THE THEORY OF DYEING. III

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Since dyeing is in general a case of selective adsorption by the fiber, we should expect to find all degrees of adsorption. If the amount of adsorption is low and if the fiber consequently shows no tendency to exhaust the bath, the dye in the fiber will wash out readily and the practical dyer will say that that dye does not dye that fiber. For practical reasons the dyer does not recognize the innumerable gradations of adsorption which actually occur with different dyes and different fibers. To him a dye either dyes or does not dye a given fiber. Thus, methylene blue is not supposed to dye cotton; but one has nevertheless to wash cotton thoroughly to remove all the methylene blue. The distinction is a good one practically; but it should not be allowed to interfere with the theoretical treatment of the subject. We are actually dealing with differences in degree, not differences in kind.

There are some dyes which are not adsorbed strongly by wool and very many which are not adsorbed strongly by cotton. Satisfactory results can be obtained only by use of mordants,¹ which are "substances by means of which we are able to fix coloring matters, which of themselves have [little or] no affinity for the fabric." The term and conception date back a good way. Thus my name-sake² says: "Adjective coloring 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 color has been applied to the dyed substance, their union becomes thereby more intimate and permanent. But in other respects, adjective colors owe their durability, as well as their lustre, to the interposition of some

¹ Crace-Calvert: "Dyeing and Calico Printing," 17 (1878).

² Bancroft: "Philosophy of Permanent Colors," I, 341 (1813).

earthy or metallic basis; which, having a considerable attraction, both for the coloring 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 coloring matters when *uncombined*. These earthy and metallic bases, having been commonly employed in a state of solution or combinations with acids, were from that circumstance denominated *mordants* (biters or corrodors) by the French, who, indeed, began to employ the term long before a theory of dyeing had been conceived; whilst even alum was supposed to act by its sulphuric 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 since been adopted in other countries. The ingenious Mr. Henry, of Manchester, has, however, lately objected to it with great reason, and has 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 coloring matters, as well as between the former and the fibers 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 sometimes 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 of fibers 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 coloring 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 coloring 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 colors."

A mordant can be defined as a substance which is adsorbed strongly by the fiber and which adsorbs the color strongly. When dyeing mordanted cloth, we really dye the mordant in most cases rather than the fiber itself. When the mordant is dyed with no fiber present, the dyed product is called a lake, though the lakes used as pigments are usually thrown down on, or together with, barium sulphate, china clay, lead sulphate, red lead, or some other suitable medium intended to modify the physical properties. For acid dyes the usual mordants are the hydrous oxides of aluminum, chromium, iron, tin, copper, lead, etc., while the basic dyes are mordanted with tannin, fatty acids, albumin, silicic acid, arsenic acid, or phosphoric acid. The basic dyes are also sometimes mordanted with the direct cotton colors.¹ Sulphur and other substances may be used as mordants in special cases. A satisfactory theory of dyeing must account for the action of the specific mordants, and also for the action of the so-called fixing agents. The metallic mordants can be fixed, or made to hold faster to the fiber by treatment with silicates, arsenates, phosphates, tannin, or fatty acids, lime, magnesia, and the hydrous oxides of zinc, nickel, and cobalt are helpful in

¹ Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 378 (1910).

conjunction with other fixing agents. Lime seems to be essential when alumina is used as a mordant for alizarine; but it is quite possible that the lime helps fix the color to the mordant rather than the mordant to the fiber. The acid mordants can be fixed by metallic mordants in general, while tartar emetic is the best fixing agent for tannin. The theory of mordants, therefore, involves four different things: the relation between the fiber and the mordant, the relation between the mordant and the fixing agent, the relation between the mordant and the dye, and the relation between the dye and the fixing agent.

Most people consider: that the mordant forms a definite compound with the fiber in the case of wool, though not in the case of cotton; that the mordant forms a definite compound with the dye; that the mordant forms a definite compound with the fixing agent; and that the dye forms a compound with the compound formed by the interaction of mordant and fixing agent. Knecht, Rawson and Loewenthal¹ say: "The name [mordant] is derived from the French word *mordre* (to bite or corrode), because the early French dyers believe that the utility of the metallic salts they employed consisted in their corrosive nature; it was believed that these substances opened the pores of the textile fibers and thus rendered them capable of absorbing the dyestuffs. At a later period it was recognized that the so-called mordants entered into a chemical combination with the dyestuffs and formed insoluble compounds or 'color lakes,' hence these substances were considered principally as fixing agents for the dyestuffs. In many cases this is true—*i. e.*, where a dyestuff dyes without the aid of mordants, and becomes simply faster to washing and milling by the application of the mordant. In most cases, however, the mordant is an essential constituent of the color, as without it no color at all or only a worthless shade is produced. We consider as mordants substances which, partly or wholly, combine with the dyestuffs to form definite compounds

¹ "A Manual of Dyeing," 2nd Ed., 4, 20, 179, 189, 224, 234 (1910).

in the fiber, thus distinguishing them from those compounds which take part in the dyeing process without entering into the composition of the ultimate color. . . .

"The mordants may be classified as *acid* and *basic* mordants. The acid mordants, of which the tannins and the oil (fatty acid compounds) mordants are the most important, serve for the fixation of basic dyestuffs and metallic oxides; they are often used for fixing basic mordants on the fiber, which latter then act as the true mordants in dyeing. Their chief application is in the dyeing of cotton and linen, and in silk weighting. The basic mordants contain the hydrated oxides of the heavy metals as their active constituents; of this class the most important are compounds (salts) of aluminum, iron, chromium, copper, and tin. In accordance with their basic character, these mordants serve for the fixation of acid or phenol-like dyestuffs.

"As far back as the eighteenth century it was observed that for the dyeing of cotton with madder and alumina mordants calcareous water was necessary; the influence of lime in water used for dyeing with other mordants and dyestuffs was also noticed. In 1882, Horace Koechlin, in a communication to the Société Industrielle de Mulhouse, pointed out that certain coloring matters could be more readily fixed on cotton by means of *double mordants* (containing two metals) than by simple ones. Such double mordants were prepared by mixing aqueous solutions of acetate of alumina, or acetate of chrome with either acetate of lime or acetate of magnesia. He showed that calico prepared with such mordants could be dyed with Phloxin, Scarlet 3R, and other coloring matters. Some years later he recommended for the fixation of St. Denis red a treble mordant consisting of alumina, magnesia, and oxide of zinc, and showed that this treble mordant was also capable of fixing other azo dyes, yielding bright shades which were comparatively fast to soap.

"Following up this subject more closely from a scientific point of view, Prud'homme, taking as his starting point Vauquelin's observation that alumina precipitated in presence

of magnesia is insoluble in caustic alkalies, discovered that, beside magnesia, other metals possess the property of producing compounds with alumina insoluble in alkalies, which are useful as mordants; and further, that other metallic oxides which are soluble in alkalies are capable of yielding, like alumina, insoluble compounds of this character of *compound mordants*. Nickel and cobalt salts, for instance, act better than magnesium salts in rendering the precipitated alumina insoluble in caustic soda, while tin and zinc salts form with each other a compound mordant which is also insoluble in caustic soda. Prud'homme maintains that in cotton dyeing compound mordants are invariably produced, either intentionally or accidentally on the fiber, and that there is no such thing as a simple mordant. The best mordants consist of compounds of sesquioxides, like alumina, chromic oxide, or ferric oxide, with monoxides, like lime, magnesia, or zinc oxide. In some cases treble mordants give even better results. Thus iron fixed with arseniate of soda or phosphate of soda gives better results with lime or magnesia than without these oxides."

"The *mordanting* of wool and silk appears to be analogous to the dyeing of these fibers, 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 constituent of the salt; but, being possessed of more pronounced acid than basic properties, it absorbs the basic constituent 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 fiber. 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 fiber. Thus, whereas the sulphates of aluminum, iron, chromium, and copper are readily taken up from the boiling solutions by the wool fiber, 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."

"The application [of the tannin-substances] in dyeing is based on the fact that they are readily absorbed by the textile fibers, notably by cotton, linen, and silk; and on the property of forming insoluble compounds in the fibers, on the one hand with the heavy metals and with antimony, and on the other hand with the basic dyestuffs."

"Tannic acid forms lakes with the basic colors, which are insoluble in pure water, but dissolve in an excess of tannin and in other acids. The tannic acids can be converted into various metallic salts, which are insoluble in tannic acid or in water, and which, when produced in the fiber, resist soaping very well. These insoluble salts possess the same property as tannic acid in the free state of forming lakes with the basic colors; but an excess of the salts has no dissolving action on the color lakes, and the products are very stable. There are in this way produced in the fiber *triple compounds* of tannic acid, a metallic oxide and a basic color, which are quite insoluble in water, and resist both washing and soaping extremely well; and they are also faster to light than the lakes of tannin and coloring matter which do not contain a metallic oxide."

"Sodium phosphate precipitates from the solutions of aluminum salts *aluminum phosphate*, AlPO_4 . $\text{Al}_2(\text{SO}_4)_3 + 2\text{Na}_2\text{HPO}_4 = 2\text{AlPO}_4 + \text{Na}_2\text{SO}_4 + 2\text{NaHSO}_4$. The precipitate forms a voluminous white mass, which is soluble in caustic soda, but not in ammonia. It also dissolves in hydrochloric or nitric acid, but not in acetic acid. Citric acid prevents the formation of the precipitate but not tartaric acid or sugar. Aluminum phosphate is soluble in the aqueous solutions of other aluminum salts. One equivalent of aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3$, can keep one equivalent of aluminum phosphate, AlPO_4 in solution, according to Liechti and Suida. This is probably the reason why sodium phosphate is not a good fixing agent for aluminum mordants. Sodium arsenate precipitates from the solutions of aluminum salts *aluminum*

arsenate as a white powder, which is insoluble in water, but soluble in acids. This reaction is used to fix aluminum mordants on the vegetable fibers. Sodium silicate precipitates from the solutions of aluminum salts aluminum hydroxide; the silicic acid does not combine under these conditions with alumina; if the silicate of soda contains an excess of caustic soda, the precipitate of aluminum hydroxide may redissolve in the precipitant."

"The composition of the mordant which is retained by the fiber varies with the different fixing processes. In almost every case aluminum hydroxide is formed either by mere dissociation of the aluminum salt, or by decomposition of the same with ammonia, or with sodium or ammonium carbonate, or with chalk, etc. In addition, arsenate and phosphate of soda generate more or less aluminum arsenate, and phosphate; soap produces stearate, palmitate, or oleate of aluminum; whereas silicate of soda forms the hydroxide only. If the material was prepared with tannic acid, oil or soap, tannate, etc., of aluminum is formed; the mordanting with stannate and alum produces only stannic hydrate and aluminum hydroxide. In case a basic sulphate is fixed exclusively by aging, very basic sulphates are formed, which, being insoluble in water, are retained, together with the hydroxide, while the neutral sulphate and free acid, which were formed by dissociation through aging, are removed by washing. It is, however, more usual to pass the goods after the aging through some fixing bath—*e. g.*, chalk or phosphate—which remove probably the whole amount of the sulphuric acid."

Parry and Coste¹ say: "The neutral color lakes may, in general, be regarded as compounds of one or more natural color acids with inorganic bases, with, at times, more or less mechanical admixture of excess of base or acid. Theoretically, however, the lake may be regarded as the true compound in the sense described. In the same way the lakes of the artificial color must be regarded as true chemical com-

¹ "The Chemistry of Pigments," 240 (1902).

pounds, although the mechanical admixture plays an important part in the preparation of the colors in actual practice.

“For the purposes of the present chapter, artificial coloring matters capable of forming lakes may be divided into three groups. These are as follows: (1) The artificial color bases containing nitrogen in combination with hydrogen, so that the base behaves as an ammonia derivative. (2) Artificial colors of a purely acid nature, capable of combining with an inorganic base. (3) Artificial colors in which both acid and basic functions exist simultaneously in a well-defined degree. Such bodies may be typified by a sulpho acid of an amido compound.

“In this sense then we understand a true lake, and it is necessary to here draw attention to the somewhat free use of the word ‘base’ in connection with this subject. As we are employing the word, it refers to a compound or an oxide of a metal capable of uniting to form a definite compound with an acid. The word is also employed (‘lake base,’ etc.) when referring to a neutral body, such as sulphate of barium or china clay, which is employed as an absorbent, or as a diluent for a color, but in the present work the word will not be employed in that sense.

“At the same time it must be admitted that the principles of lake formation are not altogether as well understood as one could wish. Although we have emphasized the importance of recognizing the principle of true chemical combination as the basis for the formation of lakes, there is considerable room for speculation as to the degree to which this combination is carried in a great number of cases which must be regarded as belonging to the class of true lakes. It is quite certain that advantageous precipitation of color bases takes place, when only a small proportion of the calculated molecular equivalent of the precipitating acid is used. This is especially the case when tannic acid is employed. Here, then, we have a case in which, whilst there is certainly a true chemical combination of the base and the acid, there exists in the compound far more base than the theoretical combination would require.

It is usual to use the expression 'mechanical combination' in such cases, and to escape from the difficulty of a lame explanation by the use of a term which is even more difficult to define than the original problem is to explain. In certain cases, where a voluminous precipitate, such as that of alumina in the hydrated state, is thrown down, a species of 'mechanical combination' is not difficult to assume. For example, when one adds a solution of ammonia to a solution of alum mixed with a salt of calcium, a voluminous precipitate is thrown down. It is of such a bulky, gelatinous nature that together with the mass of water which assists to make up the 'jelly,' there is a considerable amount of lime salts; it is next to impossible to completely remove these lime salts by ordinary washing with water, and when the alumina is filtered off and dried, it will be found that there still remains an appreciable amount of lime in a state of intimate admixture with the alumina. But the quantity is not sufficient to explain the almost complete precipitation of a considerable excess of base by a small quantity of the precipitating acid, as in the case we have quoted.

"From a prolonged experience of compounds of the inorganic elements, which are more easily manipulated than the organic compounds from this point of view, we are acquainted with well-defined basic compounds, *i. e.*, compounds of a base with an acid which are not of normal constitution, but contain definite molecular proportions of the base in excess of that required for the normal compound. In our present imperfect state of knowledge concerning the exact nature of the combination existing between many organic compounds, it appears to us that the most feasible explanation of the somewhat erratic combinations of these lake bodies is the existence of an analogous series of compounds to those which, as just mentioned, are well recognized between inorganic elements. This, however, is merely a matter of speculation, and need not, therefore, be further discussed here. We now pass on to the consideration of the coal-tar lakes, and in doing this we have arranged the lakes in groups according to their colors,

without taking their chemical constitution into consideration, a practice which, as evident in the earlier chapters, would not have been convenient when dealing with the pigments of inorganic origin."

Friend¹ also considers that lakes are or should be definite compounds. "Most natural coloring matters are acidic in character, and can, therefore, combine with basic bodies, such as the oxides and hydroxides of metals. The products thus obtained are colored, and insoluble in water; they, therefore, possess two of the qualities necessary to render them serviceable as pigments. Theoretically, the amount of basic substance should be exactly sufficient to neutralize all the acid color—neither more nor less—to form a true lake. Practically, however, this rule is not adhered to, an excess of base being usually employed in such quantities as to produce the desired shade. The greater the proportion of the base, the lighter will be the tint, for obvious reasons. As the color and metallic base have such a strong affinity for one another, it is generally sufficient to mix solutions of the two, when the lake separates out. Sometimes, however, the addition of small quantities of sodium carbonate is necessary to effect the precipitation."

Knecht and Hummel² do not even discuss the possibility of the fixing agents not forming definite compounds with the mordants. "Silk may be often mordanted in the same manner as wool, but as a rule it is treated like cotton. The silk is steeped for several hours in cold, neutral, or basic solutions of chromium chloride, alum, ferric sulphate, etc., then rinsed in water slightly, and passed into a cold dilute solution of silicate of soda, in order to fix the mordants on the fiber as insoluble silicates. Cotton does not, like wool and silk, possess the property of decomposing metallic salts, hence the methods of mordanting this fiber are more complex, and vary according to the metallic salts and coloring matters employed,

¹ "An Introduction to the Chemistry of Paints," 101 (1910).

² "Encyclopedia Britannica," 11th Ed., 8, 748 (1910).

as well as the particular effects to be obtained. One method is to impregnate the cotton with a solution of so-called 'sulphated oil' or 'Turkey red oil;' the oil-prepared material is then dried and passed into a cold solution of some metallic salt—*e. g.*, aluminum acetate, basic chromium chloride, etc. The mordant is thus fixed on the fiber as a metallic oleate, and after a passage through water containing a little chalk or silicate of soda to remove acidity, and a final rinsing, the cotton is ready for dyeing. Another method of mordanting copper is to fix the metallic salt on the fiber as a tannate instead of an oleate. This is effected by first steeping the cotton in a cold solution of tannic acid or in a cold decoction of some tannin matter, *e. g.*, sumach, in which operation the cotton attracts a considerable amount of tannic acid; after squeezing, the material is steeped for an hour or more in a solution of the metallic salt and finally washed. The mordants employed in this case are various—*e. g.*, basic aluminum or ferric sulphate, basic chromic chloride, stannic chloride (cotton spirits), etc. There are other methods of mordanting cotton besides those mentioned, but the main object in all cases is to fix an insoluble metallic compound on the fiber. It is interesting to note that whether the metallic oxide is united with the substance of the fiber, as in the case of wool and silk, or precipitated as a tannate, oleate, silicate, etc., as in the case of cotton or silk, it still has the power of combining with the coloring matter in the dyebath to form the colored lake or dye on the material."

I propose to show that no definite compounds are formed as a rule when dyeing with mordant colors. The fiber adsorbs the mordant, the mordant adsorbs the dye, and the mordant adsorbs the fixing agent. It is not impossible that definite compounds are formed with special substances or under special conditions; but I claim that these are merely unimportant cases and that they have no significance for the general theory of dyeing.

The taking up of mordants by wool is like the case of the adsorption of alkali or acid, with the exception that the ad-

sorbed bases are practically insoluble in water and consequently do not tend to wash out in water to any appreciable extent. It is perhaps desirable to give some data, in support of this, though it must be admitted that the experiments have never been done in the proper way. Pelet-Jolivet¹ gives figures for wool with aluminum chloride, potassium bichromate, potassium chromate, and chrome alum, Table I.

TABLE I

3 g wool, 200 cc solution		5 g wool, 200 cc solution	
Aluminum chloride		Potassium bichromate	
Grams in solution	Grams adsorbed	Grams in solution	Grams adsorbed
0.007	0.0037	0.0976	0.0024
0.0038	0.0183	0.1902	0.0098
0.0304	0.0138	0.2324	0.1676
0.1256	0.0956	0.304	0.206
0.8596	0.0252	1.101	0.299
2.1465	0.655	—	—
3.832	0.392	—	—
5 g wool, 200 cc solution		5 g wool, 200 cc solution	
Potassium chromate		Chrome alum	
Grams in solution	Grams adsorbed	Grams in solution	Grams adsorbed
0.1887	0.0113	0.1818	0.0182
0.5861	0.0139	0.5831	0.0169
0.9807	0.0193	0.9766	0.0234
1.3749	0.0251	1.159	0.241
—	—	1.743	0.257

One difficulty with these data is that they do not really represent the facts. In the case of aluminum chloride, a certain amount of this substance purports to have been adsorbed. Though it is not so stated, it is certain that the author determined the amount of alumina adsorbed and then cal-

¹ "Die Theorie des Färbeprozesses," 78, 79 (1910).

culated this into aluminum chloride. It is quite impossible that the aluminum chloride could have been adsorbed without decomposition. The irregularity of this series is in itself a proof of disturbing factors. A similar criticism applies to the other cases in Table I. In spite of these defects, it is quite clear that there is no evidence for the existence of two solid phases, and that, consequently, the taking up of alumina and of hydrous chromium oxide by wool is a case of adsorption.

An independent way to check this conclusion is to postulate the adsorption and then to see to what extent this enables us to account for and to criticize the results obtained by other people. Aluminum salts hydrolyze to a certain extent cold and to a greater extent when the solution is heated. The hydrous oxide set free may remain apparently dissolved but really as a colloidal suspension; or it may coagulate and precipitate, depending on the conditions of the experiment. Other things being equal, the tendency of the alumina to coagulate will be greater the higher the concentration of the hydrous alumina. Excess of acid will force back the hydrolysis and the hydrolysis will be less the stronger the acid that is used. Since the fiber adsorbs hydrous alumina, by hypothesis, the hydrolysis will proceed farther in presence of the fiber than when no fiber is present. While it is true that the hydrolysis will proceed farther the less acid the solution, it does not follow that the ideal condition for mordanting is a neutral or alkaline solution. We must consider also the rate of hydrolysis because it is essential for the fiber to hold the hydrous oxide as well as to set it free. Consequently it may be beneficial to have in the solution substances which retard the precipitation or coagulation of the hydrous oxide. From a neutral or basic aluminum sulphate solution, the alumina might easily precipitate in relatively large masses which would be chiefly on the surface of the fiber and which would not be held fast by it. Adding organic acids might very well retard coagulation sufficiently to enable the alumina to be taken up in a more satisfactory form of the fiber. If one impregnates the fiber with a solution of aluminum acetate and then steams

the fiber, the acetate will be driven off gradually, and hydrous alumina will be set free slowly, thus permitting of a very effective adsorption. Since the object of getting the mordant into the fiber is to have something there which will adsorb the coloring matter, the ideal thing would be to precipitate the alumina in the form in which it would hold fastest to the cloth, would have the maximum transparency, and would adsorb the greatest amount of dye. It is not probable that the mordant can be obtained in such a form that it would satisfy all these requirements to the highest degree simultaneously. We shall, therefore, expect to find that the properties of the mordant vary with the treatment and that one strikes a balance so as to get the mordant in the form which is most generally useful.

Liechti and Suida¹ have done some work on the behavior of the solutions of some salts of alumina and iron. "The operation of mordanting textile fibers with aluminum, iron, and chromium salts consists in presenting solutions of these in such a condition to the fiber, that it shall be readily and completely impregnated with them, so that under the influence of the fiber itself and by certain physico-chemical processes the oxides or very basic salts are precipitated thereupon. The insoluble metallic compounds thus deposited in, on, or among the fibers form the mordant in its narrowest sense, combining, as they do, with the coloring matters either chemically or mechanically, thus rendering it possible to dye the fiber. Alizarine, for example, is a yellow-colored body which alone does not dye, but which can combine chemically with the oxides of aluminum, iron, and chromium, to form the actual colors—red, pink, black, violet, and reddish brown. The authors' task has been to study what influences the various acids, combined with the sesquioxides (R_2O_3) of iron, aluminum, etc., would have upon the behavior of the salt solutions with respect to the fiber to be mordanted. This necessitated the study of the dissociation of various normal and basic solutions,

¹ Jour. Soc. Chem. Ind., 2, 537 (1883).

and also their behavior towards the fibers under conditions similar to those which obtain in the practical operations of the dyeing and printing. The present paper deals only with the phenomena of dissociation of various alumina and iron salts, in which the amount of alumina or ferric oxide was exactly the same. Soluble basic salts were prepared from concentrated solutions of the normal salts by adding to the latter various amounts of sodium carbonate, sodium bicarbonate, or the corresponding hydrated oxide. There was also prepared a number of normal and basic salt solutions in which the base is apparently in combination with only two molecules of acid radicals, because such salts play an important part in practice. In determining the dissociation point by heating, equal volumes of the solutions were put into test-tubes of equal diameter, and these were partially immersed in a large glass beaker filled with water, and containing a thermometer. The water was heated very gradually to the boiling point, and the dissociation point was determined from this thermometer, an experiment having shown that it registered exactly 1° lower than if placed in the solution in the test-tube. The dissociated mordant solutions were allowed to cool in order to see if the precipitate would redissolve or not. In determining the dissociation point by dilution, equal volumes of the mordants were mixed with gradually increasing amounts of water, and the mixtures were allowed to stand for five minutes. In this way the exact amount of solution was ascertained which was just necessary to cause turbidity or the beginning of dissociation. To determine the amount of water necessary to precipitate the alumina completely the separate liquids were filtered and the amount of alumina in the filtrate was estimated. In these experiments of dilution a natural water containing 0.0748 g. CaO and 0.0114 g. MgO per liter was taken, in order to give a practical bearing to them. In all cases the dilution was limited to such an amount that the CaO and MgO of the water could have no appreciable action. With respect to the behavior of the various aluminum mordants, no decomposition took place with any of the normal

salts, either in boiling or diluting. With an increase in their basic condition the sulphates and acetates, and in a less degree the sulphocyanates, showed an increasing liability to decomposition by heating, while the basic chlorides were not dissociated either by boiling or by dilution, even when four molecules of acid radicals were withdrawn. By dilution with water there were decomposed only the basic sulphates, sulphoacetates and those basic acetates which contained in solution a sulphate, *e. g.*, Na_2SO_4 ; whereas, acetates (even when basic), free from H_2SO_4 , also chlorides, nitrates, and sulphocyanates, could be diluted with water at the ordinary temperature without undergoing decomposition. Since it appeared to be of practical importance to gain some definite information as to the behavior of the mordants to the fiber, and the amount of mordant fixed on the latter during such operations as are actually adopted in practice, experiments were made with the most usual mordants in the following manner: A weighted quantity of cotton was evenly impregnated with, say, an alum mordant until its weight was exactly doubled, and then hung in a dry place on glass rods for 36 hours. A certain portion was then incinerated in order to determine the amount of alumina which the fiber had at its command. Another portion of the prepared fiber was then dried in a constant air current for six hours at a temperature of 40°C . The fiber was then washed for six hours with a definite amount of distilled water, and the amount of alumina in it was carefully estimated. From the number obtained it was possible to determine the percentage of alumina which had become fixed on the fiber.

“Aluminum Sulphates.”—Crystalline aluminum sulphate from the Baden Aniline and Soda Works in Ludwigshafen, and also a melted commercial sulphate, were used in order to prepare other alumina mordants. These commercial salts had as nearly as possible the composition $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. Basic aluminum sulphates were prepared by partially neutralizing a solution of the above with carbonate of soda crystals, Solvay soda, or sodium bicarbonate, or by dissolving

aluminum hydrate in normal aluminum sulphate. The strength of the solutions corresponded either to 200g or 150g normal sulphate per liter. The following mordants, among others, were prepared:

(1) $\text{Al}_2(\text{SO}_4)_3$. 200g normal aluminum sulphate dissolved in one liter H_2O .

(2) $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$. 200g normal sulphate + 31.82g Na_2CO_3 per liter, according to the equation:

(3) $\text{Al}_2(\text{SO}_4)_2(\text{OH})$ as No. 2, but only 150g normal sulphate per liter.

(4) $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$. 200g normal sulphate and 75.7g sodium bicarbonate per liter, according to the equation:

$$2\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 6\text{NaHCO}_3 = \text{Al}_4(\text{SO}_4)_3(\text{OH})_6 + 3\text{Na}_2\text{SO}_4 + 3\text{CO}_2 + 36\text{H}_2\text{O}$$

(5) $\text{Al}_2(\text{SO}_4)(\text{OH})_4$. 300g normal sulphate and 151.3g NaHCO_3 according to the following equation:

TABLE A

Formula	Dissociation on heating			Dissociation on dilution	
	Start	At 100°	On cooling	Start	End
1. $\text{Al}_2(\text{SO}_4)_3$	—	—	—	—	—
2. $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$	—	—	—	14 vols.	30 vols.
3. $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$	—	—	—	10 vols.	22 vols.
4. $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$	68°	Jelly	Ppt. remains	2 vols.	25 vols.
5. $\text{Al}_2(\text{SO}_4)(\text{OH})_4$	Keeps only a short time			1/2 vol.	—

Formula	Attraction of the fiber during mordanting and drying		
	Al_2O_3 presented to the fiber, grams	Al_2O_3 fixed by the fiber grams	Percentage
1. $\text{Al}_2(\text{SO}_4)_3$	0.6971	0.0901	12.92
2. $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$	0.4473	0.2283	51.04
4. $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$	0.1527	0.0897	58.74

From Table A it will be seen that the more basic the mordant the more readily is it dissociated either on heating or on diluting with water, and the greater is the proportion of alumina fixed on the fiber by steeping, hanging, and drying. Other experiments showed that the dissociation was accelerated by the presence of Na_2SO_4 in the mordant solution.

Aluminum Sulpho-acetates.—These mordants were prepared either by double decomposition of the normal aluminum sulphate with lead acetate or by adding acetic acid to solutions of basic sulphates. The following mordants among others were prepared:

(1) $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_4$. 200g normal sulphate and 227.6g lead acetate per liter according to the equation:

(2) $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_3(\text{OH})$. 200g normal sulphate, 25.2g sodium bicarbonate and 170.6g lead acetate per liter, according to the equation:

(3) $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_2(\text{OH})_2$. 200g normal sulphate, 31.8g Na_2CO_3 and 113.8g lead acetate, per liter, according to the equation:

(4) $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)(\text{OH})_3$. 200g normal sulphate, 100.9g NaHCO_3 , 61.1g 29 percent acetic acid per liter, according to the equation:

(5) $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)(\text{OH})_3$ as No. 4, but only 150g normal sulphate per liter.

TABLE B

Formula	Dissociation on heating			Dissociation on dilution	
	Start	At 100°	On cooling	Start	End
1. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_4$	89°	Jelly	Ppt. dissolves	—	—
2. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_3(\text{OH})$	70°	Jelly	Ppt. almost dissolves	12 vols.	50 vols.
3. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_2(\text{OH})_2$	52°	Jelly	Ppt. remains	4 vols.	24 vols.
4. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)(\text{OH})_3$	48°	Jelly	Ppt. remains	1 vol.	10 vols.
5. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)(\text{OH})_3$	40°	Jelly	Ppt. remains	$\frac{3}{4}$ vol.	7 vols.

Attraction of the fiber during mordanting and drying

Formula	Al_2O_3 presented to the fiber, grams	Al_2O_3 fixed by the fiber, grams	Percentage
1. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_4$	0.5750	0.5190	90.26
2. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_3(\text{OH})$	0.5012	0.4957	98.90
3. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_2(\text{OH})_2$	0.1851	0.1688	91.19
4. $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)(\text{OH})_3$	0.1987	0.1914	96.33

From Table B it will be seen that with the sulpho-acetates of alumina any increase in basicity lowers the dissociation point both on heating and diluting with water. All these mordants yield nearly the whole of their alumina to the fiber during mordanting and drying, and act therefore much stronger than the sulphates.

Aluminum Acetates.—The normal acetate was prepared by double decomposition of aluminum sulphate and lead acetate, and the basic acetates were made by adding sodium bicarbonate to solutions of the normal acetate. The following mordants, among others, were prepared:

(1) $\text{Al}_2(\text{CH}_3\text{CO}_2)_6$. 200g normal aluminum sulphate and 341.4g lead acetate per liter, according to the following equation:

(2) $\text{Al}_2(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$. 200g normal aluminum sulphate with 31.8g Na_2CO_3 , and 227.6g lead acetate per liter, according to the following equation:

(3) $\text{Al}_2(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$. 200g normal aluminum sulphate with 341.4g lead acetate per liter, and, after filtering, 50.5g NaHCO_3 added, according to the equation:

(4) $\text{Al}_2(\text{CH}_3\text{CO}_2)_2(\text{OH})_4$. 200g normal aluminum sulphate with 341.4g lead acetate, and 101g NaHCO_3 per liter, according to the following equation:

TABLE C

Formula	Dissociation on heating			Dissociation on dilution	
	Start	At 100°	On cooling	Start	End
1. $\text{Al}_2(\text{CH}_3\text{CO}_2)_6$	—	—	—	—	—
2. $\text{Al}_2(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$	65.5°	Ppt. dense	powdery Ppt. remains	4 vols.	50 vols.
3. $\text{Al}_2(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$	74°	Ppt. dense	powdery Ppt. remains	—	—
4. $\text{Al}_2(\text{CH}_3\text{CO}_2)_2(\text{OH})_4$	44°	Jelly	Ppt. remains	—	—
Attraction of the fiber during mordanting and drying					
Formula	Al_2O_3 presented to the fiber, grams		Al_2O_3 fixed by fiber, grams	Percentage	
1. $\text{Al}_2(\text{CH}_3\text{CO}_2)_6$	0.2631		0.1349	51.27	
2. $\text{Al}_2(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$	0.2213		0.2201	99.46	

This series of experiments (Table C) shows also that increase in the basicity of aluminum acetate lowers the dissociation point on heating, but that by diluting with water they are not dissociated, not even when basic. Another series of experiments showed that the dissociation point of the basic acetate on heating was ever raised by dilution. The readier dissociation of No. 2 mordant is caused by the presence of Na_2SO_4 . No. 4 mordant contains no Na_2SO_4 . It is worthy

of notice that the basic acetate deposits the whole of its alumina in the fiber, whereas the normal acetate gives up only half. Since the basic acetate experimented with contains sodium acetate, the authors purpose determining its influence in this respect.

“Aluminum Sulphocyanates.—These were prepared by double decomposition of barium sulphocyanate with normal aluminum sulphate, the basic ones being made by adding NaHCO_3 to the normal aluminum sulphocyanate. The following were prepared:

(1) $\text{Al}_2(\text{SCN})_6$; (2) $\text{Al}_2(\text{SCN})_4(\text{SO}_4)$; (3) $\text{Al}_2(\text{SCN})_5(\text{OH})$; (4) $\text{Al}_2(\text{SCN})_4(\text{OH})_2$; (5) $\text{Al}_2(\text{SCN})_3(\text{OH})_3$; (6) $\text{Al}_2(\text{SCN})_2(\text{OH})_4$

Contrary to statements which have been made that normal aluminum sulphocyanate solutions decompose when heated to $40^\circ\text{--}50^\circ\text{C}$, it was found that they could be boiled even without decomposition, and only when evaporated over the naked fire to a syrupy consistency was there a slight separation of alumina. A solution of normal salt made from 200g aluminum sulphate per liter only yielded 33.37 percent of its alumina to the fiber by steeping and drying, much less, therefore, than in the case of all the mordants already tested in this respect with the exception of $\text{Al}_2(\text{SO}_4)_3$. With the exception of No. 3 mordant, which did not dissociate, all the basic sulphocyanates dissociate only on boiling, and increase of basicity simply renders the decomposition more complete. None are dissociated on diluting with water.

“Aluminum Chlorides.—Normal Al_2Cl_6 was prepared by dissolving aluminum hydrate in the calculated amount of HCl . Basic mordants were made by adding Na_2CO_3 to the normal solution. The following were prepared:

(1) Al_2Cl_6 ; (2) $\text{Al}_2\text{Cl}_5(\text{OH})$; (3) $\text{Al}_2\text{Cl}_4(\text{OH})_2$; (4) $\text{Al}_2\text{Cl}_3(\text{OH})_3$; (5) $\text{Al}_2\text{Cl}_2(\text{OH})_4$

None of these mordants dissociate either by heating or by diluting with water. The solubility of aluminum hydrate in Al_2Cl_6 was tested and the following results were obtained. To a solution of Al_2Cl_6 a quantity of aluminum hydrate was

added sufficient to form the basic salt $\text{Al}_2\text{Cl}_4(\text{OH})_2$. The alumina dissolved only on heating, and the solution remained clear on cooling. To this clear solution a further quantity of aluminum hydrate was added sufficient to form the compound $\text{Al}_2\text{Cl}_2(\text{OH})_4$. It was, however, found that no more alumina could be made to dissolve, the precipitate even increasing, and on filtering it was found that the solution contained equal molecules of normal Al_2Cl_6 and of HCl . The nascent $\text{Al}_2\text{Cl}_2(\text{OH})_4$ had apparently decomposed according to the following formula:

In the same way it was found that, on adding aluminum hydrate to $\text{Al}_2(\text{SO}_4)_3$ solution sufficient to produce the basic compound $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$, no alumina at all dissolved, the filtrate only containing $\text{Al}_2(\text{SO}_4)_3$. Here, too, we must suppose that the nascent basic compound decomposes as follows:

Because of the excellent results in the steam alizarine reds yielded by the following mordant its dissociation qualities and behavior to the cotton fiber were ascertained. The mordant is an aluminum-chloride-acetate, $\text{Al}_2\text{Cl}_2(\text{CH}_3\text{CO}_2)_4$ prepared according to the following equation:

200g normal aluminum sulphate, 227.6g lead acetate, and 73.3g barium chloride were dissolved in one liter of water. This mordant dissociated neither on heating nor on diluting with water, and yields to the cotton fiber the remarkably low amount of 3.26 percent alumina.

"*Aluminum Nitrates*.—The normal salt was prepared in solution by double decomposition of normal aluminum sulphate with lead nitrate. Basic mordants were prepared by addition of NaHCO_3 to the normal mordant. The following mordants were prepared:

(1) $\text{Al}_2(\text{NO}_3)_6$; (2) $\text{Al}_2(\text{NO}_3)_5(\text{OH})$; (3) $\text{Al}_2(\text{NO}_3)_4(\text{OH})_2$; (4) $\text{Al}_2(\text{NO}_3)_3(\text{OH})_3$; (5) $\text{Al}_2(\text{NO}_3)_2(\text{OH})_4$

All the solutions corresponded to 200g normal sulphate per liter water. None of these mordants dissociated either on heating or diluting with water.

"Aluminum Phosphate in Solution.—It was ascertained, contrary to the statements appearing in textbooks, that sodium phosphate, Na_2HPO_4 , produces no permanent precipitate in presence of an excess of $\text{Al}_2(\text{SO}_4)_3$. It was further proved by experiment that two molecules of $\text{Al}_2(\text{SO}_4)_3$ are the smallest quantity which is capable of retaining one molecule of $\text{Al}_2(\text{PO}_4)_2$ in solution."

The first point to be considered in regard to this paper is whether these basic salts represent anything more than the ratio of added sodium salt to the aluminum salt in solution. Liechti and Suida evidently believe that they are dealing with dissolved basic salts which are definite compounds. Though they do not so state it, their course of reasoning evidently is that alumina is insoluble in water, that alumina did not precipitate, and that, therefore, a soluble basic salt must have been formed. The flaw in the reasoning is the assumption that the alumina must precipitate because it is insoluble. It may stay in apparent solution as colloidal alumina. It is, therefore, very much of a question what one has in the case of a solution of any aluminum salt. In Thorpe's Dictionary of Applied Chemistry,¹ I find the statement that "the triacetate or normal [aluminum] acetate $\text{Al}_2(\text{CH}_3\text{CO}_2)_6$ is not known. A solution corresponding to this compound, but which appears to be a mixture of the diacetate and acetic acid, is the only acetate of commercial importance. It is known as 'red liquor' or 'mordant rouge,' and is largely used in dyeing and calico printing, especially for the production of red colors, madders and pinks (whence its name of red liquor); for the production of dense lakes, and for waterproofing woolen fabrics."

No one would guess the non-existence of the normal acetate from anything in Liechti and Suida's paper, and yet

¹ "Dictionary of Applied Chemistry," 2nd Ed., I, 14 (1912).

Crum¹ was familiar with the fact. "On the question, as to which of the soluble acetates of alumina can be considered as a definite compound, it has already been stated of the teracetate, that when evaporated rapidly enough, and at a heat just low enough to prevent the formation of the insoluble salt, it leaves a product whose composition is nearly that of a binacetate. It may be added that the solution of teracetate gives off acetic acid as freely in the cold, as if a third part of its acid were free. On making an experiment with two solutions of acetate of lead—one of which was decomposed by sulphuric acid and the other (which was three times as strong) by tersulphate of alumina—it was found that the aluminous solution gave a smell of acetic acid considerably stronger than that in which the acid was known to be free. It may be doubted, then, whether there exists a combination of acetic acid with alumina corresponding to the tersulphate of alumina. The solution of binacetate has no smell of acetic acid at ordinary temperatures."

Crum considers that the diacetate, $\text{Al}(\text{CH}_3\text{CO}_2)_2\text{OH}$ or $\text{Al}_2(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$, is a definite compound, and this view has been held by all other writers since his time. It is an open question whether this is correct or not because there is said to be a soluble and an insoluble form of the so-called diacetate. This in itself sounds like a case of colloidal suspension and of coagulation. However this may be, Crum's work on colloidal alumina² shows that one cannot draw any conclusion as to the existence of definite compounds from the fact that no visible precipitation occurs.

"By the continued action of heat on a weak solution of binacetate of alumina, a permanent separation of the constituents of the salt takes place, although no acid escapes, and no alumina is precipitated. The properties of the alumina are at the same time materially changed. A solution of binacetate of alumina, diluted so as to contain not more than

¹ Jour. Chem. Soc., 6, 224 (1854).

² Crum: Ibid., 225 (1854).

1 part of alumina in 200 of water, was placed in a close vessel which was immersed to the neck in boiling water, and kept in that state day and night for ten days. It had then nearly lost the astringent taste of alum, and acquired the taste of acetic acid. Being afterwards boiled in an open capsule acetic acid was freely given off, and when the boiling had continued about five hours (the loss of water being continually restored), the liquid was found to have retained not more than $\frac{1}{11}$ of its original quantity of acetic acid, or about 1 equiv. to $5\frac{1}{2}$ of alumina.

"The solution of hydrate of alumina thus obtained has nearly the same transparency as before the loss of its acid, and is slightly oily. It is nearly tasteless. By longer boiling it may be deprived of considerably more of its acid, but there is a danger of coagulation. A solution containing $\frac{1}{4}$ percent of alumina is converted into a solid transparent jelly, when mixed with half its bulk of water acidulated with $\frac{1}{2500}$ of sulphuric acid. The jelly has, therefore, only $\frac{1}{600}$ of its weight of alumina, and $\frac{1}{7500}$ of sulphuric acid. By pressure in a bag the liquid part of this jelly was readily separated, and the solid was reduced to $\frac{1}{60}$ or $\frac{1}{70}$ of its original volume. Pure water did not dissolve this residue, neither did an excess of sulphuric acid, even at a boiling heat. On examination it was found that the solid portion had imbibed almost the whole of the sulphuric acid. It existed there in the proportion of about 1 equiv. of acid to 15 of alumina.

"The coagulating power of the various agents may be ascertained with tolerable accuracy by employing an aluminous solution so dilute as to contain not more than 1 part of alumina in 800 of water, and shaking it in a phial with about half its volume of a coagulating solution. In this manner it was found that 1 atom of citric acid (tribasic) coagulates as powerfully as 3-atoms of sulphuric acid, and tartaric acid (bibasic) as much as 2. Two atoms of oxalic acid are required to produce the same effect as 1 of sulphuric acid. Of muriatic and nitric acids, not less than 300 equiv. must be employed to produce an effect equal to that of 1 equiv. of sulphuric acid

—the volume of the acid being always half that of the aluminous solution. No acid has the power of redissolving the coagulum.¹

“The alkalies have a strong coagulating power. About 2 equivs. of potash produce an effect equal to 1 of sulphuric acid, and the same is the case with soda, ammonia, and lime. The coagulation takes place before the acetic acid which remains in the aluminous solution is fully saturated; for when the alkali, in a very dilute state, is added with caution, the coagulum which it produces has still an acid reaction. This coagulum, like that from sulphuric acid, is insoluble in any acid, whether cold or hot, as well as in pure water. It dissolves, however, in a boiling solution of potash or soda, and when the alkaline solution is afterwards saturated by an acid, the ordinary terhydrate of alumina is thrown down. Large quantities, however, of the acetic salts (already formed) may be added before they coagulate the aluminous solution.² When the solid part of the coagulum produced by a strong solution of acetate of soda was afterwards freed from that salt by pressure, it redissolved in pure water, and the solution was again coagulated by a fresh addition of the salt. An experiment with acetate of lime gave the same result. The nitrates and chlorides coagulate also with great difficulty.

“Solutions of sulphate of soda, magnesia, and lime coagulate as readily as a liquid containing the same quantity of sulphuric acid in the free state. On examining one of these mixtures, the sulphuric acid was found in the solid part of the coagulum as before, and the alkali in the fluid part, united with the acetic acid which had remained in the aluminous solution after boiling. The digested solution of alumina,

¹ Since these experiments were concluded, it has been found that by employing a wider and shallower porcelain vessel, it is possible to boil off, in an hour and a half, a much larger proportion of acetic acid than that which is mentioned in the text as being done in five hours; and to obtain a product equally fluid.

² Hence, in preparing the binacetate of alumina, which is to be used in obtaining the bihydrate, it is better to employ an excess of acetate of baryta, than to leave in the solution the slightest trace of sulphuric acid.

which has not been deprived of its acetic acid by boiling, requires about twice as much sulphuric acid to coagulate it as does the boiled solution, and thirty or forty times as much alkali. The coagulation is complete before the acetic acid is entirely saturated. One of the most characteristic properties of the digested and altered acetate of alumina is its loss of the power of acting as a mordant. The ordinary acetate, as is well known, forms a yellow opaque precipitate with decoction of quercitron. That which has been thoroughly digested is merely coagulated by the decoction—the color of which is but little altered, and the coagulum is translucent. The same effect is produced with decoctions of logwood, brazilwood, etc....

“It has been already mentioned that when the precipitated [insoluble] binacetate is kept for an hour or two in 200 parts of boiling water, it is changed into the soluble binacetate. The substance so produced may be converted, like the original solution, into the peculiar bihydrate. Thirty to thirty-six hours' digestion is sufficient to complete the change, for after that time the solution has no longer any taste of alum, and the power of coagulating with acids does not increase. A portion of it was boiled in an open vessel eleven hours, being retained at the strength of $\frac{1}{2}$ percent of alumina by successive additions of water. The solutions remained quite clear, and became very slightly oily. It then contained only about 1 equiv. of acetic acid to 19 of alumina. This preparation may be considered as free from all other foreign matter, with the exception of a trace of iron, which still adheres to it. As compared with the solution prepared at once from the soluble binacetate, smaller quantities of the reagents are sufficient to coagulate it, and the coagulum produced has not more than half the density. 0.03g of sulphuric acid, or 0.06g of sulphate of soda is sufficient to coagulate 1.5g of alumina in 600g water, being in the proportion of about 1 equiv. of sulphuric acid to 35 of alumina. An equal quantity of the solution was completely coagulated by 0.034g of potash and by 0.020g of ammonia. In both of these experiments the

acetic acid was not fully saturated. The alkalies then are equivalent in coagulating power to sulphuric acid when a very small quantity only of acetic acid is present in the solution....

"It is well known that when teracetate of alumina is boiled along with sulphate of potash, a gelatinous precipitate is formed, which redissolves when the solution becomes cold. M. Koechlin-Schouch found it to be a subsulphate of alumina. When alum, dissolved in six times its weight of water, was treated with 3 equiv. of acetate of lead—enough to decompose its tersulphate of alumina, but not the sulphate of potash—a large proportion (74 percent) of the sulphate of potash was found to be carried down by the sulphate of lead formed in the process. To a solution so prepared, the loss was restored by an addition of sulphate of potash, and a mixture formed of

KO_2SO_3 together with $\text{Al}_2\text{O}_3.3\text{A}$.

This solution, diluted so as to contain about 0.3 percent of alumina (from 5 oz. of alum per gallon), was exposed to heat. At about 90° Fahr., the gelatinous precipitate began to form; and after two hours' boiling, when scarcely a trace of alumina remained in solution, it was thrown upon a filter of calico, which was kept hot within a steam-pan until the filtrate passed through. The collected precipitate was pressed between numerous folds of bleached calico, and brought up gradually to the state of a stiff clay occupying no more than $\frac{1}{10}$ of the volume of the original solution. It was then divided into portions which could conveniently be shaken and thoroughly mixed in bottles with quantities of water equal in all to the original solution. The mixture was filtered as before and pressed between folds of calico; and another repetition having been made of the same process, the precipitate was deprived of every admixture of soluble matter.

"A portion being dissolved in nitric acid and filtered, gave an abundant precipitate with nitrate of baryta. Exposed to a white heat, and the residue pulverized and boiled in water, the filtered liquor gave no longer a precipitate with

nitrate of baryta, and no indication, or a very doubtful one, of alkali to litmus paper; proving that the sulphuric acid indicated by the first test had been combined, not with potash, but with alumina. Mixed with sulphuric acid, the substance gave no smell of acetic acid, and when burned with oxide of copper it yielded no more carbonic acid than could readily be accounted for by the few fibers of cotton-wool that were to be distinguished in the liquid. The substance dried into a hard, whitish, semi-transparent matter, easily pulverized."

An analysis of this product gave results agreeing very well with the formula $\text{Al}_4\text{O}_5\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Crum assumes that he actually has this basic salt. While this is possible, it is not proved, and one is rather sceptical about it in view of the fact that three slightly differing methods of preparation gave varying percentages of alumina, 43.51, 44.16, and 50.71. Crum¹ also found that a solution of so-called aluminum acetate is precipitated by sodium chloride.

"A solution of teracetate of alumina was produced from 1 pound of acetate of lead in 10 pounds of water, decomposed by tersulphate of alumina. After purification, common salt was added to it in the proportion of 1 equiv. to 1 of tersulphate of alumina. The solution, when heated in the water bath, became of an opaque white from the deposition of a powder so very fine that the mixture passed through the filter almost without change. Neither heat nor any other application could alter this character. It was left at rest, and after some weeks, the liquid, having become nearly clear, was poured off, and the precipitate, which had contracted into $\frac{1}{64}$ of the bulk of the liquid was mixed again with fresh water 11 times its volume. After several weeks more the precipitate fell again to the bottom of the vessel, when it was mixed with a third portion of the fresh water, which again, after four weeks, was decanted, and the precipitate dried in a capsule at 100° Fahr."

On analysis the product was found to contain acetate,

¹ Crum: Jour. Chem. Soc., 6, 231 (1854).

chloride and sodium even after all this washing. Crum states very frankly that he could not make a formula which could be stated in atomic proportions. It is quite clear that the precipitate was alumina which had adsorbed some acetic acid, some hydrochloric acid, and some sodium chloride.

Graham¹ has confirmed these results of Crum. "We are indebted to Mr. Walter Crum for the interesting discovery that alumina may be held in solution by water alone in the absence of any acid. But two soluble modifications of alumina appear to exist, alumina and metalumina. The latter is Mr. Crum's substance. A solution of the neutral chloride of aluminum (Al_2Cl_3) placed on the dialyser, appears to diffuse away without decomposition. But when an excess of hydrated alumina is previously dissolved in the chloride, the latter salt and free hydrochloric acid are found to escape by diffusion in a gradual manner, and the hydrated alumina, retaining little or no acid, to remain behind in a soluble state. A solution of alumina in chloride of aluminum, consisting at first of 52 parts of alumina to 48 of hydrochloric acid, after a dialysis of six days, contained 66.5 percent of alumina; after eleven days 76.5 percent; after seventeen days 92.4 percent, and after twenty-five days the alumina appeared to be as nearly as possible free from acid, as traces only of hydrochloric acid were indicated by an acid solution of nitrate of silver. But in such experiments the alumina often pectizes in the dialyser before the hydrochloric acid has entirely escaped. Acetate of alumina with an excess of alumina gave similar results. The alumina remained fluid in the dialyser for twenty-one days, and when it was pectized was found to retain 3.4 percent of acetic acid, which is in the proportion of 1 equivalent of acid to 28.2 equivalents of alumina.

"Soluble alumina is one of the most unstable of substances,² a circumstance which fully accounts for the difficulty of pre-

¹ Phil. Trans., 151, 207 (1861); Jour. Chem. Soc., 15, 247 (1862).

² [This refers to the highly purified substance. It is possible that Liechti and Suida considered that the statement applied to all solutions containing an excess of base.]

paring it in a state of purity. It is coagulated or pectized by portions, so minute as to be scarcely appreciable, of sulphate of potash and, I believe, by all other salts; and also by ammonia. A solution containing 2 or 3 percent of alumina was coagulated by a few drops of well-water, and could not be transferred from one glass to another without gelatinizing; unless the glass was repeatedly washed out by distilled water. Acids in small quantity also cause coagulation; but the precipitated alumina readily dissolves in an excess of the acid. The colloids gum and caramel also act as precipitants.

"This alumina is a mordant, and possesses indeed all the properties of the base of alum and the ordinary aluminous salts. A solution containing 0.5 percent of alumina may be boiled without gelatinizing, but when concentrated to half its bulk, it suddenly coagulated. Soluble alumina gelatinizes when placed upon red litmus paper, and forms a faint blue ring about the drop, showing a feeble alkaline reaction. Soluble alumina is not precipitated by alcohol or by sugar. No pure solution of alumina, although dilute, remained fluid for more than a few days. Like hydrated silicic acid, then, the colloid alumina may exist either fluid or pectous, or it has a soluble and insoluble form, the latter being the gelatinous alumina as precipitated by bases. It is evident that the extraordinary coagulating action of salts upon hydrated alumina must prevent the latter substance from ever appearing in a soluble state when liberated from combination by means of a base.

"Colloidal alumina possesses also, I believe, a high atomic weight, like cosilicic acid. The chloride of aluminum with excess of alumina referred to above appears to be, either in whole or in part, a colloidal hydrochloride of alumina, containing the latter substance with its large colloidal equivalent, and may be really neutral in composition. The soluble persalts of iron, tin, etc., are likewise all colloidal, and have no doubt a similar constitution. Such colloidal salts are themselves slowly decomposed on the dialyser, being resolved into the

crystalloidal acid which escapes and the colloidal oxide which remains behind.

"Soluble Metalumina.—Mr. Crum first pointed out a singular relation of acetic acid to alumina, which has never been explained. Sulphate of alumina, when precipitated by acetate of lead or baryta, gives a binacetate of alumina, with one equivalent of free acetic acid, the neutral teracetate of alumina not appearing to exist. It was further observed that, by keeping a solution of this binacetate in a closed vessel at the boiling point of water for several days, nearly the whole acetic acid came to be liberated, without any precipitation of alumina occurring at the same time. Mr. Crum boiled off this free acetic acid, or the greater part of it, and thus obtained his soluble alumina. The same result may be obtained by dialysing a solution of acetate of alumina that has been altered by heat. In three days the acetic acid was reduced on the dialyser to 11 percent, giving 1 equiv. acetic acid to 8 equiv. alumina; in six days to 7.17 percent acid; in thirteen days to 2.8 percent acid, or 1 equiv. acid to 33 equivs. alumina. The alumina exists in an allotropic condition, being no longer a mordant; and forming, when precipitated, a jelly that is not dissolved by an excess of acid. Metalumina resembles alumina in being coagulated by minute proportions of acids, bases, and of most salts. Mr. Crum found the solution of metalumina to require larger quantities of acetates, nitrates, and chlorides to produce coagulation than of sulphates. The solution of metalumina is tasteless, and entirely neutral to test paper, according to my own observation. Like alumina, the present colloid has therefore a fluid and a pectous form, the liquid soluble metalumina, and the gelatinous insoluble metalumina."

Liechti and Suida¹ commented on the fact "that the basic acetate precipitated the whole of its alumina in the fiber whereas the normal acetate gives up only half." This is not due to any property belonging exclusively to the fiber.

¹ Jour. Soc. Chem. Ind., 2, 539 (1883).

Graham¹ notes that "to facilitate the separation of hydrochloric acid from the perchloride of iron, for instance, that salt is first rendered basic by the addition of peroxide of iron. The comparatively stable perchloride of iron is transformed by such treatment, into a feebly constituted colloidal hydrochloride. The latter compound breaks up under the purely physical agency of diffusion, and divides on the dialyser into colloidal peroxide of iron and free hydrochloric acid."

The same thing apparently takes place with chromic chloride though it is not stated so definitely.² "The definite terchloride of chromium, being a crystalloid, diffuses away entirely when placed in solution upon the dialyser. This salt dissolves, with time, a certain portion of freshly precipitated hydrated chromic oxide, and becomes of a deeper green color. Such a solution, after dialysis for twenty-two days, contained 8 hydrochloric acid to 92 chromic oxide; and after thirty days, 4.3 acid to 95.7 oxide, or 1 equiv. acid to 10.6 equivs. oxide. After thirty-eight days, the solution gelatinized in part upon the dialyser and then contained 1.5 acid to 98.5 oxide, or 1 equiv. acid to 31.2 equivs. chromic oxide. This last solution, which may be taken to represent soluble chromic oxide, is of a dark green color, and admits of being heated, and also of being diluted with pure water without change. It was gelatinized with the usual facility by traces of salts and other reagents which affect colloid solutions, and was then no longer soluble in water, even with the assistance of heat. It appeared to be the green hydrated oxide of chromium, as that substance is usually known. A metachromic oxide may possibly be obtained by heating and dialysing the acetate, but I have not attempted to form it."

Tommasi³ has studied the action of aluminum on cupric chloride. "Aluminum acts rapidly, even at ordinary temperatures, on a solution of cupric chloride, with liberation

¹ Jour. Chem. Soc., **15**, 265 (1862).

² Graham: *Ibid.*, **15**, 254 (1862).

³ Bull. Soc. chim. Paris, [2] **37**, 443 (1882); Jour. Chem. Soc., **44**, 19 (1883).

of hydrogen and copper, and formation of an aluminum oxychloride, the composition of which depends on the concentration of the copper solution. With a 31.25 percent solution of cupric chloride, the aluminum oxychloride had the composition $2\text{Al}_2\text{O}_6\text{H}_6.3\text{Al}_2\text{Cl}_6$, and with a 7.81 percent solution, the composition $\text{Al}_2\text{O}_6\text{H}_6.4\text{Al}_2\text{Cl}_6$. These oxychlorides are easily decomposed and will not crystallize. They are not true compounds, but variable mixtures of aluminum chloride and oxychloride. The action of metallic aluminum on these oxychlorides yields as a final product the compound $\text{Al}_2\text{Cl}_6.6\text{Al}_2\text{O}_6\text{H}_6.12\text{H}_2\text{O}$. To obtain this compound, a 31.25 percent solution of cupric chloride is treated with aluminum until all the copper is precipitated; the liquid is filtered, the filtrate heated, and aluminum added in successive small quantities until it ceases to dissolve, water being added from time to time to make up for evaporation. The clear liquid is then evaporated to a syrup, and finally dried at $40^\circ\text{--}50^\circ$. In this way the oxychloride is obtained in white flakes resembling those of potassium boro-tartrate. A solution of this oxychloride, like that of ferric oxychloride, is precipitated by sulphuric acid and by certain salts, such as the sulphates of sodium, ammonium, potassium, magnesium, zinc, copper, and iron; but it is not precipitated, even on boiling, by the chlorides of potassium, ammonium, sodium, copper, or barium, by potassium iodide, potassium bromide, ammonium nitrate, or potassium bromide. The aluminum hydroxide thrown down is but slightly soluble in sulphuric acid, and appears to be an isomeric modification, probably the modification δ , described¹ by the author."

There is no proof for the statement that the oxychlorides of varying composition are mixtures of aluminum chloride and of a definite oxychloride; and there is no proof that there is any definite oxychloride. The fact that the so-called oxychloride is precipitated by sulphate is what one would expect of a colloidal suspension and is not characteristic of a true

¹ Tommasi: *Comptes rendus*, 91, 231 (1880).

solution. It is probable, therefore, that we are dealing entirely with adsorption phenomena. Schneider¹ also gives experiments which show that a solution of aluminum chloride really contains some or all of the alumina in colloidal suspension. "It is a familiar fact² that traces of sulphuric acid precipitate alumina from solutions of basic aluminum chloride. I think that it is new that acid aluminum chloride solutions are coagulated by sulphuric acid. Addition of a trace of sulphuric acid to an acid aluminum chloride solution containing 0.1894g alumina in 400 cc (1 mol Al_2O_3 to 7.2 mol HCl) caused the precipitation of 0.0486g alumina, or 25.6 percent of the total alumina.

"I have also found it stated in the textbooks that the solubility of alumina in acids decreases if the alumina is allowed to stand a long time under a solution of ammonia. I have not found any reference to the fact that when an aluminum chloride solution is formed by dissolving in hydrochloric acid an alumina which had stood for a long time under aqueous ammonia, the addition of sulphuric acid causes a greater precipitation than when the solution is prepared from alumina which has been freshly precipitated with ammonia."

This last statement would be quite impossible if we were dealing with a true solution. It is quite natural if we consider that Schneider was really peptonizing alumina with hydrochloric acid and that he was peptonizing a more hydrous, or less dense, alumina in one case than in the other. It is the same difference that we have on precipitation, Graham's method giving so-called alumina while Crum's method gives so-called metalumina. I shall come back to this again when I come to the question of burned mordants.

Müller³ has shown definitely that an alumina hydrosol is obtained by peptonizing freshly precipitated alumina with

¹ Ber. chem. Ges, Berlin, **23**, 1353; Liebig's Ann., **257**, 368 (1890).

² Ordway mentions that basic aluminum chloride solution precipitates alumina on addition of small amounts of sulphuric acid (Am. Jour. Sci., [2] **26**, 203 (1858)).

³ Zeit. anorg. Chem., **57**, 311 (1908).

N/20 hydrochloric acid. "That we are dealing with colloidal hydrosols is proved by the behavior of these solutions. They are microscopically homogeneous and resemble other colloidal sols by passing readily through filter paper. The effect of electrolytes is typical. Dilute solutions of univalent acids or of salts with univalent cations may be added without producing important changes. Acids with multivalent anions and salts of these acids (sulphuric acid and sulphates, for instance) cause the coagulation of a gelatinous hydrogel even when added in very small amounts." Müller¹ also points out that the "basic aluminum salts" obtained by Ordway² and others are mythical.

From all this evidence we are justified in concluding that aluminum salts hydrolyze more or less completely when dissolved in water. This change takes place slowly at low temperatures and more rapidly when the solutions are heated. The reaction products are colloidal alumina and free acid; there is no satisfactory evidence of the formation of any basic salts in solution though the absolute non-existence has also not been proved. With aluminum acetate the hydrolysis takes place so rapidly that it seems certain that no appreciable amount of the normal acetate is formed when equivalent solutions of aluminum sulphate and lead acetates are mixed. Liechti and Suida were certainly not working with the basic salts which they thought they were studying. Since they made up their solutions synthetically and did not analyze after filtering, it seems possible that none of the solutions had the composition that Liechti and Suida have given. Since lead sulphate may carry down as much as 74 percent of the potassium sulphate from a potash alum solution,³ it is unsafe to assume that nothing is carried down from an aluminum sulphate solution.

Liechti and Suida's experiments on the dissociation of aluminum sulphate solutions are just what one would ex-

¹ *Zeit. anorg. Chem.*, **57**, 320 (1908).

² *Am. Jour. Sci.*, [2] **26**, 203 (1858).

³ *Crum: Jour. Chem. Soc.*, **6**, 229 (1854).

pect (Table A). With increasing addition of sodium carbonate, a precipitate is formed more readily both on heating and on dilution. The more dilute solution, No. 3, coagulates more readily than the more concentrated one, No. 2. The sulpho-acetates, Table B, also behave as they should. The hydrolysis proceeds farther with a weaker acid, acetic acid, than with sulphuric acid and there is enough sulphate present to act as a coagulating agent. The sulpho-acetates are more readily decomposed both on heating and on dilution than the corresponding sulphate solutions. The acetates, Table C, do not coagulate on dilution, presumably owing to the absence of a precipitating agent. No. 2 solution seems an exception but the reason for this was pointed out by Liechti and Suida though they did not understand it. This solution contained sodium sulphate. I have not been able to find any special experiments on the effect of sulphocyanates on colloidal alumina. To account for the fact as noted by Liechti and Suida, one must assume that sulphocyanates have a lesser precipitating power or a greater peptonizing power than acetates. This assumption is a plausible one because we find that acetates come between sulphates and sulphocyanates in their action on gelatine and on albumin.¹ The chlorides, chloride-acetates, and nitrates of aluminum all behave as they should in view of what was shown by Crum in regard to the coagulating action of the various acid radicals. If we wanted any further proof that we are not dealing with definite basic salts, we could find it in the fact that Liechti and Suida were able to prepare what they called $\text{Al}_2\text{Cl}_2(\text{OH})_4$ by adding sodium carbonate to an aluminum chloride solution but were not able to go beyond what they called $\text{Al}_2\text{Cl}_4(\text{OH})_2$ by dissolving alumina in aluminum chloride. Of course this is not absolutely conclusive because Liechti and Suida did not add sodium chloride to the second solution and consequently the solutions were not strictly comparable; but this difference is probably not of much importance.

¹ Freundlich: *Kapillarchemie*, 418, 425 (1909).

Liechti and Suida's experiments on the behavior of solutions of aluminum salts in presence of cotton are very disappointing. They had the right idea in making up most of the solutions to contain the same amount of alumina per liter; but, after that, they seem to have gone all to pieces and to have tried to make their experiments as little comparable as possible. Instead of leaving the cotton in the solution until equilibrium was reached, they impregnated the cotton with an alum mordant until its weight was exactly doubled. Heermann¹ showed that with silk "the maximum increase in weight (fiber and mordant) is reached after periods of mordanting ranging from six hours to two days," the salts used being those of tin, iron, chromium, and aluminum. While it is not legitimate to assume that cotton would behave exactly like silk, the very fact that Liechti and Suida took pains to stop the treatment when the weight was exactly doubled, shows that they did not await equilibrium. The experiments in any single series are therefore not comparable and the different series are not comparable because Liechti and Suida determined the amount of alumina fixed on the fiber after drying in a constant air current for six hours at 40°. This may of course give results with a volatile acid like acetic acid which differ from those obtained with sulphuric acid. As might be expected, one can draw any conclusions one likes from the experiments. In Table A the percentage alumina fixed on the fiber increases from 12.9 with aluminum sulphate to 51.0 with so-called $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$, and to 58.7 with so-called $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$. From this Liechti and Suida draw the conclusion that the more basic the mordant, the greater is the proportion of alumina fixed on the fiber by steeping, hanging, and drying. The absolute amounts of alumina fixed on the fiber are shown by Table A to be 0.0901g, 0.2283g, and 0.0897g from which we could draw the conclusion that more alumina is fixed from a moderately basic mordant than from one that is either more or less basic. When we look up in

¹ Jour. Soc. Chem. Ind., 22, 361 (1903).

Table A the total amount of alumina taken up by the fiber while the cotton is doubling in weight, we find that the figures are 0.6971g, 0.04473g and 0.1527g from which we could conclude that alumina is taken up (not fixed) more rapidly the less basic the mordant. These three sets of conclusions show how futile the experiments of Liechti and Suida are so far as giving us any real information. The matter is almost equally bad with the sulpho-acetates, Table B. With the most basic mordant the percentage of alumina fixed is 96.3 as against 90.3 with the least basic but the absolute amount fixed is 0.1914g with the most basic mordant and 0.5180g with the least basic. In all the cases where acetate and sulphate are both present in the solution, Tables B and C, the percentage alumina fixed by the fiber varies between 90 and 99. In the only case in which a straight acetate mordant was used the percentage alumina fixed was only 51. No experiments are therefore available on a basic acetate mordant containing no sulphate. It is difficult to see of just what use Liechti and Suida's experiments with cotton are.

The question as to the form in which mordants are taken up has been answered by Heermann¹ for the case of silk. "Raw and boiled-off silks which had been mordanted at 30° with stannic chloride, basic ferric sulphate, chromic chloride, and aluminum acetate were examined with a view to ascertaining in what form the mordant was present in the fiber. The silk was mordanted, washed thoroughly with water, and titrated directly with standardized sodium hydroxide solution; this method gives a direct determination of the amount of acid radical present in the mordanted fiber in the form of basic salt; its accuracy was checked by fusing the fiber with alkali hydroxide, and determining the amount of acid radical in the usual manner. A deduction was necessary from these results since traces remain adhering mechanically to the fiber, even after most careful washing, and this was ascertained by substituting for the mordanting a treatment with a solution

¹ Jour. Soc. Chem. Ind., 23, 1143 (1904).

of the acid of which the radical was present in the mordant, the other conditions of the process, and the analytical method being the same as above. It was found that considerable range in the concentration of the acid solution used has no effect on the amount of acid adhering to the fiber; *e. g.*, treatment with 1, 5 and 10 percent solution of hydrochloric acid resulted in the same percentage of acid being retained in each case. The analytical data were completed by a determination of the amounts of metallic oxide present in the fiber. The results were as follows: in the case of the tin mordant, the raw silk was found to contain 155 mols of stannic oxide to each atom of chlorine, corresponding to a formula of $\text{SnCl}_{4.619}\text{Sn}(\text{OH})_4$, and a basicity number of 0.0019; boiled-off silk contained 143 mols of stannic oxide to each atom of chlorine, corresponding to $\text{SnCl}_{4.571}\text{Sn}(\text{OH})_4$ and a basicity number 0.0021. With the iron mordant on raw silk, 111 mols of ferric oxide were present to each mol of SO_3 , *i. e.*, $\text{Fe}_{222}\text{SO}_3\text{OH}_{664}$, basicity number 0.008; on boiled-off silk, 91 mols Fe_2O_3 to 1 mol of SO_3 , or $\text{Fe}_{182}\text{SO}_3(\text{OH})_{544}$, basicity number 0.0096. Chromium mordant on raw silk, 40 mols of chromic oxide to 1 atom of chlorine, or $\text{Cr}_{80}\text{Cl}(\text{OH})_{239}$, basicity number 0.009; on boiled-off silk, 44 mols of Cr_2O_3 to each atom of chlorine, or $\text{Cr}_{88}\text{Cl}(\text{OH})_{208}$, basicity number 0.008. Aluminum mordant; in neither raw nor boiled-off silk could any acid radical be detected, showing that the aluminum was present as hydroxide. It would thus appear that for all practical purposes, the mordant is not present in the fiber in the state of a basic salt, but in the form of the hydroxide."

We do not seem to have corresponding data for cotton; but there seems to be good reason for assuming that the basic mordants really are the hydrous oxides¹ proper and are not, in general, basic salts.

Heermann² has also studied the effect of temperature on the amounts of various mordants taken up by silk. "Silk

¹ Cf. Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 234 (1910).

² Jour. Soc. Chem. Ind., 22, 623 (1903); 23, 57 (1904).

was mordanted for six hours at temperatures ranging from 0° to 30° C, at intervals of 5° with tin, iron, chromium, and aluminum mordants. At temperatures between 0° and 5° , iron and chromium mordants were adsorbed with great difficulty; tin mordants slightly more easily. With iron and tin mordants, the temperature has practically no effect on the amount adsorbed by boiled-off silk, but the amount adsorbed by raw silk increases considerably with the temperature, reaching a maximum at 30° . Chromium mordants act in just the reverse manner, *viz.*, the temperature has no effect on mordanting raw silk; but boiled-off silk adsorbs more of the mordant as the temperature rises; with aluminum mordants, raw and boiled-off silks adsorb increasing quantities up to 20° , when a maximum is reached." "It is found that at low temperatures, 0° – 5° , the penetration of the fiber (previously moistened with water) by the mordanting salts and the adsorption by it of metallic oxides take place slowly and with difficulty, owing to the reduction in the power of diffusion of the salts in solution at such temperatures. Hence the silk tends to become unevenly mordanted. At 15° – 20° the fiber is penetrated with ease by the salts, and mordanting takes place more regularly."

We can now consider some of the problems that come up in the actual mordanting of wool.¹ "Wool differs essentially from cotton in its behavior toward the aluminum salts and is mordanted in a totally different way. The investigations of Liechti and Schwitzer² have thrown much valuable light on the reactions which take place in mordanting wool. Experiments have shown that wool takes up sulphuric and hydrochloric acids in the free state, retaining them with such force that they are only imperfectly removed by repeated boiling out with water. In a similar manner salts are taken up. The wool fiber possesses both basic and acid character, and seems to dissociate the salt by combining both with

¹ Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 236 (1910).

² Jour. Soc. Chem. Ind., 5, 526 (1886).

the acid and with the base, the base being taken up either in the free state or in the form of a basic salt. This reaction takes place most completely at the boiling point. Aluminum sulphate, for instance, is most readily decomposed by the wool fiber into basic sulphates and free acid, especially at or near the boiling temperature. The alumina which is thus taken up is retained in an insoluble form with considerable force by the fiber; no fixing agents are required as in the case with cotton; the fixation takes place simultaneously with the impregnation in the mordanting bath under the influence of the elevated temperature. The basic salts, which are fixed on the fiber, undergo a further decomposition by washing with water; they lose acid, and become more basic, while the acid is removed by the wash water.

"The wool fiber attracts, also, finely-divided precipitates from liquids, and retains them with great energy. This power of attraction is comparatively weak in cold liquids, but it increases with the temperature, so that considerable amounts of such precipitates can be attached to the wool by prolonged boiling, although not fast enough to resist washing and rubbing. By the action of the wool fiber on aluminum sulphate a precipitate of basic aluminum sulphate may be produced and boiled on to the wool fast enough to resist washing with water, although it is only mechanically fixed on the surface of the fiber. These superficially fixed mordants produce, in dyeing, color lakes, which adhere still more loosely to the surface of the fiber, and possess in a high degree the defect of rubbing.

"On the contrary, mordants which have entered into an intimate combination with the substance of the fiber are less liable to produce color lakes which rub off. To attain this end the mordanting salt must possess a certain resistance to the dissociating action of the wool, so as to allow of its penetrating into the interior of the fiber before it is decomposed and fixed, and of the dissociation and absorption taking place simultaneously, without the intermediate formation of a precipitate in the liquor, which might be attracted and mechanically fixed by the wool.

"Taken as a whole, the salts of oxalic and tartaric acid fulfill these conditions best—a fact that reminds us of the property of the non-volatile organic acids to impede the precipitation of aluminum hydroxides by alkalies or other agents. On the other hand, the basic aluminum sulphates are entirely unsuitable for the mordanting of wool, because they dissociate before they are taken up by this fiber.

"Liechti and Schwitzer have compared *the action of sulphate, oxalate, and tartrate of aluminum in mordanting*. They prepared solutions of oxalate $\text{Al}_2(\text{C}_2\text{O}_4)_3$, and of aluminum tartrate, $\text{Al}_2(\text{C}_4\text{H}_4\text{O}_6)_3$, by dissolving two equivalents of aluminum hydroxide, $\text{Al}(\text{OH})_3$, in three equivalents of oxalic and tartaric acid, respectively. If wool is boiled in a solution of *normal aluminum sulphate* the bath becomes exhausted if less than 5 percent sulphate (of the weight of the wool) is used. Larger amounts leave increasing proportions in the liquor. The mordanting baths become turbid on boiling by separating an insoluble aluminum salt. A part of the precipitate thus formed becomes mechanically fixed, and is removed on washing, the wash waters being turbid; a part remains in the mordanting liquor. The wool which has been mordanted gives an acid wash water on treatment with boiling water—thus proving that the aluminum sulphate has been decomposed, and that not merely alumina but free acid has been extracted from the mordanting bath. If *sulphuric acid is added to the mordanting bath*, the decomposition of the mordant is less rapid, and it is better fixed than when the normal sulphate is used alone. Comparatively large quantities of sulphuric acid are necessary—more than three equivalents H_2SO_4 of the sulphate, $\text{Al}_2(\text{SO}_4)_3$, and the effect of the acid decreases with an increasing dilution of the bath.

"*Alum* is a somewhat less efficient mordant than aluminum sulphate; this is evidently due to the dissociating effect which is exerted by the alkaline sulphates present in the former salt.

"*Normal aluminum oxalate*, $\text{Al}_2(\text{C}_2\text{O}_4)_3$, is almost completely taken up from the mordanting bath. A smaller

amount of precipitate remains in the liquor, and less can be removed from the wool than in the case of mordanting with the normal sulphate. The wool, on treatment with boiling water, gives, in this case also, an acid wash water.

"Normal aluminum tartrate, $\text{Al}_2(\text{C}_4\text{H}_4\text{O}_6)_3$, if used as the wool mordant, leaves scarcely any precipitate in the bath, and does not give up any to the wash water. On treatment with hot water, the wool imparts also to the latter an acid reaction. Boiling water does not remove the mordant proper. Wool which had been boiled out several times with distilled water after mordanting, gave, on dyeing with alizarine, more brilliant and fuller colors than wool which had been simply rinsed in water. The normal tartrate can be replaced, with excellent results, by a mixture of one equivalent of aluminum sulphate and three equivalents of tartar (acid potassium tartrate)

In this case, as shown by the equation, a mixture of normal aluminum tartrate and acid potassium sulphate is formed. If the normal tartrate is prepared by double decomposition, *e. g.*, with normal potassium-sodium tartrate (Rochelle salt), as in the following equation:

the results obtained are not as good as those with the pure tartrate or with the mixture produced with tartar. These facts lead to the conclusion that the tartrate is similar to other aluminum salts, and is more rapidly dissociated in the presence of alkaline sulphates than in the pure state; and that in the case of a mixture of aluminum sulphate and tartrate being used, the acid sulphate prevents a premature dissociation.

"An examination of the spent mordants and dye-baths shows that the mordanting is most perfect in the case of the tartrate, the whole of the alumina being fixed in a permanent manner. It appears that not only the hydroxides but also true basic aluminum salts are deposited by the mordanting processes in the fiber, as on dyeing the well-washed wool with

alizarine, the spent dye-liquors invariably show an acid reaction. These theoretical considerations and experiments are in perfect harmony with practical experience.

"Basic aluminum sulphates are not used as wool mordants, neither are the acetates nor sulphate-acetates, as they dissociate too rapidly and give poor results. By depositing too much of the mordant on the surface, they make the wool harsh and give rise to uneven dyeing and rubbing. Thiocyanate of aluminum, which is not as sensitive as the acetates, is a very good wool mordant; but its general employment is prevented by its high price.

"The aluminum mordant *par excellence* for wool is aluminum sulphate, either alone or in conjunction with acids or acid salts. In some cases the sulphate is used without any additions. Most generally, however, a mixture of the sulphate with the tartar substitutes is required to obtain full and brilliant colors which do not rub off. These tartar substitutes are sodium bisulphate or oxalates, or they consist of tartar which has been prepared with sufficient sulphuric acid to convert all of the potassium into potassium sulphate. From the foregoing it appears that none of these 'substitutes' can replace the tartar completely, because the action of the latter depends on the formation of *aluminum tartrate by double decomposition*. They have, of course, some effect, as has also sulphuric acid. For a full shade about 6 to 8 percent aluminum sulphate and 5 to 7 percent tartar (of the weight of the wool) are necessary. The quantity of tartar may be reduced to about half this amount, or it may be partly or even wholly replaced by sulphuric, hydrochloric, oxalic acid, bisulphate or sodium, etc., with very good, though not equally fine, results. About 4 percent of sulphuric acid (of the weight of the wool) is used, if the amount of water does not exceed 50 to 60 times the weight of the wool; otherwise more acid must be applied. When sulphuric acid has been used in mordanting, it is often beneficial to add about 5 percent sodium acetate to the ultimate dye-bath to neutralize the mineral acid which always remains in the wool fiber (and

which otherwise would be converted into potassium sulphate if tartar had been employed). The mordanting bath is prepared with the necessary quantities of aluminum sulphate and tartar (or its substitutes) and the wool is entered at a low temperature. During one to one and a half hours the bath is heated gradually to boiling and boiled for half an hour more. When the bath has cooled down the wool is taken out and thoroughly washed in water; boiling out with water is beneficial. It has been shown that washing is absolutely necessary to remove all loosely adhering mordants and to prevent rubbing of the ultimate color. The washing, moreover, removes some of the acid, which is absorbed by wool, and would be injurious in dyeing. The washed wool is ready for dyeing; it should not be allowed to dry, as it is then very difficult to wet out again."

In the chapter on mordants Herzfeld¹ says: "It is well known that wool has acid and basic properties; the latter [?] enables it, when boiled in a bath of aluminum sulphate, to decompose the salt and to precipitate basic salt or alumina on the fiber. This takes place very rapidly and the precipitate is not properly adsorbed by the fiber. The precipitation takes place more slowly and more regularly if organic acids are present, wherefore oxalic acid, lactic acid, tartar, or something similar, is always added when mordanting wool. These counterbalance the effect of the mineral acid set free in the process."

Beech² discusses the mordanting of wool. "The mordanting method is one of the most generally useful. It consists in first causing a combination of the metal with the wool fiber. This is carried out by boiling the wool in a solution of the metal, such as bichromate of potash, chrome alum or chrome fluoride, when chrome is to be used as a mordant, with alum or sulphate of alumina when alumina is required to be deposited on the fiber, and with copperas when iron

¹ "Das Färben und Bleichen der Textilfasern," 58 (1900).

² "The Principles and Practice of Wool Dyeing," 71 (1902).

is to be the mordant. It is best to add a little oxalic acid, cream of tartar or tartaric acid to the mordanting bath, which addition helps in the decomposition of the metallic salt by the wool fiber, and the deposition of the metallic oxide on the wool. With bichromate of potash, sulphuric acid is often used, much depending upon the character of the mordant required. Some dye-stuffs, such as logwood for blacks, work best when the wool is mordanted with chromic acid, which is effected when sulphuric acid is the assistant mordant. Other dye-stuffs, such as fustic, Persian berries, and alizarine yellow, are best dyed on a basic chrome mordant, which is effected when tartar or oxalic acid is the assistant mordant used, or when some other form of chrome compound than bichromate is employed.

"The actual mordanting is done by boiling the wool in a bath of the mordant, the quantity of which should be varied according to the particular mordant that is being employed and to the quantity of dye-stuffs which is to be used. It is obvious that for fixing a deeper shade of, say, alizarine on the wool, a larger quantity of mordant will be required than to fix a pale shade; sometimes this point is overlooked and the same amount of mordant employed for pale or deep shades. The best plan of carrying out the mordanting is to enter the wool in the cold bath or at a hand heat, and then raise to the boil and continue the boiling for one hour; of course the goods should be kept turned over during the process to facilitate the even mordanting of the wool. A great deal of the success of dyeing with the dye-stuffs now under consideration depends upon the efficiency with which the mordanting has been carried out. If this is at all unevenly done, then no amount of care in the succeeding dyeing process will lead to the development of an even dyeing. After the mordanting is finished, the goods should be rinsed with water, but it is not necessary to dry them."

These results are exactly what one can predict according to the adsorption theory of mordanting because the theory was designed with that in mind. The more basic the solution

the greater the hydrolysis and the more rapid the precipitation. Consequently so-called basic solutions cannot be used with wool. While aluminum sulphate does not hydrolyze so much as the aluminum salt of a weaker acid, the coagulating effect of sulphate causes the alumina to precipitate more rapidly and in a less satisfactory form. Addition of sodium sulphate increases the concentration of sulphate and makes matters worse. Addition of sulphuric acid tends to work both ways. The increase in acidity cuts down the hydrolysis and tends to prevent precipitation of alumina. Increase in the sulphate concentration tends to increase the rate of coagulation. The effect due to the increasing acidity is the more important one and consequently an aluminum sulphate solution, acidified with sulphuric acid, works better than an aluminum sulphate solution which has not been acidified at all, and very much better than an aluminum sulphate solution to which sodium sulphate has been added. If we acidify with an organic acid the two factors work together, because the organic acid acts as a peptonizing agent on alumina instead of peptizing it as sulphates do. Those organic acids are the most satisfactory which are the most effective in preventing rapid coagulation of the alumina. It is worth while to compare the three quoted statements in regard to this point. Knecht, Rawson and Loewenthal say that the aluminum salts of oxalic and tartaric acids possess a certain resistance to the dissociating action of wool, which is not true because these salts hydrolyze considerably more than the sulphate. Beech says that addition of oxalic acid, cream of tartar or tartaric acid to the mordanting bath helps in the decomposition of the wool salt by the wool fiber, which is not true, because increasing the acidity cuts down the hydrolysis. Herzfeld is perfectly right in saying that precipitation takes place more slowly and more regularly if organic acids are present; but this is not especially helpful because he does not make any attempt at an explanation why organic acids should have such an effect. Instead of this jumble of contradictory explanations, the adsorption theory straightens the whole matter

out; what happens is just what one would expect from a knowledge of the chemistry of the reacting substances. What has been said about oxalic and tartaric acids applies with suitable modifications to formic acid¹ and to lactic acid.²

Having taken up the case of alumina mordant in such detail, it hardly seems necessary to discuss the other metallic mordants now. The same principles are involved and the slight differences in behavior do not seem to present anything new.³ The difference between the mordanting of wool and of cotton is what one would expect from the lesser adsorbing power of cotton. With cotton the solutions must be more basic and the use of a fixing agent for the mordant is more important.

There is one more point about alumina mordants which I wish to establish before bringing this first paper on mordants to a close. The brilliancy of a mordanted color will depend very largely on the transparency of the mordant. The most brilliant colors are obtained with a tin mordant⁴ apparently because this mordant is the most transparent. Cajar⁵ finds that when soda is added to a cold aluminum sulphate solution, the precipitate is white and has a distinct covering power. If the precipitate is heated or if soda is added to a hot solution the precipitate is more transparent. This is in line with the general fact that precipitates are less amorphous and more crystalline the higher the temperature of precipitation⁶ provided the other conditions are kept the same. Raising the temperature of the mordanting bath therefore gives a more transparent mordant. It also helps to fix the mordant better on the fiber; but that is a point which can be postponed until I take up the whole question of fastness of dyes.

Since we get a more transparent mordant by raising the

¹ Boehringer and Soehne: *Zeit. Farbenindustrie*, **9**, 237, 353 (1910).

² Schwalbe: *Zeit. Kolloidchemie*, **5**, 129 (1909).

³ Liechti and Suida: *Jour. Soc. Chem. Ind.*, **5**, 526 (1886).

⁴ Herzfeld: "Das Färben und Bleichen der Textilfasern," 73 (1900); Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 276 (1910).

⁵ *Zeit. angew. Chem.*, **24**, 793 (1911).

⁶ Cf. Owens: *Jour. Phys. Chem.*, **18**, 461 (1914).

temperature of the bath, the question arises whether it might not be better to raise the temperature still more if possible or to keep the bath longer at the boil. This might be desirable if transparency were the only thing to be considered. It so happens that another factor comes in. At high temperatures the alumina becomes denser, presumably losing water, and loses its mordanting powers.¹ This fact is recognized by practical dyers² "Goods which have been impregnated with the acetates and sulphate-acetates must not be dried at high temperatures, since these compounds are most readily dissociated on the fiber by heat, when acetic acid escapes and the base remains on the fiber in a form which renders it less capable of combining with the coloring matter in the subsequent dye-bath; poor and irregular colors would thus result. This fact may be due to the generation of aluminum oxide instead of the hydroxide, as shown by either of the following equations:

Another explanation is that a basic acetate or a less hydrated aluminum hydroxide is formed, neither of which forms color lakes. Mordants that have been spoiled by overheating are said to have been burned."

The general results of this paper are as follows:

1. A mordant is a substance which is adsorbed strongly by the fiber and which adsorbs the dye strongly.
2. There is no evidence that any definite compounds are formed when the metallic mordants are taken up by wool, silk or cotton.
3. The difference between the behavior of wool and of cotton is merely one of degree.
4. Aluminum salts hydrolyze more or less completely

¹ Cf. Crum: *Jour. Chem. Soc.*, 6, 227 (1854).

² Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2nd Ed., 235 (1910).

when dissolved in water, the change being more rapid at high temperatures.

5. When aluminum salts hydrolyze, or when small amounts of sodium carbonate are added to the solution, colloidal alumina is one of the reaction products.

6. With aluminum acetate the hydrolysis is so rapid that no considerable amount of normal acetate is formed when equivalent solutions of aluminum sulphate and lead acetate are mixed.

7. Coagulated alumina causes so-called aluminum acetate to hydrolyze further and hydrous ferric oxide has a similar effect on ferric chloride.

8. The fact that aluminum chloride will hold in solution more alumina than it can carry into solution is proof that we are not dealing with a definite basic salt.

9. The solutions used by Liechti and Suida did not contain the basic salts that were supposed to be there.

10. Since Liechti and Suida did not approximate equilibrium conditions in their mordanting experiments, the results are too uncertain to have any value.

11. The metallic mordants are hydrous oxides and not basic salts.

12. The rate of coagulation is more important than the degree of hydrolysis.

13. Normal and so-called basic aluminum sulphates coagulate too readily to be satisfactory with wool.

14. Addition of sodium sulphate increases the rapidity of coagulation from normal or basic aluminum sulphate solutions.

15. Addition of sulphuric acid retards the coagulation of alumina; addition of organic acids is still more helpful.

16. The upholders of the chemical theory of dyeing give diametrically opposed explanations for the action of organic acid.

17. More transparent mordants are obtained from hot solutions than from cold solutions; but they have less mordanting power.

18. Alumina mordant may be taken as a typical basic mordant. What is true of this is true of the other mordants with slight and obvious changes.

19. The differences in the mordanting of wool and of cotton are what would be expected from the lesser adsorbing power of cotton.

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