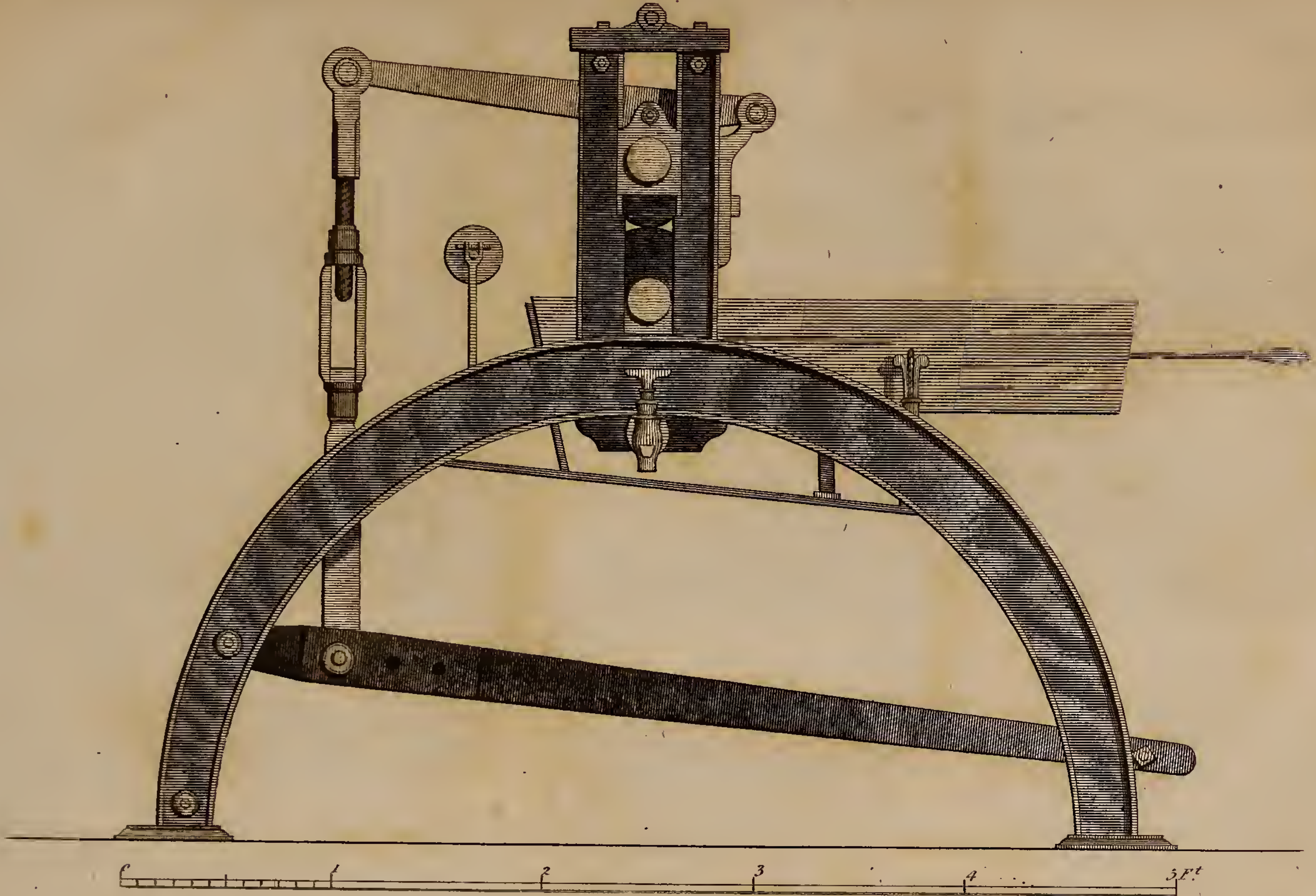
PLATE. I.



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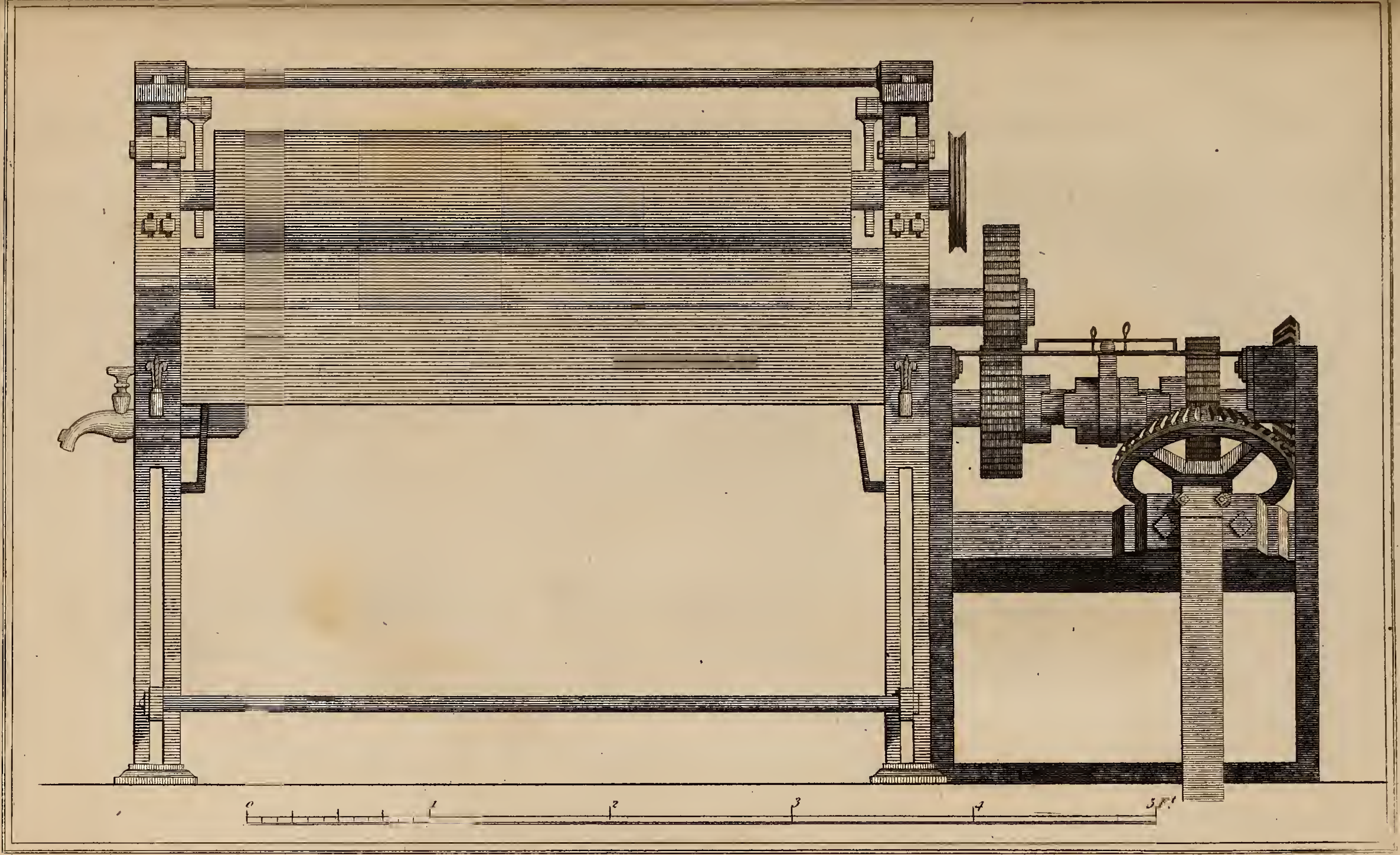

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PLATE. III.

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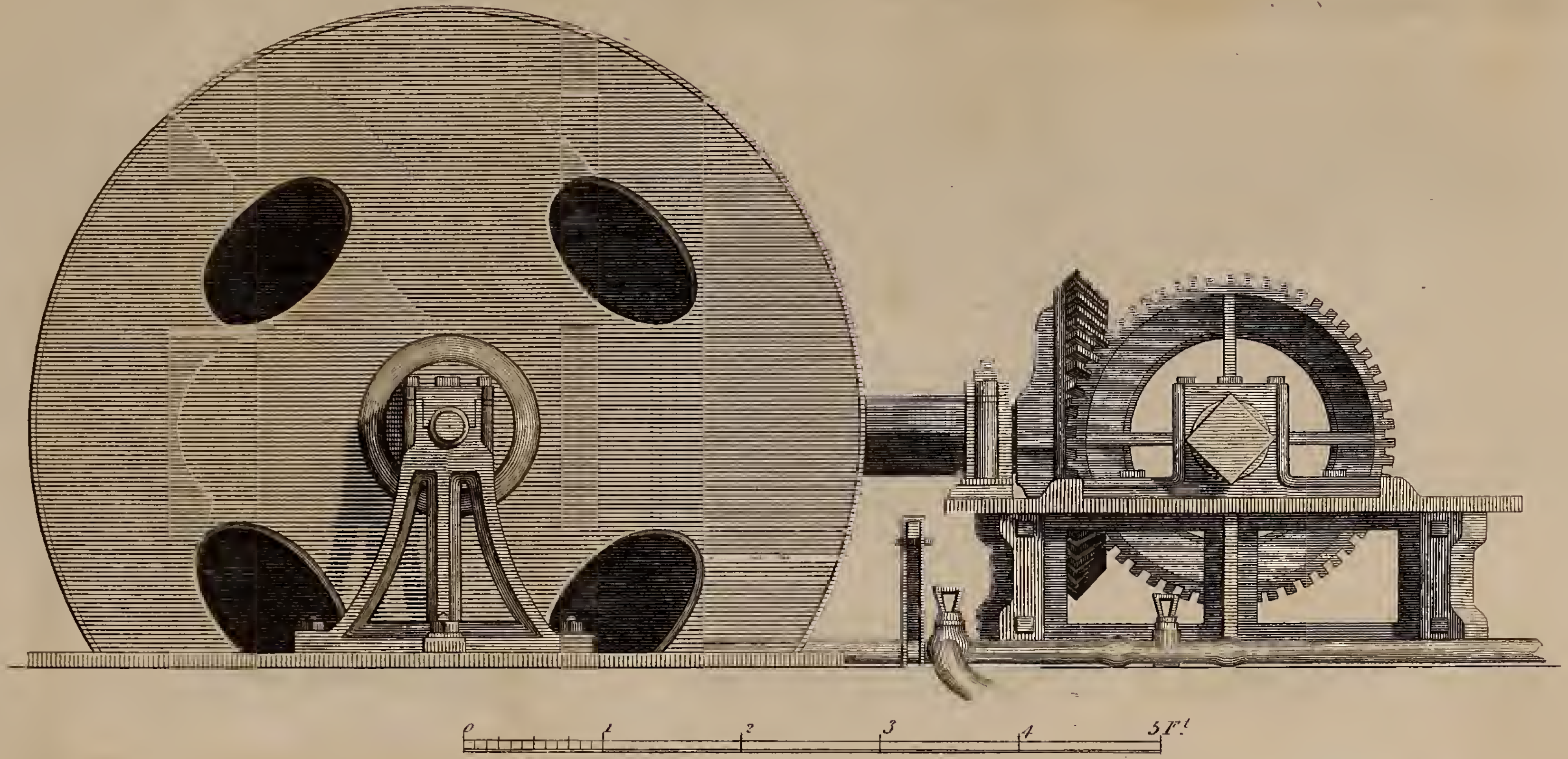

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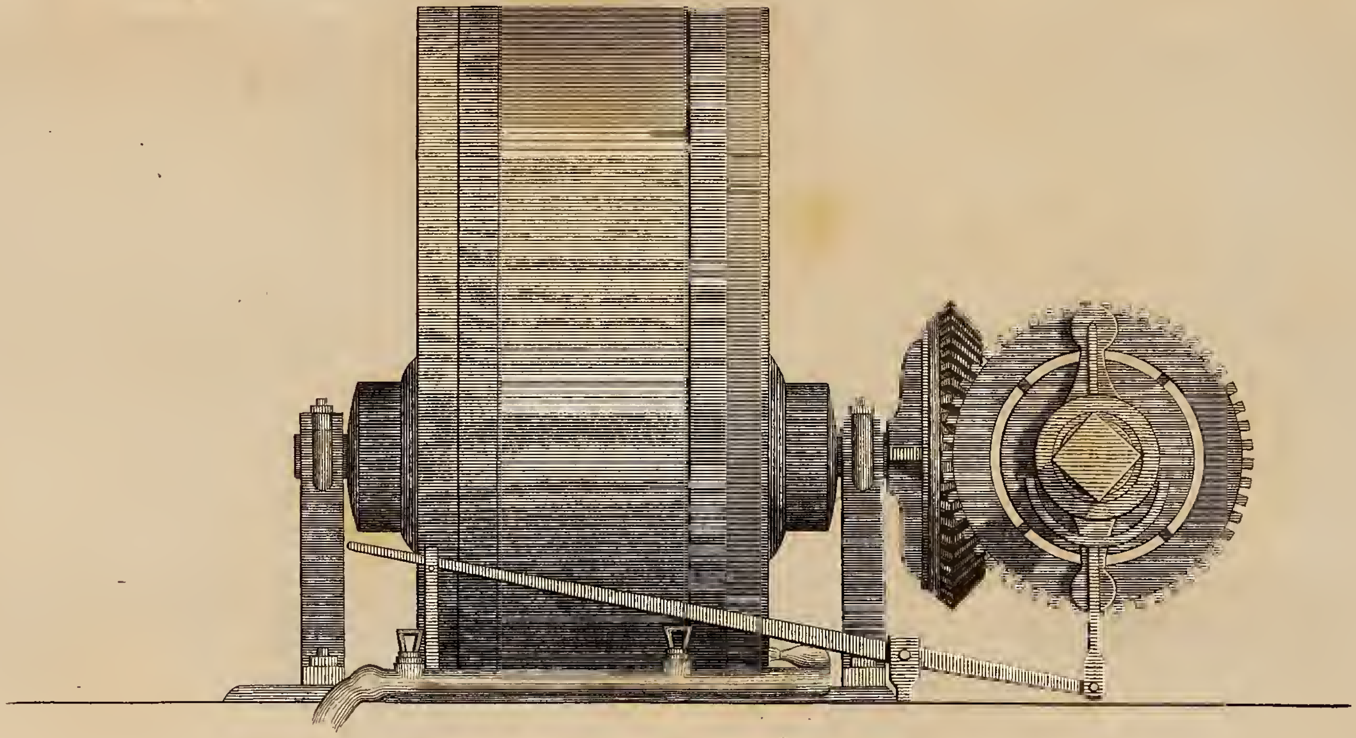

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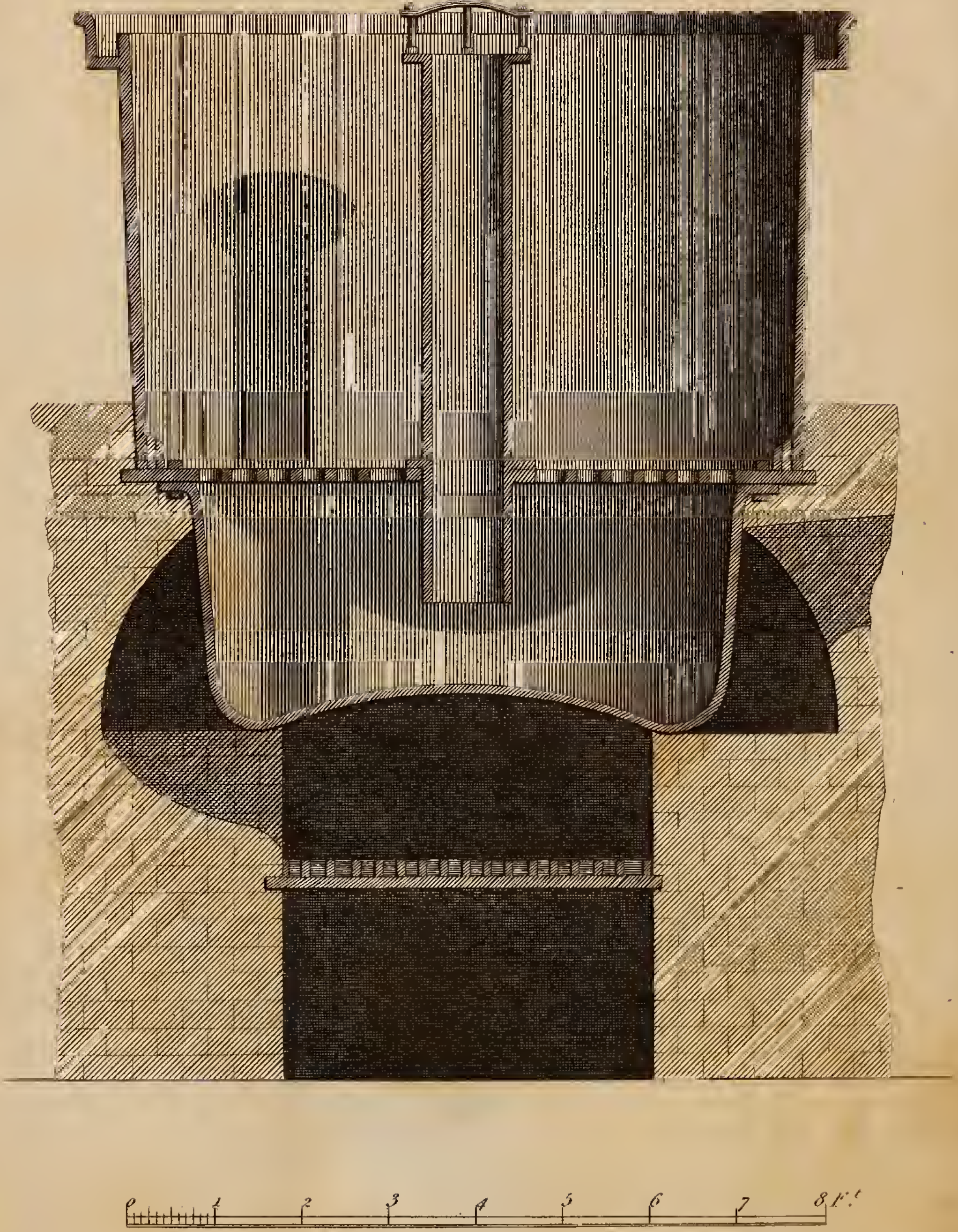

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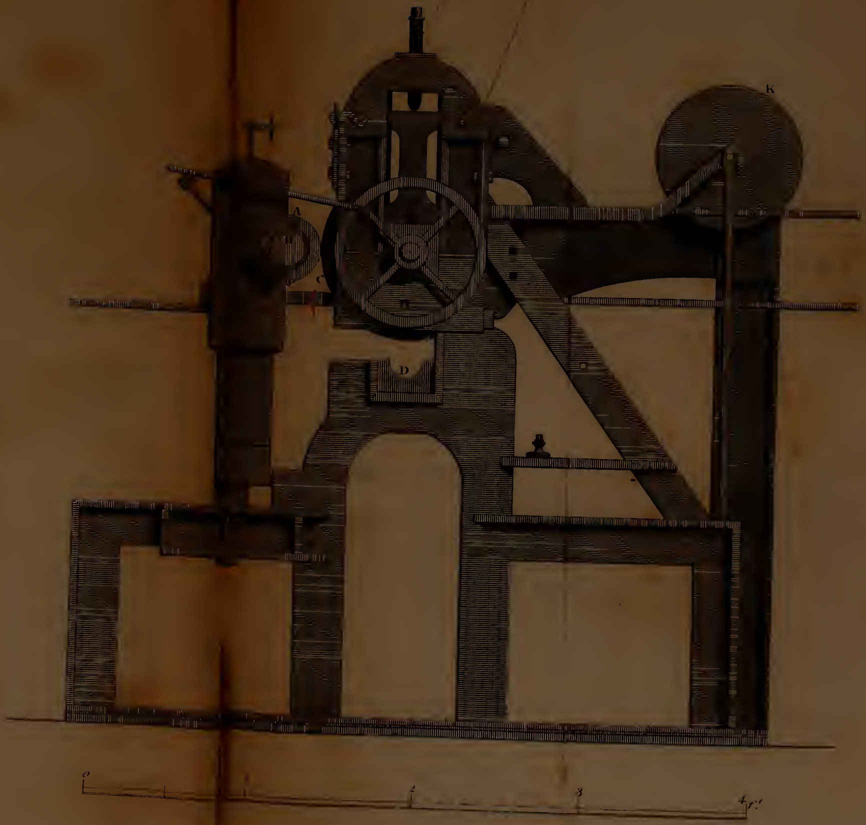
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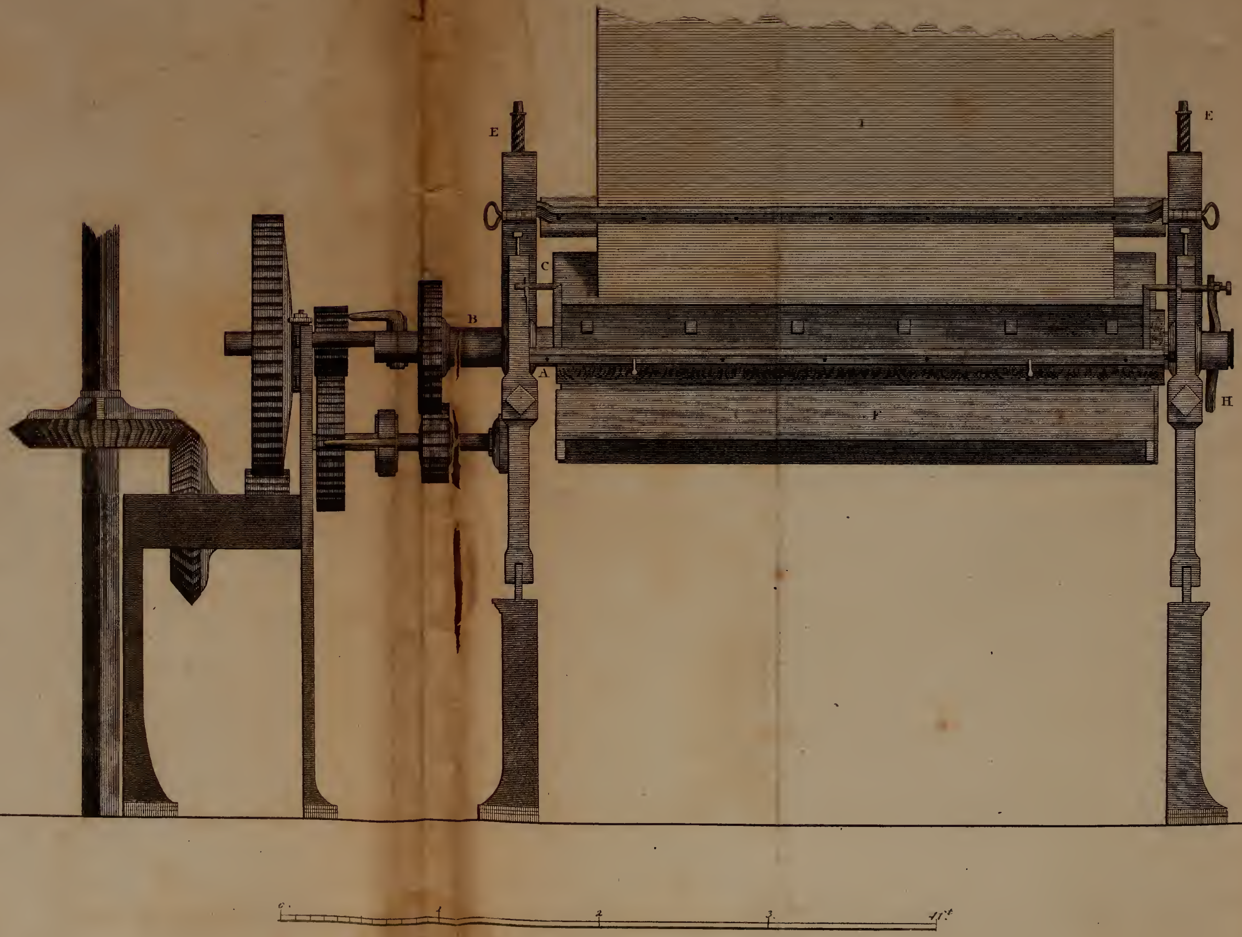

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