MORDANTS. I

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Introduction

In 1875 Napier¹ wrote: "If the various colouring matters used in dyeing had an affinity for the fibre the process would be very simple: it would only be necessary to make a solution of the dye-drug, and immerse the goods in it to ensure their being dyed. But so far from this being the case, if we except indigo and safflower, there is scarcely a dye-stuff that imparts its own colour to goods; nay, the greater part of the dye-drugs used have so weak an affinity, especially for cotton goods, that they impart no colour sufficiently permanent to deserve the name of a dye. The cause of this is obvious. If, for example, we take a decoction of logwood, the colouring matter is held in solution by the water; by putting a quantity of cotton into this solution the fibres become filled with the coloured solution, but if the cotton has no power to render that colouring matter insoluble, and retain it within its fibres it is plain that, by taking out the cotton and putting it into water, the colouring matter within and upon it will be diffused in the water—in other words, the dye, having no attraction for the fibre, is washed out. This want of affinity makes dyeing sufficiently intricate, and renders it more dependent upon science; indeed, it is only by the nicest arrangement of a few chemical laws that the dyer is enabled to turn to advantage the various colouring matters of which he is in possession. When the dyer finds that there is no affinity between the goods and any colouring substance which is put into his possession, he endeavours to find a substance which has a mutual attraction for the cloth and colouring matter, so that by combining this substance with the cloth, and then passing the cloth through the dyeing solution, the colouring matter combines with the

¹ "A Manual of Dyeing," 186 (1875).

substance which is upon the goods, and constitutes a dye. This third substance used, which acts as a mediator, combining two inimical bodies, is termed a mordant, from the French *mordre*, to bite—from an idea which the old dyers had that these substances bit or opened a passage into the fibres of the cloth, giving access to the colour. And although the theory of their action is now changed, the term is still continued and perhaps further investigation will prove the term not altogether inapplicable.”

In the first English book on dyeing, Bancroft¹ distinguished between substantive and adjective colours.¹ “To me, however, colouring matters seem to fall naturally under two general classes; the first including those matters which, when put into a state of solution, may be fixed with all the permanency of which they are susceptible, and made fully to exhibit their colours in or upon the dyed substance, without the interposition of any earthy or metallic basis; and the second, comprehending all those matters which are incapable of being so fixed, and made to display their proper colours, without the mediation of some such basis. The colours of the first class I shall denominate ‘substantive;’ using the term in the same sense in which it was employed by the great Lord Verulam, as denoting a thing solid by, or depending only upon itself; and colours of the second class I shall call ‘adjective,’ as implying that their lustre and permanency are acquired by their being adjected upon a suitable basis.”

Bancroft’s views on mordants² are practically those held many years later by Napier. “Adjective colouring matters are generally soluble, in a great degree at least, by water; though some of them derive their solubility from an intermixture of what has been called ‘extractive’ matter; which being separated in the dyeing process, after the adjective colour has been applied to the dyed substance, their union becomes thereby more intimate and permanent. But in

¹ *Philosophy of Permanent Colours*, 1, 118 (1813).

² Bancroft: *Philosophy of Permanent Colours*, 1, 341 (1813).

other respects, adjective colours owe their durability, as well as their lustre, to the interposition some earthy or metallic basis; which, having a considerable attraction, both for the colouring matter and the stuff to be dyed, serves as a bond of union between them, and obviates that disposition to suffer decomposition and decay, which naturally belongs to such colouring matters when uncombined. These earthy and metallic bases, having been commonly employed in a state of solution or combination with acids, were from that circumstance denominated mordants (biters or corrodors) by the French who, indeed, began to employ the term long before anything like a true theory of dying had been conceived; whilst even alum was supposed to act by its sulfuric acid, and not by the pure clay upon which its usefulness depends, and whilst in truth all the other matters called mordants were supposed to be useful only by their solvent or corroding powers; and the term, having been thus employed, has been since adopted in other countries. The ingenious Mr. Henry, of Manchester, has, however, lately objected to it, with great reason, and proposed in its stead to employ the term 'basis,' which seems defective only, inasmuch as it does not express the particular affinity, or power of attraction, manifestly subsisting between these earthy and metallic substances, and the several adjective colouring matters, as well as between the former and the fibres of wool, silk, cotton, etc. I confess, however, that no other more suitable term has occurred to me; and being unwilling to propose new terms, without some cogent reason, I shall some times employ that of mordant as well as that of basis; though not indiscriminately in all cases; since I shall generally use the former to signify earthy and metallic substances when actually dissolved by some acid, alkaline, or other solvent, and when of course they will commonly prove more or less corroding or biting, according to the original meaning of the term. But the denomination of basis will be most frequently used to designate the same earthy and metallic substances, distinctly and separately from any acid or other solvent, when actually fixed in the

pores or fibres of wool, silk, etc., or when it is not intended to notice any property in them, which may more immediately result from their combinations with any particular menstruum. M. Berthollet, indeed, gives the term mordant a much more extensive signification, as meaning all the different chemical agents capable of serving as *intermedia* between the several colouring particles and the stuffs so dyed with them, either for the purpose of assisting their union, or of modifying it. This last effect (of modification) may, however, be produced by a variety of matters besides those which are of the earthy or metallic kinds, and indeed by everything capable, not of fixing, but of merely varying the shades of adjective colouring matters. These, therefore, I think it more proper to designate, not as mordants or bases, but as 'alterants' whose use and application may in this respect be extended to substantive as well as to adjective colours."

A mordant is thus a substance which is adsorbed strongly by the fibre and which adsorbs the dye strongly. If one is a purist, it is necessary to say that adjective colours dye the mordant and not the fiber; but nobody does this because the difference can only be detected by careful microscopic observation.¹

The word mordant has prevailed over Bancroft's word, basis, so far as the dyeing industry is concerned; but the latter term has survived in the paint trade, where we speak of the carriers for lakes as bases,² this having nothing to do with the chemist's use of the word to denote an oxide or hydroxide. In fact a particular precipitated barium sulphate³ has been given the trade name of Lake Base because it was "of great value as a base upon which to precipitate lakes."

At the present time we distinguish acid and basic mordants the tannins and the so-called oils being the acid mordants⁴ while the hydrous oxides of the heavy metals are classed as the

¹ Minajeff: *Zeit. Farben-Ind.*, 6, 233 (1907).

² Thorpe: *Dictionary of Applied Chemistry*, 3, 236 (1912).

³ Toch: "Chemistry and Technology of Paints," 117 (1916).

⁴ Knecht, Rawson and Lowenthal: "A Manual of Dyeing," 5 (1910).

basic mordants. This distinction is a comparatively recent one, for the basic mordants used to be considered as practically the only ones.¹

"All the mordants, with one or two exceptions, are found among the metallic oxides. It may be supposed from this that, as metals are the most numerous class of elements, mordants are also very numerous; it is not so, however. In order that the substance may act as a mordant, it must possess certain properties: it must have an attraction for the colouring matter, so as to form with it an insoluble coloured compound; and it must be held easily in solution in order to enter within the fibre. It may also have an affinity for the fibre, a tendency to unite with it, but this property is not essentially necessary; only the two first properties are so, and they limit the mordants almost wholly to what are termed the insoluble bases—that is, substances which are not by themselves soluble in water.

"The bases or oxides which are in general use as mordants, and which appear to succeed best, are alumina and the oxides of tin and iron; the two first are colourless, and the peroxide of the latter is brown, and imparts to white goods a buff or nan-keen colour; which in many cases affects to a considerable extent the colour of the cloth, a circumstance which must also be attended to by the dyer. Indeed, the principal part of all dyeing operations is the proper choice and application of mordants; there being a chemical union between them and the colouring matter, a new substance is formed, not only differing in properties, but differing in colour, from any of the originals, consequently a very little alteration in the strength or quality of a mordant gives a decided alteration in the shade of colour. However, this gives the dyer a much wider field for variety of shades, and at the same time a less number of colouring substances are required; as, for example, logwood alone gives no colour to cotton worthy the name of a dye; yet by the judicious application of a few different kinds of

¹ Napier: "A Manual of Dyeing," 186, 192 (1875).

mordants, all the shades from a French white to a violet, from a lavender to a purple, from a blue to a lilac, and from a slate to a black, are obtained from this substance."

"The property which the fibre possesses of fixing portions of the dye-stuff within its pores will have to be often referred to, as it bears a very important relation to mordants. What are termed astringent substances have a strong action in this way in combining with the fibres of cotton goods. A piece of cotton put into a hot solution of sumach, and remaining in it until cool, there is a quantity of the astringent principle, probably gallic or tannic acid, fixed upon the fibre which no washing will remove. We have seen goods thus treated passed afterwards through all the regular operations of bleaching, and still retaining so much of these substances as was sufficient to impart a black tint on passing them through protosulphate of iron. Hence the astringent matters in many vegetable dyes act a very important part in the dyeing operations. Whether such substances as galls and sumach, which are used only for their astringent principle, may be termed mordants, is a question we need not discuss; but they are essentially necessary for fixing within the fibre such quantities of the metallic base or mordant as are required to give depth and permanency to the colour; and as these astringent matters produce tints with the bases, they give a wider scope for variety of colour. Thus, if we pass a piece of cotton through a solution of protochloride of tin, and then wash it in water, we will have a great quantity of oxide of tin fixed within the fibre by the operation of washing; and by passing this cloth through a decoction of Brazil-wood, and then 'raising' with a little spirits, there is a fine though not permanent, rose-red produced. If we pass the cotton through bichloride of tin, and then wash, there is very little of the oxide of tin fixed; for the bichloride is not decomposed, as the protochloride is, by water. If, then, it is passed through the Brazil-wood in the same manner as the other, a colour of less depth is produced; but if the cloth be previously steeped in sumach, and be then passed through the tin solution, even the bichloride, the astrin-

gent principle of the sumach combines with the tin, and forms an insoluble compound; and there is thus fixed a great quantity of the metallic base within the fibre, which gives the colour with the Brazil-wood, so that, when immersed into the wood decoction, there is obtained a colour of great depth and permanency. But the compound formed between the tin and sumach gives a yellow, and thus peculiar tints of the colour are obtained; instead of having a rose colour, as was obtained without the sumach, a deep rich red, between rose and scarlet, is produced. Thus sumach, galls, etc., are extensively used, in connection with metallic bases, to fix, modify, and impart depth to colours for which these bases are applied. The nature of these astringent substances will be given under the distinctive names of the matters which contain them."

While the oxides of aluminum, tin, and iron were practically the only basic mordants in use in Napier's time, chromic oxide is probably today the most important of all the mordants, unquestionably so for wool. Nearly all possible oxides have been studied at one time or another. Liebermann¹ reports on experiments with the oxides of aluminum, antimony, beryllium, bismuth, cadmium, cerium, chromium, cobalt, copper, iron, lead, manganese, nickel, thorium, tin, uranium, yttrium, zinc, and zirconia. Titania² is used as mordant on leather hat-bands. Alumina was the first mordant used, and in the old days the oxides of aluminum and tin were the most important, with iron oxide a poor third because people were interested in obtaining bright colours. Nowadays the oxides of chromium and aluminum are the important ones, with the oxide of iron a fair third and the oxide of tin a poor fourth. The possibility of using other oxides had been considered more than a century ago, for Bancroft³ says: "It will be ascertained hereafter, by my own particular experiments, that all the metals, properly so called, as far as they have been tried, are capable of attracting adjective colouring

¹ Ber. deutsch. chem. Ges., **35**, 1493 (1902).

² Barnes: Jour. Soc. Dyers and Colourists, **35**, 59 (1919).

³ Philosophy of Permanent Colours, **1**, 392 (1813).

matters in some degree, and of serving as bases to them; and this is also true of most of the earths; though none of them is so efficacious and useful in this way as alumine; indeed this and the oxide of tin, seem to be the only bases suited, by their perfect whiteness, to reflect the rays of light so as to exhibit adjective colours with their utmost lustre and brightness, every other falling short of these in that respect, and almost all of them appearing to sadden or darken the colours which they serve to fix. Probably, the oxides of zinc and antimony do this less than any of the others: the former, however, (zinc) does not appear, by my experiments, capable of giving much stability and permanency to any colour dyed with it."

Until near the end of the fifteenth century the alum used for dyeing in Italy came from the Turks, there being an alum works near Constantinople and a famous one near Smyrna.¹ "About the year 1460, Bartholomew Perdix (by some called Pernix) a Genoese merchant, who had become acquainted with the preparation of alum in Syria, when returning thence to Italy, happened, at the island of Aenaria, now called Ischia or Hiscla to observe large alum stones among the substances which had been thrown up, more than one hundred years before, in consequence of the eruption of a destructive volcano there; and, having calcined some of these stones in a furnace, he extracted from them excellent alum." Pure alum was apparently given the additional appellation in Italy of *rocca* or *roccha*, whence come the French name of *alun de roche* and the English one of roach alum.

A few years after Perdix had begun to produce alum from the stones which he found at Ischia, the famous deposit at Tolfa near Civita Vecchia was discovered by John di Castro. The account of this throws such a light on the trade in the heavy chemicals in those days that it is worth quoting² in spite of its having nothing to do with the theory of mordants.

"This John di Castro, being fond of travelling, had re-

¹ Bancroft: *Philosophy of Permanent Colours*, 1, xxxi (1813).

² *Ibid.*, 1, xxxiii (1813).

sided some time at Constantinople, and acquired much wealth by dyeing cloth made in Italy, which was transported thither and committed to his care, on account of the abundance of alum in that neighborhood. Having by these means an opportunity of seeing daily the manner in which alum was made, and from what stones, or earth, it was extracted, he soon learned the art. When, by the will of God, that city was taken and plundered, about the year 1455, by Mahomet II, Emperor of the Turks, he lost his whole property; but, happy to have escaped the sword of these cruel people, he returned to Italy, after the assumption of Pius II, to whom he was related, and from whom he obtained, as an indemnification for his losses, the office of commissary-general over all the revenues of the Apostolic Chamber, both within and without the city. While in this situation, he was traversing all the hills and mountains, searching the bowels of the earth; he at length found some alum stones in the neighborhood of Tolfa; and having made experiments by calcining them, he obtained alum, and repairing to the pontiff, said to him: 'I announce to you a victory over the Turk. He draws yearly from the Christians above three hundred thousand pieces of gold, paid to him for the alum with which we dye wool of different colours, because none is found here, but a little at the island of Hiscla, formerly called Aenaria, near Puteoli, and in the cave of Vulcan at Lipari, which having been exhausted by the Romans, is now almost destitute of that substance. I have, however, found seven hills, so abundant in it, that they would be almost sufficient to supply seven worlds. If you will send for workmen sufficient, and cause furnaces to be constructed and the stones to be calcined, you may furnish alum to all Europe; and that gain which the Turks used to acquire by this article being thrown into your hands, will be to him a double loss, etc.' These words of Castro appeared to the pontiff as the mere result of idle dreams. He, however, employed skilful people, who found that the stones really contained alum; but least some deception might have been practised, others were sent to the place where they had been found, who met with abun-

dance of the like kind. Artists, who had been employed in the Turkish mines in Asia, were then brought from Genoa; and these, having closely examined the nature of the place, declared it to be similar to that of the Asiatic mountains, which produce alum; and, shedding tears for joy, they kneeled down three times, worshipping God, and praising his kindness in conferring so valuable a gift on our age. The stones were calcined, and produced alum more beautiful than that of Asia, and superior in quality. Some of it was sent to Venice and to Florence; and being tried, was found to answer beyond expectation. The Genoese first purchased a quantity of it, to the amount of twenty thousand pieces of gold; and Cosmo, of Medicis, for this article laid out afterwards seventy-five thousand. On account of this service, Pius thought Castro worthy of the highest honours, and of a statue, which was erected to him in his own country, with this inscription: 'To John di Castro, the inventor of alum;' and he received, besides, a certain share of the profit; immunities and a share also of the gain, were granted to the two brothers, Lords of Tolfa, in whose land the aluminous mineral has been found. This accession of wealth to the Church of Rome was made, by the divine blessing, under the Pontificate of Pius II; and if it escape, as it ought, the hands of tyrants, and be prudently managed, it may increase; and afford no small assistance to the Roman pontiffs, in supporting the burthens of the Christian religion."

"The wealth which the pope obtained from the discovery and working of the mines of Tolfa, encouraged and produced similar undertakings in other parts of Italy, particularly at Volterra, in the district of Pisa, though their success was greatly obstructed by the obstacles which the pope contrived and employed against them, in order that he might monopolize all the benefits to be derived from the manufacture and sale of alum; of which he raised the price so exorbitantly, that alum procured from the Turks was found much cheaper than that of Tolfa, and, therefore, employed. But to obviate this interference, the pope pretended to devote the revenue produced

by his alum works to the defence of Christianity against the Turks, and menaced all who should act so unchristianly, as to purchase or procure, alum from these infidels, with excommunication; which prohibitions were renewed by several of his successors."

"In England the first alum work was that of Gisborough, in Yorkshire, begun near the end of Queen Elizabeth's reign, upon lands belonging to Sir Thomas Chaloner, who secretly procured workmen from the alum works at Tolfa, no person in England then knowing how to produce it. This seduction of his workmen so enraged the pope, as we are told by Pennant, in his Tour to Scotland, that his holiness endeavored to frighten and recall them, by curses, or anathemas, in the very form left us by Ernulphus."

Bancroft¹ states that "this alum continues to be known under the name Roman alum and esteemed above all others; principally because it contains about half as much iron as most other alums: the latter, however, may be rendered equally pure and valuable, by calcining, then dissolving, and afterwards recrystallizing them. Stahl, Newman, Pott, and other eminent Chemists consider alumine as a calcareous earth, and not as being an earth, which it is, *sui generis*, nearly related to clay, but differing from it."

According to Bersch,² under the name of Roman alum, "or that of 'cubical alum,' a variety of alum is sold, generally at a rather higher price than ordinary alum from which it is distinguished by its crystalline form. Ordinary alum forms octahedral crystals often the size of a child's head, but cubic alum well-formed cubes. The property of crystallizing in cubes may be imparted to any alum solution by the addition of a little potash.³ Much so-called Roman alum is made in German works in this way. When this alum contains very little iron, it is quite equal in quality to the best Roman alum, for the higher value of the latter is due entirely to its low con-

¹ Philosophy of Permanent Colours, 1, xxxv (1813).

² "The Manufacture of Mineral and Lake Pigments," 46 (1901).

³ Cf. Napier: "A Manuel of Dyeing," 120 (1875).

tent of iron. The alum prepared in the province of Naples is still better than Roman alum; it contains less iron."

We are so familiar with metallic aluminum and so accustomed to look upon Sir Humphry Davy's preparation of the alkali metals as one of the great discoveries of the period that it is rather a shock to learn that this view was not shared by all of his contemporaries.¹

"I have in the course of this work, commonly adopted the language, and with a few exceptions, the principles or explanations of modern chemistry, not as being wholly unobjectionable but as according best with known facts, and being most likely to become parts of a more perfect system, when future discoveries shall have laid a sufficient foundation for the construction of one. I have not, however, been convinced of the expediency of adopting some of the opinions promulgated by Sir Humphry Davy; though I hope and believe, that I am properly disposed to admire his extraordinary talents, and acknowledge the important additions made by him to chemical science. This is not the place to discuss, and, therefore, it would be improper to dispute any of his facts; but I hope it may not be deemed improper for me to mention a few of the objections to which some of his conclusions seem liable.

"He supposes himself to have proved that the fixed alkalies (and several of the earths) are metals combined with oxygene, or, in other words, metallic oxides; and that when the oxygene has been separated by the powerful agency of opposite electricities, from the bases of these alkalies, the latter are reduced, each to its proper metallic state, and though the supposed metallic globules so produced, cannot be retained in this state for a single minute without burning, and again becoming potash and soda, and are besides much lighter than water, he has thought it right to consider and arrange them as metals, under the names of potassium and sodium.² He,

¹ Bancroft: *Philosophy of Permanent Colours*, 1, vii (1813).

² Gay-Lussac and Thenard have supposed these productions to be compounds of potash and soda with hydrogen (or hydrures), and Curadai has thought them to be compounds of charcoal, or charcoal and hydrogen, with potash and soda.

(Sir H. Davy) admits that 'a considerable degree of specific gravity was formerly considered as an essential character of metallic substances, but (he adds) I have discovered bodies lighter even than water, which agree in all other essential qualities with metals, and which consequently must be arranged with them.' See 'Elements of Chemical Philosophy,' p. 319. How it should follow that bodies which agree with metals in all but one essential character, must be arranged with them, I am unable to conceive: for to my understanding, an opposite inference seems the most natural, and indeed, the only allowable one. But is it true that the bodies in question do really possess all the other characters which are deemed essential to the constitution of a metal? Is not the strong propensity of potassium and sodium to burn instantaneously in the air, and as instantaneously to decompose water, without acquiring in either case, the properties of metallic oxides, at variance with all former ideas of the nature and essential characters of a metal? Even the shining quality of these supposed metals, which more than anything else seems to give them a metallic appearance, belongs equally to petroleum, when diffused upon the surface of water, and to indigo when dissolved for topical application by calico-printers, as is hereafter described. Sir. H. Davy has admitted (p. 321 of his Elements) that 'the common metals, in consequence of their fusibility, malleability, hardness, and durability, have been the most important instruments of the arts;' and that 'the uses of them have been essential to the progress of civilization:' after such an admission, it may, I think, be reasonably asked, why they are to be confounded with matters which have none of these characters?

"Surely, if it be expedient (which I do not perceive) to comprehend things so dissimilar, under one common or general denomination, it would be much more convenient to invent a new name for that purpose, and allow us to designate matters of such high importance as the metals, properly so called, by that which has been so long appropriated to them. To confound, by one appellation, substances so unlike each other,

as those commonly called metals, earths, and salts, must be highly inconvenient for the ordinary purposes of life, as well as for the operations of human intellect; and it must be no small addition to the evils of this confounding, to have it extended even to water, and to that fluid of which our atmosphere chiefly consists, nitrogene; both of which, as a consequence of these doctrines, are to be deemed metallic oxides (i. e., of hydrogen). It cannot, I think, be necessary for the advancement of science that we should thus perplex our language and ideas, and subvert those distinctions which have long regulated the actions and opinions of mankind; and I have, therefore, abstained from these innovations in the following pages. There is, indeed, an additional reason for not considering in this work the alkalies as metallic oxides; which is, that their effects in dyeing are as opposite as possible to those of the oxides of metals, properly so called: and in regard to alumina (or the earth of alum), which is supposed to contain a peculiar metal, called by Sir H. Davy 'aluminum,' I must declare that the evidence of probability of its existence, appears to me much more feeble even than that which regards the supposed metals of the alkaline earths; which last, in my judgment, is far from being sufficient to warrant his arrangement of them in the class, and under the denomination, of metals."

It is worth noting that Bancroft uses the word aluminum and not aluminium. Davy¹ says in one place that if he had succeeded in isolating the metal he was going to call it alumium; but he actually does call it elsewhere² aluminum. Graham³ uses the same spelling, while Silliman⁴ writes aluminium though adding that "aluminum would seem preferable, but I adopt the orthography already introduced." The truth of the matter seems to be that aluminum is the proper English spelling, analogous to platinum, stannum, and glucinum, while aluminium is a later and German version.

¹ Collected Works, 5, 122, from Phil. Trans., 1808

² Ibid., 4, 262; from "Elements of Chemical" Philosophy, 1812.

³ "Elements of Inorganic Chemistry," 419 (1858).

⁴ Elements of Chemistry, 1, 293 (1830).

The earlier experiments on the mordanting of wool and with aluminum sulphate or with alum do not seem at all in accord with what we now find; but the discrepancy is more apparent than real. According to Bancroft:¹ To impregnate wool or woollen cloth with aluminous basis, it is commonly boiled in water, with from one-fourth to one-sixth of its weight of alum, and from one-twelfth to one-sixteenth of its weight of crude tartar, putting the latter first into the water, and, afterwards, the powdered alum: the heat of the water being gradually raised, is kept at the boiling point for an hour and a half, or two hours, during which the cloth is turned through the boiling liquor on a winch, that the mordant may be equally applied; and being afterwards taken out and drained, it is commonly left until the next day, and then rinsed in clean water, for dyeing. In the early collection of recipes, printed in 1605, and already mentioned, sour bran liquor is commonly directed to be employed in this way with alum; and it seems to have answered the purpose of tartar, which, when it came to be generally used in this way with alum, was supposed by the older dyers to do good by softening and correcting the acrimony of the latter: probably, however, the purposes which it answers, are not yet clearly ascertained; one of them seems to be, that of increasing the solubility of alum, and enabling it more completely and intimately to penetrate the fibres of the wool, with which it moreover enters into a permanent union, and thereby contributes efficaciously to modify, vary, and in some cases to brighten the colours with which it is employed, as will be seen hereafter.

"It was until very lately believed, even by those who had most knowledge of the subject, that woollen cloth boiled in this way, with alum, decomposed the latter, in a considerable degree at least, attaching to itself the alumine, though not without a small portion of the sulphuric acid in combination therewith.² Very recently, however, MM. Thenard and Roard

¹ *Philosophy of Permanent Colours*, 1, 384 (1813).

² Berthollet, tom. i. p. 80, after saying, that in aluming stuffs the latter decompose the alum, and combine with the alumine, whilst the acid, which held it dissolved, separates and remains in the bath, adds, "Mais il ne faudrait pas conclure de là, qu'aucune portion de l'acide ne reste dans la combinaison de l'étoffe où elle peut avoir quelque influence sur la couleur."

(of whom, the latter is director of the dyeing department at the imperial manufactory of the Gobelins at Paris), appear to have acquired more correct ideas on this point, by a series of experiments, of which they have given a minute statement, in a memoir read at the Physical and Mathematical class at the French National Institute (see *Ann. de Chimie* tom., 74, p. 267 [1810]).

"These experiments were principally made with alum, acetate of alumine, tartar, and the solutions of tin, applied to wool, silk and cotton; and by these, it was fully ascertained that alum and cream of tartar do not decompose each other when dissolved in water, and boiled with wool, (a fact which had, indeed, been previously asserted by Berthollet); that in this boiling, the wool combines with the alum, without decomposing it in any degree,¹ and also with the tartar; that equal parts of alum and tartar would dissolve in two-fifths less of water, than would be required to dissolve them separately.

"They found that wool, as it is commonly cleansed for being alumed, was not deprived of the carbonate of lime naturally combined with it; and that this wool being boiled the usual time, with one-fourth of its weight of alum and one sixteenth of its weight of cream of tartar, rendered the bath or water, troubled or muddy, and produced (as is, indeed,

¹ It was completely ascertained that when wool had been so alumed, the alum employed might be all recovered, partly from the bath or liquor in which the aluming had been performed, and partly from the wool itself, by repeatedly washing the latter in pure boiling water: commonly a dozen separate washings were sufficient to remove completely all the alum which had united itself to the wool; and the alum, so separated, was susceptible of a distinct crystallization, as if it had never been so employed. After the last of these washings, the wool or cloth, so washed, was found to be as incapable of receiving colours by dyeing, as if it had not been so alumed; and, indeed, before the last, it was always found, that the colour attempted to be dyed upon it, was feeble, in proportion to the number of washings which had taken place.

It became evident, therefore, from these experiments, that wool or cloth boiled with alum (and tartar) attached to itself the undecomposed alum only, and that a decomposition of the latter does not take place until the subsequent operation of dyeing, when the affinity of wool, being assisted in the dying vessel, by the affinity of the adjective colouring matter, their co-operation separates the alumine, in a great degree at least, from the sulphuric acid.

commonly observed) a copious white sediment, which being collected, washed, and analysed, was found to consist chiefly of a sulphate of lime, and a saturated sulphate of alumine. That when wool had been properly cleansed, and deprived of its carbonate of lime, no sulphate thereof was found. Such wool or cloth, being boiled in pure distilled water, with the proportions just mentioned of alum and tartar, and the bath or liquor with which the boiling had been performed being carefully evaporated, a residuum was found, consisting of alum, cream of tartar, and a compound, difficultly crystallizable, of tartrate of potash and animal matter. The wool itself, when so boiled, afforded, by repeated washings, alum, and a small quantity of cream of tartar, besides a very sour combination of tartaric acid, alum, and animal matter. As the acid of tartar combines so copiously with wool, MM. Thenard and Roard have inferred, that it ought not to be employed in this way with alum, except for colours which acids contribute to raise and improve: and among such colours they rank those of cochineal, kermes, and madder; but those of weld, logwood, and Brasil wood, not resisting acids as they suppose, wool, intended to be dyed from either of these, ought, as they think, to be alumed, without any addition of tartar. The accuracy of these opinions will be tried by facts when the several colouring matters here mentioned shall claim our particular attention."

Napier¹ quotes the following theory of mordants by M. Dumas:

"Cream of tartar, or bitartrate of potash, constitutes by itself a feeble mordant, but which is very often used in dyeing light woollen stuffs, to which we may wish to give a delicate but brilliant shade. It is also employed in the dyeing of ordinary woollen goods, but here it is associated with alum, sulphate of iron, chloride of tin, etc. Its influence, under these circumstances, consists evidently in determining a double decomposition, from which we have produced a sulphate of potash or

¹ "Manual of Dyeing," 200 (1875).

chloride of potassium, whilst the tartaric acid combines with the alumina, the peroxide of iron, or the oxide of tin. Now it is very probable that the colouring matters remove the alumina, the peroxide of iron, or the oxide of tin, more readily from tartaric than from sulphuric acid. Moreover, the presence of free sulphuric acid would certainly prove injurious, as well to the stuff as to the colouring matter, whilst free tartaric acid can exercise no unfavorable action over them.

“The operation of subjecting wool to the alum mordant is always effected at the boiling point; the mixture used in this process is a compound of alum and of cream of tartar. One of the objects of this addition is to free the bath of the carbonate of lime which the water generally retains in solution, and which, acting on the alum, would determine its partial decomposition by producing an insoluble subsulphate of alumina and potash, and this accumulating on the stuff, and becoming unequally fixed upon its surface, would lead to stains or blotches on passing the material through the dye-bath. But, independently of the above effect, which might be produced by any acid, cream of tartar appears to be capable of effecting a further object, by inducing a double decomposition, which transforms the alum into a tartrate of alumina. However this may be, after one or two hours' boiling in the alum-bath, the cloth which should be constantly agitated so as to cause a more equal application of the mordant, is withdrawn from the copper, and, after thoroughly draining, it should be put aside for two or three days, when we wish to dye it with any full-bodied colour. Experience has proved that this repose after the use of the mordant greatly favours the union of the latter with the stuff. In applying the tin mordants we also make use of cream of tartar. It is, moreover, an indispensable addition where we desire to fix the salts of iron previously to dyeing in black.

“Woolen cloth, on being dipped into a cold aqueous solution of alum, appropriates to itself a part of this salt, but without undergoing any very sensible alteration. MM. Thenard and Roard have, indeed, proved that cloth, when thus

treated by a cold solution of alum, gives up this salt to boiling water, and that, after a few washings performed at the boiling point, it will have parted with the whole of the alum which it had received in the cold bath. When, however, cloth is boiled in a solution of alum, it yields to this liquid a portion of its organic matter, which becomes dissolved; but at the same time it absorbs an equal amount of the alum.

"We have now merely to shew the action which wool undergoes when brought into contact with alum and cream of tartar at one and the same time. It is very possible that there may be in this case a simultaneous fixation of alum, as well as of the double tartrate of alumina and potash, and of tartaric acid. The presence of alum in the cloth when taken from the boiling solution is very evident; that of the tartrate of alumina and potash and of free tartaric acid is only presumable.

"Silk, in like manner, unites itself with alum when placed in a cold solution of this salt, and afterwards parts with it to boiling water; it may be reproduced from this liquor by evaporation. The action of silk on acetate of alumina is identical with that of wool. It at first absorbs this salt in its pure form; then, by desiccation it loses some acetic acid, and retains a mixture of the acetate together with alumina in its free state; it gives up a further portion of this acetate to boiling water.

"The alum mordant is always used cold with silk: if employed hot, it would destroy its lustre. The bath should not contain cream of tartar when it is intended for this material; on the contrary, we here have recourse to a variety of alum of as neutral a character as possible.

"The theory of the action of mordants is connected in the closest manner with that of dyeing. It may, in fact, be viewed under two very different aspects. Sometimes we admit that there exists a true combination between the stuff and the colouring matter—a combination which can only be determined by a veritable affinity between these two bodies, and which will present a condition analogous to that which occurs in all chemical combinations—that is to say, a state of saturation,

beyond which the union of these bodies becomes of a very unstable character; at other times, on the contrary we regard the dyeing of stuffs as produced by a nearly mechanical phenomenon, by virtue of which the colouring matters become imprisoned in the meshes of the organic filaments contained in the material to be dyed. This latter opinion is evidently the better founded. It approximates the theory of dyeing to some analogous phenomena which we find manifested by animal charcoal on coloured solutions; for, as the animal charcoal seizes upon the colouring matters contained in an aqueous solution, and renders them insoluble by fixing them in a purely mechanical manner within its own pores: so may the wool, the silk, and the cotton, appropriate the colouring matters held in solution, and, by fixing them in their pores, render them more or less insoluble to water. Experience, however, shews that dyeing thus produced is wanting both in intensity and in fixity—two qualities which it derives by the previous application of a mordant. Now, we can readily see that the mordants themselves may become fixed in the tissues by similar causes to those which determine the fixation of the colouring matters by animal charcoal. We know, in fact, that this latter body possesses the property of removing from water not only the colouring matters, but also certain salts. There will, therefore, be no difficulty in imagining that silk, wool, and cotton may, in their character of porous bodies, purely and simply seize upon the alum, and that this salt, when once imprisoned in the meshes of the tissue, may subsequently react upon the colouring matter according as this latter, in its turn, penetrates the interior of these materials.

“We may then refer the phenomena of absorption, which characterise the fixation of the mordants and the penetration of the colouring principles into the tissues, to the same cause as that which determines the action of animal charcoal on certain soluble salts and colouring matters. But if one of these stuffs be impregnated with alum and then dipped in a bath of soluble colouring matter, it acquires a very deep tint, which appears to be essentially produced by a kind of lac,

formed by means of the colouring matter and the base of the mordant. On the other hand, in a great number of cases, the mixture of the above mordant with the dye-bath fails in producing an insoluble precipitate. Thus, when we mix together alum and a decoction of Brazil-wood, no precipitate is formed, and, to obtain a lac from this liquor, we are obliged to add some alkali or alkaline carbonate, such as ammonia; in a word, we must render the alumina free. While admitting, then, in accordance with the experiments of MM. Thenard and Roard, that the stuffs fix the alum in its natural state, we must acknowledge, at the same time, that, by some special action, the tissue subsequently determines the union of the base of the mordant with the colouring matter. This special action is equivalent to that of the alkali.

“Now, it is certain that the above-mentioned stuffs possess in a high degree the faculty of seizing upon the insoluble colouring matters when these are presented to them in their nascent state. It is thus that cotton becomes dyed of a rose colour in a liquor which contains carthamic acid in suspension, arising from the decomposition of a carthamate of soda by an acid. In like manner we find wool acquires a black colour, when placed in a boiling solution of a salt of iron and tannin, by attracting to itself the black precipitate resulting from their admixture. Consequently, although the dyer generally endeavors to produce the insoluble compound, on which the colouring stuff depends, within the very pores of the tissue, still we may affirm that, in many cases, the cloth or other material, when placed in presence of the nascent precipitate, has the property of seizing upon it, and thus acquiring a shade of greater or less intensity.

“It is to this property (which is due to some hitherto undetermined cause) that we must undoubtedly refer the reaction which takes place between the alum and the soluble colouring matters, as well as some of these more mysterious phenomena which are manifested in dyeing. How else, indeed, are we to account for the fact that wool so readily takes a scarlet colour, while cotton and silk are unable to fix it? How

explain the cause of wool so easily appropriating the black precipitate formed by tannin and the salts of iron, while silk, under the same circumstances, acquires a black colour only by great trouble and expense? How, in one word, can we understand why certain colours should fix themselves better on certain materials than on others, unless it be by virtue of some special action, wrongly designated by the name of affinity, but which does not the less constitute a force, or rather a consequence of diverse forces of which we must take full account during the operations of dyeing? To confound, in fact, a chemical affinity properly so called, such as is evidenced in ordinary chemical combinations when produced in definite proportions, with the phenomena of dyeing, is certainly to mix together two very distinct ideas. The union of silk with Prussian blue, or of wool with indigo, is quite a different thing to the combination of sulphur with lead. But to consider the tissue as a simple filter, capable of retaining in its pores certain principles, and of receiving from them peculiar colours, is to go equally far in an opposite direction; nor would this supposition at all explain the mode in which the coloured lac is formed in most of the operations of dyeing, operations which are effected by an aluminous salt and a colouring bath, altogether incapable of producing any lac, except by the addition of an alkali for the purpose of setting the alumina at liberty, or of a stuff which has the power of taking up the lac, as quickly as it is formed.

“Among the reasons which induce us to regard the insoluble colouring matters and the stuffs as capable of uniting together by virtue of some special force, we must mention the facts elicited by the recent experiments of M. Chevreul, who has found that the stuffs and colours, when once united form products which are endowed with properties differing, according to the nature of the stuff, in the same given colour. The properties of the dyeing matter are, then, greatly modified by the peculiar action of the tissue on the dye. Numerous examples place the truth of this assertion beyond all question. It becomes, therefore, perfectly clear that it is only by an

attentive and systematic study of the specific properties of the stuffs, in their relation to the various dyeing matters which we may desire to fix upon them, that we can hope to direct the future progress of the art of dyeing."

On the other hand¹ "Chevreul denied that the alum could be washed out by water, and Bolby stated that actual decomposition took place; a basic salt being deposited on the fibre, leaving the solution more acid."

Knecht, Rawson and Loewenthal² consider that "the mordanting of wool and silk appears to be analogous to the dyeing of these fibres, and to depend upon their acid and basic properties. Thus, wool boiled with a solution of aluminum sulphate fixes both the acid and the basic constituents of the salt; but, being possessed of more pronounced acid than basic properties, it absorbs the basic constituents more energetically than the acid one, and some free acid is left in the solution. By subsequent treatment with boiling water, more acid is extracted, and the alumina becomes more firmly combined with the substance of the fibre. It is noteworthy that only such salts which contain the acid and basic constituents in a comparatively loose state of combination are absorbed by the wool fibre. Thus, whereas the sulphates of aluminum, iron, chromium, and copper are readily taken up from the boiling solution by the wool fibre, sodium sulphate or sodium chloride are not taken up at all. Chromic acid, on the other hand, is readily taken up by wool, and, like the acetates of the heavy metals, is precipitated from its aqueous solution by lanuginic acid."

Thenard and Roard believed that aluminum sulphate or alum is adsorbed by wool unchanged and that the elimination of the sulphate radical takes place when the mordanted fibre is dyed. Most of the work since then has been to the effect that wool does decompose aluminum sulphate more or less. If the recent writers had read the original paper by Thenard and Roard, there would have been no discrepancy to explain.

¹ Dreaper: "The Chemistry and Physics of Dyeing," 61 (1906).

² "A Manual of Dyeing," 20 (1910).

Havrez¹ showed that when relatively concentrated solutions of alum are used in mordanting wool, the mordant washes out readily and the wool is not dyed so deeply as when more dilute solutions of alum are used. He recommends not going above ten percent alum, referred to the amount of wool. It has been found by von Georgievics² that from relatively dilute solutions of alum, more alumina than sulphate is taken up by wool while the reverse is true for relatively concentrated solutions. At twenty-four percent alum, referred to wool, the two are taken up in equivalent quantities. Thenard and Roard used twenty-five percent alum, referred to the wool, so that their results are absolutely in accord with the most modern data. The whole trouble arose from their using a more concentrated solution of alum than is now customary.

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¹ Dinger's Polytech. Jour., 205, 491 (1872).

² Jour. Soc. Chem. Ind., 14, 653 (1895).