

MORDANTS. II

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ALUMINA

Hydrolysis of Aluminum Salts

Over a century ago, Gay-Lussac¹ found that if one heats a solution of aluminum acetate, it soon becomes turbid and a large amount of alumina precipitates. If the solution is allowed to cool, the precipitate dissolves slowly and becomes transparent. On the reheating and recooling these changes repeat themselves and this can be kept up indefinitely. With a dilute solution of aluminum acetate the turbidity begins at about 50° and a precipitate forms at a little higher temperature. The precipitate must change gradually because it dissolves more slowly, when the solution is cooled, the longer the heating has lasted. With a more concentrated solution of aluminum acetate the temperature must be raised somewhat higher before turbidity occurs; but this solution also clears up when cooled.

“To determine the amount of alumina precipitated from an acetate solution by heating and the variation with the temperature, there were taken two equal portions of aluminum acetate made by mixing in the cold two solutions of alum and of lead acetate. One of these portions was raised to the boiling-point and filtered at once, while the other portion was precipitated by ammonia. The two precipitates were washed and dried; after which it appeared that the first weighed about half as much as the second.

“These observations may be very important for the makers of dyed fabrics for they use the hot solutions of alum and lead acetate in order to get as concentrated solutions of the mordant as possible. A great deal of alumina must precipitate, and the loss will be considerable if the solution is filtered at once. To

¹ *Annales de Chimie*, **74**, 193 (1810).

avoid this it is necessary to let the solution cool completely before filtering or decanting off the mother liquor, and it is also necessary to stir vigorously so as to be certain that all the alumina redissolves. Unless these precautions are taken, the aluminum acetate will be very acid, which is probably the reason for usually adding chalk. It is nevertheless easy to prevent the precipitation of alumina when an aluminum acetate solution is heated, by adding alum. As is well known, alum dissolves alumina and therefore keeps the solution of aluminum acetate from becoming turbid. A large excess of acid will accomplish the same result."

"The precipitation of alumina on boiling and the redissolving at a lower temperature are facts which are of interest to the general theory of chemistry and which are rather exceptional. If the precipitation were due to volatilization of the acetic acid, the alumina would not redissolve when the temperature is lowered. As a matter of fact similar changes can be observed in a strongly acid solution or in hermetically sealed flasks. Since the precipitation does not depend on the volatilization of the acid, it is evident that it is due to the heat which wrenches apart the molecules of acid and alumina, carrying each out of the sphere of action of the other, and causing their separation. With less heat the same molecules come within each other's sphere of activity and combine."

Gay-Lussac is practically saying in other words what we now designate as reversible hydrolysis. In 1854 Crum¹ prepared colloidal alumina from a weaker and more basic solution than that used by Gay-Lussac. "By the continued action of heat on a weak solution of binacetate of alumina, $\text{Al}_2\text{O}_3 \cdot (\text{CH}_3\text{CO}_2)_4(\text{OH})_2$, 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 one part of alumina in two hundred of water, was

¹ Jour. Chem. Soc., 6, 225 (1854).

placed in a closed 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 one-eleventh of its original quantity of acetic acid, or about one equivalent to five and a half of alumina."

The theory of this is very simple. Water will hydrolyze any salt until the product of the concentrations of the hydrogen and hydroxyl ions reaches a value of about 10^{-14} . If either base or acid is very sparingly soluble, the hydrolysis will run farther than if both are strong electrolytes. Equilibrium will be reached much more rapidly if the solution is heated. Whether the insoluble base precipitates or remains in colloidal solution will depend on the conditions of the experiment. That hydrolysis has taken place can be shown in a number of different ways. Gay-Lussac deduced it from seeing the precipitated alumina and Crum from the change in the taste of the solution. One could measure the change in acidity in other ways than by the sense of taste. Debray¹ showed that if a dilute solution of ferric chloride is heated to 70° it no longer reacts with potassium ferrocyanide to form Prussian blue. The reason for this is that there is no more ferric salt in solution, it having been converted completely into colloidal ferric oxide. Colloidal ferric oxide is not blackened by hydrogen sulphide. On the other hand it is precipitated from apparent solution either by sodium sulphate or by sulphuric acid, a behavior which is distinctly not characteristic of ferric chloride. Wiedemann² has used the magnetic properties as a means of following the hydrolysis, because the atomic magnetism of the iron in colloidal ferric oxide is only one-fifth that of the iron in a strongly acid

¹ *Comptes rendus*, **68**, 913 (1869).

² *Pogg. Ann.*, **135**, 218 (1868); *Wied. Ann.*, **3**, 45 (1878).

solution of ferric chloride. Colloidal solutions of the hydrous oxides can be obtained by hydrolysis of the acetates, nitrates, or chlorides; but not in general by hydrolysis of sulphates, because sulphuric acid precipitates the colloidal solutions more readily than does hydrochloric, nitric, or acetic acid.

In 1883 Liechti and Suida published some work on the hydrolysis of solutions of aluminum salts. Their original paper is not in the John Crerar Library, the Library of Congress, or the Library of the Franklin Institute. I have therefore made use of the lengthy abstract by J. J. Hummel.¹ With aluminum sulphate ($\text{Al}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 200 g per liter) there was no visible hydrolysis on heating or on diluting. With $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$ made from 200 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 31.82$ g Na_2CO_3 per liter, there was no visible change on heating; but a precipitate formed when the solution was diluted fourteenfold. With a solution three-quarters as concentrated, there was no visible change on heating, but dissociation took place on diluting tenfold. Since three-fourths of fourteen is ten and a half, this shows the error in determining the beginning of visible hydrolysis. With $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$, made from 200 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 45.7$ g NaHCO_3 per liter a jelly was formed on heating and a precipitate remained on cooling. Diluting to one-half caused a precipitate to appear in the cold. With $\text{Al}_2(\text{SO}_4)(\text{OH})_4$, made from 300 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 151.3$ g NaHCO_3 per liter, the solution kept only a short time. The general results are that hydrolysis takes place more readily on heating and on diluting, the more basic the solutions. The statement is made that sodium sulphate accelerates the dissociation. If this is true, it must be because the sodium sulphate decreases the hydrogen ion concentration by reacting with the sulphuric acid to form acid sodium sulphate. Since sodium sulphate coagulates colloidal alumina, it may be that it has practically no effect on the hydrolysis; but causes the precipitate to become visible sooner. In other places Liechti

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

and Schwitzer¹ say that they have proved that sodium sulphate retards the decomposition. There must be a misprint somewhere. A retarding of the decomposition would be more in line with the observation by Schmid² that sodium sulphate retards the precipitation of alumina by sodium carbonate.

With what they call a sulpho-acetate, $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_4$, made from $200 \text{ g } \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 227.6 \text{ g } \text{Pb}(\text{CH}_3\text{CO}_2)_2$ per liter, a precipitate formed on heating to 90° and a jelly on heating to 100° . The solution cleared up on cooling. There was no precipitate on diluting sixtyfold. On adding sodium bicarbonate to this so-called sulpho-acetate, Liechti and Suida obtained solutions of what they called basic sulpho-acetates, from $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)_3(\text{OH})$ down to $\text{Al}_2(\text{SO}_4)(\text{CH}_3\text{CO}_2)(\text{OH})_3$. There is no real reason for assigning these formulas to these solutions. In the first place there is no obvious reason why the sodium bicarbonate should take acetate rather than sulphate out of the aluminum salt. It would be distinctly more reasonable to consider the basic compounds as varying from $\text{Al}_4(\text{SO}_4)(\text{CH}_3\text{CO}_2)_4(\text{OH})_2$ to $\text{Al}_2(\text{CH}_3\text{CO}_2)_3(\text{OH})_3$. Probably the reason for not doing this was that these solutions did not behave like basic acetate solutions obtained by adding sodium bicarbonate to aluminum acetate; but that does not prove anything because these latter solutions do not contain sodium sulphate. In the second place there is no reason to suppose that Liechti and Suida ever had a sulpho-acetate solution. The so-called sulpho-acetate solution was undoubtedly merely a mixture of $\frac{1}{3} \text{Al}_2(\text{SO}_4)_3$ and $\frac{2}{3} \text{Al}_2(\text{CH}_3\text{CO}_2)_6$. Similarly there is no satisfactory evidence of the existence of any of the alleged basic compounds. They may perfectly well have been aluminum sulphate or aluminum acetate or a varying mixture of both with peptized alumina. Liechti and Suida undoubtedly thought they were dealing with true basic salts because of

¹ Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, **3**, 59, 60 (1886).

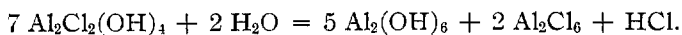
² Jour. Soc. Chem. Ind., **14**, 654 (1895).

their getting an apparent solution; but it is quite evident even from the abstract that they know nothing about colloidal solutions. The formulas which are written therefore indicate the relative amounts of sodium bicarbonate which have been added to the original solution and nothing more than that. This point seems to have been overlooked by all the people who have discussed this work.

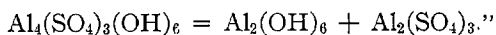
The so-called basic sulpho-acetates all formed jellies on heating and all formed precipitates on dilution, the temperature at which the first turbidity occurred being lower the more basic the solution. Less water had to be added to cause precipitation as the solution became more basic. With straight aluminum acetate, made from $200 \text{ g Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 341.4 \text{ g Pb}(\text{CH}_3\text{CO}_2)_2$ per liter, there was no turbidity on heating and no precipitation on cooling. This result does not contradict that of Gay-Lussac because he was working with a more dilute solution. All the so-called basic aluminum acetates formed precipitates or jellies on heating which did not dissolve when the solutions were cooled. The one with the alleged formula $\text{Al}_2(\text{CH}_3\text{O}_2)_4(\text{OH})_2$ precipitated on dilution; but the more basic ones did not. This may only be a question of a time factor. If not, sodium acetate must peptize alumina strongly.

By adding sodium carbonate to aluminum chloride, solutions were obtained having the analytical compositions, $\text{Al}_2\text{Cl}_5(\text{OH})$, $\text{Al}_2\text{Cl}_4(\text{OH})_2$, $\text{Al}_2\text{Cl}_3(\text{OH})_3$, $\text{Al}_2\text{Cl}_2(\text{OH})_4$. None of these solutions become turbid either on heating or on diluting. Liechti and Suida were not able, however, to make these alleged solutions synthetically. "The solubility of aluminum hydrate in aluminum chloride was tested, and the following remarkable 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 proved 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:



We know that hydrous ferric oxide, if present in excess, will remove from suspension all the chromic oxide¹ peptized by caustic alkali; but nobody has studied the removal from suspension of a substance by an excess of itself, unless perhaps we have such a case in the Bayer process for the purification of alumina. Since Liechti and Suida were obsessed with the idea of basic compounds, they made no experiments to see whether addition of sodium chloride would cause more alumina to go into apparent solution. According to Schmid² sodium sulphate retards the precipitation of alumina.

A whole series of so-called basic nitrate solutions were made up by adding sodium bicarbonate to aluminum nitrate solutions. None of these solutions became turbid either on heating or on dilution. The sum total of all these experiments is that basic aluminum acetate solutions hydrolyze very readily because the resulting acetic acid is a weak acid; that basic aluminum sulphate solutions become turbid because of the coagulating action of the sulphates, this more than counterbalancing the effect due to the strength of sulphuric acid; and that basic aluminum chlorides and nitrates do not become markedly turbid because the acids are strong ones having low coagulating powers.

Although Liechti and Suida got no cloudiness with their

¹ Nagel: Jour. Phys. Chem., 19, 331 (1915).

² Jour. Soc. Chem. Ind., 14, 654 (1895).

aluminum sulphate solution on heating, that may have been a question of concentration or of time for Naumann¹ reports that "when a solution of potash alum is heated to the boiling point of water, a white precipitate is formed, which, after washing with water, is an amorphous powder, with an admixture of glittering laminae, and dissolves with difficulty in strong hydrochloric acid, but easily in potash. The precipitate contains 31.2–32.6 percent of alumina, about 11 percent of potash, 30–40 percent of sulphuric acid, and water; and is therefore a more or less basic compound of alumina, potash, and sulphuric acid, with water. It was found that with pure alum solutions the decomposition was most rapid at first, gradually becoming less for equal intervals of time, so that a state of equilibrium in the liquid was reached only after a very long time. Dilution of the solutions favored decomposition. Free sulphuric acid, added to alum solutions, prevented the decomposition, partially or entirely, according to the amount added. Neutral potassium sulphate, on the contrary, expedited the decomposition."

There is a good deal of uncertainty as to what compounds are formed when salts of aluminum are boiled or are treated with soda. Cajar² states that the action of soda on cold aluminum sulphate solution gives a white precipitate which covers well; whereas a more transparent precipitate is obtained when the soda is added to a hot sulphate solution. Underwood³ states that alumina precipitated cold with sodium carbonate contains basic sulphate and dries soft and powdery; but that it dries horny when precipitated hot. Jennison⁴ says that the hydrate of aluminum, $\text{Al}_2(\text{OH})_6$, "is produced when caustic soda or potash, ammonium hydrate or carbonated alkalies is added to a solution of an aluminum salt; it is soluble in caustic alkalies, and therefore is usually obtained by

¹ Ber. deutsch chem. Ges., **8**, 1639 (1875); Jour. Chem. Soc., **29**, 682 (1876).

² Zeit. angew. Chem., **27**, 793 (1911).

³ Underwood and Sullivan: "Printing Inks," 81 (1915).

⁴ "The Manufacture of Lake Pigments from Artificial Colours," 51 (1900).

means of the carbonates. When produced from cold, dilute solutions, it is of a transparent, gelatinous nature; but, on heating, becomes opaque and more contracted in bulk. With carbonated alkalies it is much denser and is very lumpy, owing to the reaction being incomplete. Aluminum hydrate when dried, forms a hard, white, horny substance, which has the composition of $\text{Al}_2(\text{OH})_6$, and only on ignition is the whole of the water driven off, leaving Al_2O_3 ."

According to Knecht, Rawson and Loewenthal¹ a crystallized basic sulphate, $\text{Al}_2(\text{SO}_4)_2(\text{OH})_2$, has been placed on the market by Messrs. Peter Spence and Co., Ltd. Schlumberger² claims that there is one basic sulphate of aluminum. On adding 4.5 mols of caustic potash to a solution containing one mol of aluminum sulphate, the supernatant liquid was still distinctly acid. On adding 5 mols KOH the solution was neutral and contained no aluminum salt. On adding 6 mols KOH the supernatant liquid was alkaline and contained some alumina, presumably as potassium aluminate. The precipitate must therefore analyze for $(\text{Al}_2\text{O}_3)_2\text{SO}_3 \cdot x\text{H}_2\text{O}$ where x is not less than six. Actually it came out seven, so Schlumberger writes the formula of the basic salt $(\text{Al}_2\text{O}_6\text{H}_6)_2 \cdot \text{H}_2\text{SO}_4$. Of course, it will be noticed that he analyzed a precipitate obtained only under one set of conditions. While it may be that he was dealing with a definite compound, there is nothing in his experiments to prove it. He should have analyzed the precipitate after adding three or four mols of caustic potash and have shown that it had exactly this same composition. Then his results could have been accepted as proving something. This is the more necessary because many basic aluminum sulphates are to be found in the books.³ Böttinger contributes a new one of his own by evaporating repeatedly to dryness a mixture of aluminum sulphate and sodium chloride at 130° – 140° . This one analyzes for $\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$ or

¹ "A Manual of Dyeing," 225 (1910).

² Bull. Soc. chim. Paris, [3] 13, 41 (1895).

³ Böttinger: Liebig's Ann., 244, 224 (1888).

$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ if we adopt Schlumberger's way of writing the formula.

Adsorption of Aluminum Sulphate by Wool

Since the different salts of aluminum hydrolyze of themselves under suitable conditions, they should hydrolyze even more readily in presence of a textile fiber which adsorbs the alumina and they do as a matter of fact. In so far as the acid radical is also adsorbed, there may be minor complications and the matter may seem less simple than it really is.

When wool is treated with aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, less than about five percent on the wool, the bath is exhausted completely, all the alumina and all the sulphuric acid being taken up.¹ With higher concentrations, more and more aluminum sulphate is left in the bath. There has been some discussion whether the wool takes up aluminum sulphate or alumina and sulphuric acid in the cases when the bath is exhausted completely. When wool mordanted in this way is boiled with water, the wash water is always acid, sulphuric acid being removed slowly and alumina left behind. This has been considered by von Georgievics² as a proof that the sulphuric acid is free. While this may be true, it does not follow, because the adsorbed aluminum sulphate might be hydrolyzing. It is much wiser to admit frankly that we have no way at present of deciding this point. In case the acid is not combined in definite proportions, the next problem is whether it is adsorbed by the alumina, by the wool, or by the two in some unspecified ratio.

Ganswindt³ gives some data by Fürstenhagen and Appleyard⁴ on the mordanting of wool by potash alum, which are reproduced and extended in Table I.

¹ Liechti and Schwitzer: Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, 3, 47 (1886).

² Chem. Centralblatt, 1895, 402; Binz and Rung: Zeit. angew. Chem., 1908, 628.

³ "Theorie und Praxis der modernen Färberei," II, 83 (1902).

⁴ Jour. Soc. Dyers and Colourists, 1888, 105.

TABLE I
25.4% sulphuric acid in potash alum.

Potash alum referred to wool	Sulphuric acid referred to potash alum		Sulphuric acid referred to wool	
	Wool percent	Solution percent	Wool percent	Solution percent
5	25.4	0.0	1.27	0.0
10	22.1	3.3	2.21	0.3
15	14.6	10.8	2.19	1.6
20	11.0	14.4	2.20	2.9

In the first column are the amounts of potash alum referred to the weight of wool. In the second and third columns are the percentages of sulphuric acid in the total amount of alum in the wool and the bath respectively. At 5% alum all the sulphate is taken up, but with higher concentrations of alum more of the sulphuric acid stays in the bath. Since determinations on the alumina adsorption are not given, we cannot tell to what extent alumina is adsorbed more than sulphuric acid. Since this method of presentation is not the usual one, I have added two columns to show the percentage of sulphuric acid referred to wool, taken up by the wool and left in the bath respectively. If these figures are to be trusted, the amount of sulphate adsorbed by the wool is practically constant when the bath contains 10%–20% alum referred to the wool. It is probable that this is not strictly true.

Knecht¹ comments on these data as follows: "It is a prevalent opinion that when wool is boiled with aluminum sulphate, for instance, the salt is decomposed by the fibre in such a manner that aluminum hydrate and sulphuric acid are formed, of which the former is assimilated by the fibre, while the latter remains in solution. Others again assume that an insoluble basic sulphate of alumina is formed on or in the fibre. Quantitative determinations, carried out by Fürsténhagen and Appleyard, show that when wool is boiled with a solution of alum no free acid remains in solution when the

¹ Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 58 (1910).

amount of alum does not exceed five percent of the weight of the wool. When larger amounts are used, a basic sulphate of alumina is fixed on the fibre. Now it has always been shown that wool possesses a considerable affinity for both acids and bases, and, in its whole behavior it evidences the properties of an amido acid—that is a substance possessing simultaneously basic and acid properties. This would explain in a satisfactory manner the fixation of both the acid and basic constituents of the alum, but in what form these are fixed still remains a matter of conjecture. It is not improbable that the phenomenon is due to actual chemical combination with the fibre or with certain constituents of the latter; just as lead or mercury, when absorbed by the system, enters into chemical combination with the albuminoids in the various organs. That a hydrate is not formed is conclusively shown in mordanting wool with copper salts. The fibre assumes a green color; but copper oxide, when boiled, is at once dehydrated and transformed into black copper oxide. If copper hydrate had been formed, the fibre would be black whereas it is green, and remains so even after prolonged boiling.”

It has already been shown that Fürstenhagen and Appleyard have not proved by quantitative determinations that a basic sulphate of alumina is fixed on the fibre. They have proved that both alumina and sulphuric acid are taken up by the fibre; but nothing more. Knecht seems to realize this unconsciously because he himself admits that it remains a matter of conjecture in what form the acid and basic constituents of the alum are fixed. That is true; but that is quite a different thing from showing that a basic aluminum sulphate is fixed on the fibre. Knecht's argument in regard to the copper hydrate is fallacious because hydrous copper oxide does not necessarily turn black when heated to 100°. Tommasi¹ showed that when a little hydrous manganous oxide is precipitated with the hydrous copper oxide, the latter does not turn

¹ Bull. Soc. chim. Paris, [2] 37, 197 (1882); Comptes rendus, 99, 37 (1884).

black when boiled. Blucher and Farnau¹ found that a similar stabilization of the blue color could be obtained by adding hydrous oxides of nickel, cobalt, aluminum, chromium, and magnesium. With zinc there was some stabilization but practically none with mercury. If the blue color is due to the state of subdivision of the copper oxide, anything which will prevent it from agglomerating will keep it blue. Schenck² has shown that a mixture of the oxides of copper and alumina containing about five percent copper oxide can be heated in a blast lamp without turning black. Owing to the lower copper content the color is a light grayish blue. With ten percent copper oxide, the blue color was deeper and withstood heating in a Bunsen burner but showed signs of turning black when heated in the blast lamp. During the winter of 1920-21 Mr. R. K. Parsell repeated Mr. Schenck's experiments and, after heating, dissolved out as much alumina with caustic soda as he could without getting any blackening. In this way he was able to get a powder which was a beautiful deep blue and which contained approximately seventy-five percent cupric oxide and twenty-five percent alumina. If one insisted on writing a formula for this, it would be approximately $(\text{CuO})_4 \text{Al}_2\text{O}_3$ which is rather absurd. There are not only no indications of a definite chemical compound; but, after standing for a year the powder has changed from blue to green. We do not know whether it will go black in time or not.

According to Havrez³ and to von Georgievics⁴ the amount of sulphuric acid taken up by wool from an aluminum sulphate or an alum bath increases relatively to the wool at high concentrations until at twenty-four percent alum referred to the wool, the alumina and the sulphuric acid are taken up in the same relative amounts as they occur in aluminum sulphate.

¹ Jour. Phys. Chem., **18**, 629 (1914).

² Ibid., **23**, 283 (1917).

³ Chem. Centralbl., **1874**, 696; Cf. Liechti and Hummel: Jour. Soc. Chem. Ind., **13**, 226.

⁴ Jour. Soc. Chem. Ind., **14**, 653 (1895):

At higher temperatures, relatively more sulphuric acid is taken up. I have never seen the original data and the abstracts are confusing and to some extent contradictory. Havrez¹ claims that with high alum concentration, the peptizing action of the alum on the alumina is so great that less alum is taken up than at lower concentrations. If this is true, the amount of alumina adsorbed passes through a maximum. On the other hand he apparently based his conclusion on the fact that wool mordanted in concentrated alum solutions did not dye to so deep a shade and this may be an effect of the sulphate taken up. Liechti and Hummel, however, "disagree with his assertion that an excess of alum acts like an acid which dissolves the alumina." Dreaper² who gets Havrez's name wrong, says that "Harvey pointed out in 1872 that in the case of very concentrated solutions of alum, more sulphuric acid than alumina is absorbed. This has been recently confirmed by von Georgievics. It appears that with a 24 percent solution of alum [referred to wool], and a proportion of water fibre of 30:1 alumina and sulphuric acid are taken up in their normal proportions. The affinity of wool for acid is stronger in dilute solutions and stronger for the alumina in strong solutions. The relative curves cross each other at 24 percent." There must be a misprint in the next to last sentence of this quotation, the words acid and alumina being transposed.

Havrez³ states, and Liechti and Hummel confirm him that addition of acid (presumably sulphuric acid)⁴ is beneficial with such low concentrations of alum as one percent on the wool. Since all the alumina is taken up at these concentrations, the object of adding the acid cannot be to increase the adsorption. The statement is made that with low concentrations of alum the bath becomes alkaline, in which case the

¹ Jour. Chem. Soc., 26, 206 (1873).

² "The Chemistry and Physics of Dyeing," 62 (1906).

³ Jour. Soc. Chem. Ind., 13, 226 (1894).

⁴ Cf. Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 237(1910).

acid is added to counteract this. It is not clear whether the alkalinity is due to lime in the wool reacting with sulphuric acid, to ammonia going out from the wool, or to a partial adsorption of sulphuric acid from the potassium sulphate of the alum. This last hypothesis could be tested by running similar experiments with aluminum sulphate. Liechti and Suida¹ state that alum is not quite as good a mordant as aluminum sulphate, though the difference is not marked. This may seem to contradict their alleged previous statement that sodium sulphate increases the hydrolysis of aluminum sulphate on boiling; but the contradiction disappears if we postulate, which seems reasonable, that the sodium sulphate, though increasing the hydrolysis of the aluminum sulphate, also increases the relative amount of sulphuric acid taken up by the wool. The first would be beneficial and the second harmful and we do not know to what extent the two balance, or even whether this is the true explanation.

One objection to alum or aluminum sulphate as a mordant is that the sulphate coagulates the hydrolyzed salt so readily that very perceptible amounts of alumina or of basic salt are precipitated in the bath or on the wool in such a form that it rubs off. It seems as though this could be got round by heating the solutions more slowly. A simpler method of getting round this difficulty is to use aluminum salts of organic acids, which hydrolyze more readily than the sulphate because the acids are weaker, and yet which keep the colloidal alumina peptized in a finer form.

Adsorption of Aluminum Tartrate, etc., by Wool

This was done more than a century ago by adding tartar (acid potassium tartrate) to a solution of alum.² "To impregnate wool or woollen cloth with the aluminous basis, it is commonly boiled in water, with from one-fourth to one-sixth of its weight of alum, and from one-twelfth to one-sixteenth of its

¹ Jour. Soc. Chem. Ind., 5, 526 (1886).

² Bancroft: "Philosophy of Permanent Colours," 1, 384 (1813).

weight of crude tartar, putting the latter first into the water, and, afterwards, the powdered alum: the heat of the water being gradually raised, is kept at the boiling point for an hour and a half, or two hours, during which the cloth is turned through the boiling liquor on a winch, that the mordant may be equally applied; and being afterwards taken out and drained, it is commonly left until the next day, and then rinsed in clean water, for dyeing. In the early collection of recipes, printed in 1605, and already mentioned, sour bran liquor is commonly directed to be employed in this way with alum; and it seems to have answered the purpose of tartar, which, when it came to be generally used in this way with alum; was supposed by the older dyers to do good by softening and correcting the acrimony of the latter: probably, however, the purposes which it answers, are not yet clearly ascertained; one of them seems to be, that of increasing the solubility of alum, and enabling it more completely and intimately to penetrate the fibres of the wool, with which it moreover enters into a permanent union, and thereby contributes efficaciously to modify, vary, and in some cases to brighten the colours with which it is employed, as will be seen hereafter."

Liechti and Suida¹ have studied the behavior of aluminum tartrate. Starting with an amount equivalent to eight percent aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$, referred to the wool, the whole of the alumina was fixed firmly on the wool. On treating the wool with hot water, the wash water became acid, showing that some tartaric acid was also taken up. The normal tartrate can be replaced without detriment by a mixture of one molecular weight of aluminum sulphate with 1.5–3.0 molecular weights of cream of tartar. If the normal tartrate is prepared by double decomposition, using the normal potassium sodium tartrate (Rochelle or Seignette salt) according to the equation,



¹ Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, 3, 48 (1886); Jour. Soc. Chem. Ind., 4, 526 (1886); Kaecht, Rawson and Loewenthal: "A Manual of Dyeing," 237 (1910).

the results were not as good as those obtained with the pure tartrate or with alum and tartar, in which latter case the bath contains some acid potassium sulphate in addition to the aluminum tartrate. "Since the general practical experience of dyers is that wool is better mordanted in an acid bath, it was thought possible, perchance, to replace the cream of tartar by an acid, sulphuric acid for instance. Experiment showed, however, that although a small addition of sulphuric acid (1 mol) increases slightly the amount of alumina absorbed by the fibre, it cannot replace the cream of tartar. Since the addition of a larger amount of sulphuric acid (3 mols) yields very unsatisfactory colors although it hinders the dissociation of the mordant solution, it is evident that the beneficial action of the cream of tartar cannot be ascribed merely to its retarding the dissociation of the mordant." The explanation undoubtedly is that the use of tartrate cuts down the degree of adsorption of the sulphuric acid.

"An experiment was made accordingly with a view to determining whether the tartaric acid used along with aluminum salts played the rôle of a carrier, so that it might be possible to use any free acid along with only a small quantity of tartaric acid. The result obtained, however, proved that the tartaric acid plays no such intermediary part in mordanting wool with aluminum salts; on the contrary, a considerable amount of tartaric acid must be present (at least half the theoretical amount necessary to form aluminum tartrate) in order to fix on the wool sufficient alumina to yield full, bright colours."

Knecht¹ evidently believes in starting with aluminum sulphate. "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 tartar or tartar substitutes is required to obtain full and brilliant colours which do not rub off. These tartar substitutes are mostly sodium bisulphate or oxalates, or they con-

¹ Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 238 (1910).

sist of tartar which has been prepared with sufficient sulphuric acid to convert all 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 of sodium, etc., with very good, although 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 fibre (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 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 colour. The washing, moreover, removes some of the acid, which is absorbed by the wool, and would be injurious in dyeing."

I am inclined to believe that accurate experiments will show that the presence of sulphate in the mordanting bath is probably always detrimental.

Aluminum oxalate behaves very much like aluminum tar-

trate but is not quite so good. According to Knecht¹ aluminum acetate decomposes too readily to be used for wool; but this can hardly be the whole truth. The use of lactic acid instead of tartaric acid has also been suggested.

Matthews² has rather a hard time with the theory of mordants, chiefly because he copies with but slight changes from Ganswindt's book published in 1903. "The mordanting of the animal fibres with metallic salts is probably for the most part a chemical process, the metallic salts or oxide forming a chemical compound with the substance of the fibre. It is usually considered in the case of mordanting wool, for instance, with metallic salts, that the metal is precipitated in the fibre as the oxide or hydroxide; in certain methods of printing, this may be the fact, but in the ordinary processes of mordanting wool for dyeing, it cannot be considered that the oxide of the metal is directly precipitated in the fibre. It is possible, for instance, to mordant the wool by boiling in a bath containing a solution of alum, squeezing, and then passing through a bath containing ammonia water; this would cause the precipitation of aluminum hydrate on and in the fibre as an insoluble body. As an actual fact, however, the mordanting is not done in this manner, but is carried out by boiling the wool with a solution of alum and tartar, which it cannot be presumed would lead to the precipitation of aluminum hydrate."

Even with Ganswindt to fall back on in silence, this paragraph is quite extraordinary; but the clue is to be found elsewhere. Matthews³ has evidently not understood any of the work of Liechti and Suida or of Knecht because he enters into an elaborate explanation that sodium chloride is dissociated electrolytically in water and thereby made more active, giving this as a help in understanding the theory of Knecht, although Knecht⁴ himself speaks of hydrolytic dissociation,

¹ Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 237 (1910).

² "Application of Dyestuffs," 602 (1920).

³ "Application of Dyestuffs," 588 (1920).

⁴ Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 15 (1910).

and the case that Matthews is discussing is the decomposition of rosaniline hydrochloride into the free base and hydrochloric acid, which is not a case of electrolytic dissociation.

Adsorption of Alumina by Silk

Silk behaves towards alumina mordants very much as wool does, though less intensely. Knecht¹ states that "in silk dyeing alum has not been replaced yet by aluminum sulphate² probably owing to the circumstance that slightly basic alum decomposes more readily than basic sulphate on account of the ammonium or potassium sulphate present. . . . Aluminum sulphate-acetate and nitrate-acetate are used in a similar way. . . . During the steeping process the silk absorbs basic sulphates or basic sulphate-acetates or nitrate-acetates. By the subsequent treatment with water or silicate of soda or soap the basic salts are decomposed and aluminum hydroxide is precipitated in the fibre." Heermann³ claims to have proved that, with silk, the basic mordants of aluminum, chromium, iron, and tin are present as hydrous oxides and not as basic salts. Heermann⁴ has discussed the various theories of mordanting and mentions favorably what he calls the catalytic theory according to which the fibers bring about the hydrolytic decomposition of the mordanting salts catalytically. It is easy enough to see what he has in mind, for the hydrolysis of the aluminum salts is increased by wool or silk; but this cannot properly be called catalytic because the fibre is not in the same condition after the process as before. It is mordanted.

Heermann also advances a theory of his own which he calls the ionatic theory of mordanting. He considers mordanting "as the electrolytic precipitation of certain ion complexes in consequence of the preponderating electro-affinity of the fibres (as opposed to that of the cations of the mordant) and

¹ Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 238 (1910).

² Both are used according to Gaiswindt: "Theorie und Praxis der modernen Färberei," II, 18 (1903).

³ Chem. Centralblatt, 1905, I, 128.

⁴ Ibid., 1904, II, 674.

in consequence of the [electrolytic?] dissociation of the mordant which is perhaps increased by the catalytic power of the fibres or of the cations of the mordant."

This can mean anything or nothing, so Heermann explains his views in more detail. "There are fibres of greater and lesser electro-affinity¹ and mordants of greater and lesser electrolytic dissociation. The affinity of a mordant to a fibre reaches its maximum when the greatest dissociation of the mordant coincides with the greatest difference between the electro-affinities of the fibre and of the ions of the mordant. The fibre, having the greater electro-affinity discharges successively the ions or ion-complexes of the mordant, since these have a lesser electro-affinity. The ion-complexes of the mordant, when thus discharged deposit themselves, while in the nascent, state, uniformly on the fibre and are at first held there in a labile state along with the acid. Washing removes most of the acid of the mordanting salt and the resulting base is fixed fast to washing." It is perhaps not surprising that no further use has been made of this theory even by the enthusiastic author.

Adsorption of Alumina by Cotton

Over a century ago it was pointed out² that "the attraction between aluminous basis and the fibres of linen and cotton is much weaker than that which subsists between the same basis and the fibres of wool and silk." The knowledge that alum cannot be used by itself to mordant cotton turns back to a very early period. Bancroft³ states that "when a solution of alum is applied to calico which has received no impregnation, it will not easily be decomposed; but, on the contrary, a great part of it will again crystallize, so soon as the water which held it in solution has evaporated; and none but feeble colours can be raised upon such a basis. But when calico has been impregnated by such astringent and animal matters as are ob-

¹ [He is referring to Bodländer and Abegg's theory of electro-affinity.]

² Bancroft: "Philosophy of Permanent Colours," 2, 148 (1813).

³ "Philosophy of Permanent Colours," 1, 357; 2, 242 (1813).

tained from myrobalans and buffaloes' milk, the alum will not only be decomposed, but the alumine will combine with the astringent and oily matters so obtained, and a basis will be laid for a colour almost as durable as the Turkey red."

"For the common madder red, linen or cotton, after being boiled in a weak lixivium of potash or soda, and well rinsed and dried, is to be macerated in a decoction of powdered galls, employed after the rate of four ounces to every pound of linen or cotton to be dyed; and being equally impregnated with the soluble matter of the galls and afterwards dried, the linen or cotton is to be alumed, by soaking it thoroughly in a saturated luke-warm solution of alum, employed also at the rate of four ounces to each pound of linen or cotton; after having previously neutralized the excess of its acidity, by adding to the solution one ounce of soda for every pound of alum: this being done, and the linen or cotton moderately and equally wrung or pressed, it is to be well dried, and afterwards alumed a second time, dissolving for that purpose half as much alum as for the first aluming, and adding to it the residue of the former solution. After this second aluming, the linen or cotton is to be again well dried, and then rinsed, to remove any superfluous part of the alum which may not have been united thereto. By substituting the acetate of alumine (formerly described) for the solution of alum, just mentioned, a more beneficial effect might be obtained; but it would be attended with a considerable increase of expense.

"The use of galls, in this operation, will be readily conceived, by recurring to what I have mentioned, at p. 356 and 357 of my first volume, concerning the effect of myrobalans, when employed by the Hindoos, in causing a more copious precipitation, and a more intimate union of the earth of alum, in or with the calico which had previously imbibed their astringent matter. That this is the only use of galls so employed, I presume, because I have found, by repeated trials, that when employed with madder in the dyeing operation, they add nothing to the durability of the colour.

"For every other purpose, except that of decomposing the alum, and increasing the precipitation of alumine, and, perhaps, its closer union with the fibres of cotton, galls appear to do harm rather than good with madder, by diminishing the vivacity of its colour, and giving it a brownish tinge, without the smallest increase of its durability; on the contrary, I have observed, that when calico printed with acetate of alumine was divided, and one half dyed with madder only, and the other with madder and galls, the colour of the latter, besides a considerable degradation, was injured by being boiled with soap and also by being exposed to the weather sooner, and in a degree considerably greater, than the half which had been dyed with madder only."

Napier¹ points out that "alum forms but a weak mordant for cotton goods, owing, probably, to the strong attraction which the sulphuric acid has for the alumina; there are three proportions of acid to every two of alumina. But if we neutralise a portion of the acid, so that no more remains than is necessary to hold the alumina in solution, which, according to experiment is not above a third of the acid contained in the common alum, its properties as a mordant are greatly improved. This may be done by taking a quantity of carbonate of soda in solution, and adding this gradually to the alum solution, stirring all the time: the alumina is at first precipitated but by keeping up the agitation, the precipitate again dissolves: continue until all the precipitate is redissolved. In this state alum is a more powerful mordant for cotton, as the base is held more feebly by the sulphuric acid and is readily detached by the superior affinity of the cloth to form a mordant; and thus prepared, it is perfectly pure—any iron formerly present is precipitated in the process. Alum in this state is known by the name of cubical or basic alum, from the form in which it crystallises. We have already referred to Roman alum being superior to other alums."

¹ "A Manual of Dyeing," 120 (1975).

Very recently Tingle¹ has claimed that alumina is not adsorbed by cellulose either from aluminum sulphate or basic aluminum sulphate solution. The first statement is not new and the second is probably not correct as a general one though it may be true for the particular experimental conditions. There is nothing to show that Tingle appreciated the necessity of having peptized alumina in his solution or that he did have it.

Aluminum acetate is usually used for mordanting cotton both in dyeing and printing.² "The most common, and we believe the best method of using alumina as a mordant for cotton, is by substituting acetic acid for sulphuric acid in combination with it. The acetate of alumina has several advantages over the sulphate: 1st, the acetic acid is not so hurtful in its action upon the vegetable colouring matters; 2nd, it holds the alumina with much less force than sulphuric acid, and consequently yields it much more freely to the cloth; and 3rd, being volatile, a great portion of the acid flies off during the process of drying. When strong colours are wanted, and the mordant is of such a nature as will admit of being dried, it is better to dry the cloth from the mordant previous to dyeing. This last property of acetic acid is, therefore, very convenient, as it frees the cloth from any superfluous acid which may have been in the mordant; besides, it has been found that during the drying by heat, the soluble acetate is converted into a less soluble subacetate. We may here put the dyer in mind that when goods containing volatile acids are drying, no other kind of goods should be allowed to be in the same apartment, as the acid will be absorbed by them, and will affect almost any colour that either has been or may be put upon them. Many unpleasant and also expensive consequences occur from the neglect of these precautions."

Bancroft³ gives an interesting account of the early use of aluminum acetate in calico printing. "By thus substituting the acetic for the sulphuric acid, in the aluminous mordant

¹ Jour. Ind. Eng. Chem., 14, 198 (1922).

² Napier: "A Manual of Dyeing," 121 (1875).

³ "Philosophy of Permanent Colours," 1, 365 (1813).

lately described, several considerable advantages are gained. The acetate of alumine being much more soluble in water than common alum, the liquor will contain a much larger proportion of alumine, than could be otherwise suspended in it; and with this advantage, moreover, that it will not be liable to form crystals in or upon the linens or cottons in drying, as would happen with a solution of common alum, the acetate of alumine being incapable of crystallization. I may add also, that the acid of vinegar being volatile, and having a much weaker attraction for its earthy basis than the sulphuric acid has, the former will be speedily separated and carried off, especially by the heat of the stoves employed for drying the pieces printed with it, and will leave behind the alumine which it has dissolved, and which, being no longer encumbered by any other attraction, will yield itself wholly to that, which subsists between it, and the fibres of linen or cotton, and will unite with them more copiously and firmly than it otherwise could do, and be thereby enabled more strongly to attract and fix the colouring matters in the dyeing vessel. This, however, will only prove true, so far as the sulphate of alumine has been really decomposed by the acetate of lead, or so far as the alumine has been combined with the acetic instead of the sulphuric acid.

“As the practice of calico-printing has been but lately introduced into Europe, and as the acetic aluminous mordant does not appear to have been previously known in any other country, we might have expected that its discovery in this, would have been deemed a matter so important, as to have constituted an area in the history of the art; and, therefore, I was not a little surprised in finding that no writer had mentioned, and that no calico-printer, of whom I have inquired, could inform me, at what time, or by whom, this mordant was first employed, as the basis of red and yellow colours in calico-printing. My wonder has, however, ceased on this subject, since I have inspected a considerable number of recipes for making the several mixtures employed as mordants, soon after the business of calico-printing began to be carried on with

some degree of success here, and in other parts of Europe. In one of these which seems to have been the earliest, alum, sal ammoniac, saltpetre, red orpiment, and kelp, were directed to be mixed with water. In another, which probably followed this, it was directed that these ingredients should be dissolved in vinegar. In a succeeding recipe, a little sugar of lead was directed to be employed, but in a quantity too small to be of any considerable use; I mean one ounce of it for every pound of alum. Afterwards, the calico-printers, without any system or reasonable motive, appear in different instances to have added verdigrise, arsenic, corrosive sublimate, blue vitriol, litharge, and white lead. By stumbling upon the two last (which alone were of any use), it happened, where vinegar had been also employed, as it commonly was in some shape, that after a variety of decompositions and recompositions, some portion of acetate of alumine was formed, the good effects of which were experienced, though without any true knowledge of the ways and means by which they have been produced. By degrees, however, the printers seem to have increased the quantity of sugar of lead, and several of them to have suspected that many of the other ingredients usually employed for making their mordants were useless. Some of them, therefore, began to omit one, and some another of these ingredients, until at length all the useless ones were laid aside, though without the aid of any chemical reasoning on the subject, and without any one having ever suspected, as indeed few of them do at this day, that the lead which they continued to employ, occasioned any decomposition of the alum, or that the mordant so produced did not really contain all the lead and other ingredients used to prepare it. Among the useless ingredients before mentioned, corrosive sublimate seems to have been retained the longest, since Mr. Wilson includes it in his recipe, which was published so lately as the year 1786.

"It is not wonderful, therefore, that no particular person or period has been noted, or remembered, as distinguishable for the first invention of the acetated aluminous mordant; since the sugar of lead, or other means of forming it, were at

first used by chance so sparingly, as to have scarcely produced any better effect than would have resulted from the mere solution of alum, and the alterations and improvements by which the mordant afterwards acquired its present form, I had almost said perfection, were made by such impreceptible gradations, and resulted so much from the random additions and omissions of different individuals (no one of whom seems to have been guided by anything approaching to a just theory), that neither the discovery nor any considerable step towards it, can properly be referred to any one person or period.

“Mr. Henry, justly sensible of the superior advantages of the acetated aluminous mordant in calico-printing, and conceiving it to have really been very anciently known and employed in those countries where the art was first practiced, concludes from thence, that it must have resulted from a very advanced state of chemical knowledge in those countries, at some very remote period, which was afterwards lost, whilst the improvements arising from it in this respect continued to be practiced and handed down, through a long succession of ages to the present time. To have invented (says he) the process of printing, in the manner described by Pliny, the inhabitants of India must probably have known how to prepare alum; they must have been acquainted with the manner of dissolving lead in the vegetable acids; they must at least have been acquainted with the component parts of these salts, and they must have had a knowledge of double elective attractions, etc. In truth, however, the inhabitants of India neither had, nor have they at present, any knowledge of the use of sugar of lead, or of any other preparation of that metal which could produce similar effects in calico-printing; a solution of common alum in water being their only aluminous mordant, and the previous application of the soluble parts of myrobalans and of buffaloes' milk, to their calicoes, aided by a very hot sun-shine, and the complete desiccation which it produces, enabling them, without anything like an acetate of alumine, to give equal durability to their colours. This fact I have learned, not only from all the accounts published,

or transmitted to Europe respecting this point, but from the positive verbal informations of eye-witnesses to the practice of calico-printing in that part of the world, and particularly of a gentleman of great veracity, as well as knowledge on this subject, who formerly carried on the business of calico-printing very extensively in Bengal (principally for account of the East-India Company): and indeed sugar of lead is so far from being used for this purpose there, that within a few weeks I have received a letter from Mr. John Adie (successor to the gentleman last mentioned) dated, "Gondelpara, near Chander-nagore, the 10th of February, 1792," and mentioning, that he had some little time before been obliged to pay twenty shillings the pound for sugar of lead, in order to prepare a particular colour which I had formerly recommended; so far was this ingredient from being in use there for any such purpose.

"We may, therefore, safely conclude, that the formation of an acetate of alumine, and its application as a mordant in calico-printing, was not an oriental discovery; and that it did not result from any knowledge of double elective attractions, or any other extensive chemical knowledge, either in ancient or modern times; since those who gradually stumbled upon and introduced the use of it, were totally ignorant of the decompositions and recompositions which took place in their mixtures, and always supposed, as all other calico-printers have till lately done, and as most of them do now, that the aluminous mordant really consisted of everything used in producing it."

We know that textiles are often made shower-proof by coating the fibers with some water-repellent hydrocarbon, wax or salt,¹ the aluminum salts being often used. We also know that the probability of electrostatic charges is greater the dryer the material we are studying. Both these facts were known empirically to Napier.² "Pieces [of cloth] mordanted with acetate of alumina and dried at a great heat, are highly charged with electricity. If the hand be suddenly drawn

¹ Weber: *Jour. Soc. Dyers and Colourists*, 17, 146 (1901).

² "A Manual of Dyeing," 125 (1875).

along the piece, a complete shower of fire is observed, with a sharp cracking noise, at the same time a prickling sensation is felt. Whether this has any effect upon the mordant, in its immediately combining with other substances we do not know but cloth in this state is very difficult to moisten—water runs off it as off a duck's wing; but we offer no explanation."

Liechti and Suida¹ have made some experiments on the amount of alumina fixed by cotton from various solutions; but it is rather hard to tell from the abstract exactly what they did. "A weighed 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 thirty-six hours. A certain portion was then incinerated in order to determine the amount of alumina which the fibre had at its command. Another portion of the prepared fibre was then dried in a constant air current for six hours at a temperature of 40° C. The fibre 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 fibre." This sounds perfectly simple; but the catch is in the phrase "evenly impregnated." The cotton was apparently steeped in the bath and then dried with the mother liquor in it. Since all the solutions had the same amount of alumina in them, an amount equivalent to 200 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ per litre, one would have supposed that the amount of alumina presented to the fiber would be approximately the same in each case. Actually it varies in a ratio of more than four to one. The data are given in Table II. In the first column is the hypothetical formula of the aluminum salt in solution. In the second column is the amount of alumina in grams presented to the fibers, an absolutely mysterious item. There is nothing to show to what weight of cotton it refers. In the third column is given the amount of alumina in grams fixed by the cotton and in the fourth the percentage fixed. The apparent accuracy is of course absolutely fictitious.

¹ Jour. Soc. Chem. Ind., 2, 538 (1883).

TABLE II
Adsorption of Alumina by Cotton

Formula	Al ₂ O ₃ presented to the fiber	Al ₂ O ₃ fixed by the fiber	Percentage Al ₂ O ₃ fixed
Al ₂ (SO ₄) ₃	0.6971	0.0901	12.92
Al ₂ (SO ₄) ₂ (OH) ₂	0.4473	0.2283	51.04
Al ₄ (SO ₄) ₃ (OH) ₆	0.1527	0.0897	58.74
Al ₂ (SO ₄)(CH ₃ CO ₂) ₄	0.5750	0.5190	90.26
Al ₂ (SO ₄)(CH ₃ CO ₂) ₃ (OH)	0.5012	0.5012	98.90
Al ₂ (SO ₄)(CH ₃ CO ₂) ₂ (OH) ₂	0.1851	0.1851	91.19
Al ₂ (SO ₄)(CH ₃ CO ₂)(OH) ₃	0.1987	0.1987	96.33
Al ₂ (CH ₃ CO ₂) ₆	0.2631	0.2631	51.27
Al ₂ (CH ₃ CO ₂) ₄ (OH) ₂	0.2213	0.2213	99.46

From these data it is not permissible to draw the conclusion, which Liechti and Suida draw, that with aluminum sulphate the percentage of alumina fixed is greater the more basic the mordant. The percentage fixed varies with increasing basicity from 13 through 51 to 59; which is all that Liechti and Suida are considering. From what we know of adsorption, however, it is safe to say that the percentage adsorption would have been much greater than 51 if 0.15 g Al₂O₃ had been presented to the cotton instead of 0.45 g. The percentage adsorption for the hypothetical Al₄(SO₄)₃(OH)₆ would have been less than 58 if 0.45 g Al₂O₃ had been presented to the fibre instead of 0.15 g. It is quite possible, therefore, that under comparable conditions the percentage of alumina fixed by the fiber would have passed through a maximum with increasing basicity just as it appears to do with the so-called sulpho-acetates. On the other hand we do not know whether such a maximum, if found, would be real or would be due to the increased amount of sodium sulphate in the solution. In other words, although these experiments were made carefully, they are utterly worthless except as showing the errors which the next experimenter must avoid. Considering the time at which they were made, it is not surprising that the experiments are no better; but it is surprising that for nearly forty years they should have been considered as good work.

Kutschera and Utz¹ made some similar experiments except that they hung the cloth, after drying, in the moist air at about 34° for forty-eight hours. They got a much more uniform mordanting of the cotton than Liechti and Suida did. One square decimeter of their cloth averaged seven grams in weight, and it seems probable, though not explicitly so stated, that this is the amount of cloth to which the figures in Table III refer.

TABLE III
Adsorption of Alumina by Cotton
100 cm² of cotton averaged 7 grams

Formula	Al ₂ O ₃ presented to the fiber	Al ₂ O ₃ fixed by the fiber	Percentage Al ₂ O ₃ fixed
Al ₂ (SO ₄) ₃ 18H ₂ O	0.1566	0.0186	11.88
Al ₂ (SO ₄) ₂ (CH ₃ CO ₂) ₂	0.1456	0.1462	100.43
Al ₂ (SO ₄)(CH ₃ CO ₂) ₄	0.1660	0.1324	79.76
Al ₂ (CH ₃ CO ₂) ₆	0.1446	0.1479	102.29
Al ₂ (SO ₄) ₂ (OH) ₂	0.1350	0.0688	51.79
Al ₂ (SO ₄)(CH ₃ CO ₂) ₃ (OH)	0.1495	0.1304	87.19

They confirm Liechti and Suida on the aluminum sulphate, and the basic aluminum sulphate. They are low (80 to 99) on the Al₂(SO₄)(CH₃CO₂)₄ and also (87 to 99) on Al₂(SO₄)(CH₃CO₂)₃OH. The great apparent difference is with aluminum acetate where Kutschera and Utz get all the alumina fixed, while Liechti and Suida get only 51 percent fixed. The difference may not be a real one because Liechti and Suida get more alumina fixed by weight than do Kutschera and Utz; but they present to the fiber 263 mg as against 145 mg. It is quite possible that all the loss in efficiency comes in at the higher concentrations. This argument cannot be used to cover the cases of Al₂(SO₄)(CH₃CO₂)₄ and Al₂(SO₄)(CH₃CO₂)₃(OH) because in both these experiments Liechti and Suida were getting higher percentages of alumina fixed with higher absolute amounts of alumina presented to the fiber.

¹ Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, 3, 110 (1886).

Sodium aluminate is not used as a mordant in dyeing cotton; but it is padded on for calico printing.¹ There is no direct mordanting and it is necessary to add ammonium chloride in order to precipitate the alumina. The use of aluminum formate² and of aluminum lactate³ has been advocated. Whether one uses an acetate, formate, or lactate does not affect the general theory of the process.

Matthews,⁴ who usually follows Ganswindt implicitly, breaks away from him on the question of mordanting cotton and comes out fairly boldly for the formation of a metallo-organic compound. "In mordanting cotton the case is somewhat different, for the metals employed as mordants are usually in the form of basic salts, and the solutions of these, by great dilution, by long exposure to the air, or by warming, may become dissociated and there may be precipitated either the hydroxide of the metal or a strongly basic salt; for example, in mordanting cotton with acetate of aluminum a hydrate or basic acetate is formed. This, however, cannot be considered as 'precipitation' in the chemical sense of the term. Although it may be shown that when cotton is steeped in a readily dissociated solution of aluminum acetate, a portion of the aluminum is withdrawn from the bath, it cannot be shown however, that aluminum hydrate as such has been precipitated in the fibre. If such were the case, washing with lukewarm acetic or hydrochloric acid would remove all the hydroxide from the fibre again; but this does not happen, which is an indication that the aluminum must be fixed in some other form. A properly mordanted fibre requires that the metallic compound with which the fibre is mordanted must be held by this in such a form and with sufficient energy that the mordant cannot be removed by water or even by dilute acids or alkalis."

After two paragraphs on the mordanting of wool with

¹ Ganswindt: "Theorie und Praxis der modernen Färberei," II, 224 (1903).

² Schwalbe: Zeit. Kolloidchemie, 5, 129 (1907).

³ Boehringer and Sons: Zeit. Farben-Ind., 9, 237, 253 (1910).

⁴ "Application of Dyestuffs," 602 (1920).

copper, aluminum, chromium and iron, Matthews concludes that "all these facts appear to show that in mordanting with metallic salts the metal is combined with the fibre in the form of a metallo-organic compound, and the fibre, thus chemically changed, then possesses the proper affinity for dyeing with the mordant dyes." The fallacy lies in the assumption that an adsorbed substance will necessarily have the same properties as the same substance in mass. If that were really the case charcoal could not take soluble substances out of solution practically completely and yet we know it does. If cotton takes alumina out of aluminum acetate, there is no reason why dilute acetic acid should take any appreciable amount of alumina out of cotton and still less out of wool which holds the alumina much more strongly.

Ganswindt¹ believes in distinguishing sharply between the mordanting of wool and of cotton. "The mordanting of cotton is quite different from the mordanting of wool and silk; it has also quite a different intention and significance. The cause of the difference is the inactivity or indifference of cotton towards solutions of salts of the metals. While silk and wool take up the metals in any form on heating, often quantitatively, and fix them chemically, that is not the case with cotton. Cotton has no affinity for metal salts and no tendency to form metallo-organic compounds; even boiling for hours has no effect. It is therefore necessary to have recourse to solutions of strongly basic salts, solutions which are so labile that a mere diluting with water, gentle heating, or just the presence of a textile fiber will cause the solution to dissociate into a normal solution and into a precipitate which latter, at the moment of precipitation, is taken up on or in the fiber. It is not necessary to decide whether the hydroxide is taken up or a more basic salt than that in the original solution, for that point has no bearing on what is to follow. It is a fact, however, that no chemical compound is formed and that the cotton fiber is not changed chemically in any way by the mor-

¹ "Theorie and Praxis der modernen Färberei," II, 214 (1903).

danting or, more properly speaking, by the steeping in the salt solution. Strictly speaking the cotton is not mordanted at all. When cotton is mordanted, the phenomenon is different from that with wool and silk, in that actually the metal hydroxide or possibly a very strongly basic salt, is precipitated mechanically on the cotton fiber and can be removed to some extent by vigorous rinsing. The hydroxide that is left is also held mechanically but in the intercellular spaces.

"The mordanting with tannin and tartar emetic must also be considered as a mechanical process, for there is only a very slight affinity between tannin and cellulose. If one mordants cotton with tannin, it is possible to wash the tannin out quantitatively by repeated treatments with hot water. That is why it is necessary to fix tannin with tartar emetic. Cotton mordanted with tannin and tartar emetic is nothing more than cotton impregnated mechanically with antimony tannate. It is exactly similar when cotton is mordanted with Turkey red oil and aluminum acetate. In all cases the cotton itself remains entirely unchanged. It is not altered or affected chemically in any way and therefore one really ought not to call the process mordanting at all. The only case where there is actually a chemical change in cotton by the action of reagents is curiously enough not called mordanting but—mercerization.

"From all this it is clear that the mordanting of cotton is not at all the same thing as the mordanting of wool. The mordanting of wool is pre-eminently a chemical process, while the mordanting of cotton is a mechanical impregnation of insoluble metallic compounds in the cell spaces and pores of the cotton fibre. For this reason the mordanting of cotton with metallic salts is nothing like as important or interesting as the mordanting of wool. The organic mordants, tannin and oil, are much more important."

This is quite an unreasonable attitude to take. The difference between wool and cotton is purely one of degree, so far as we now know. Wool adsorbs alumina more strongly than cotton does and is therefore able to take up alumina from less basic solutions than cotton can. Since it adsorbs

alumina more strongly than cotton does, it also holds it more firmly, thus makes a fixing of the mordant unnecessary. That point will be discussed in detail in a later paper. There is no satisfactory experimental evidence as yet of the formation of any definite chemical compound between alumina and either wool or cotton. Specific adsorption will account satisfactorily for all the phenomena which have been observed as yet.

It is interesting to note that the one case where Ganswindt is willing to admit a chemical change and a consequent mordanting is that of mercerized cotton; and Leighton¹ has since shown that all the earlier work on the theory of the process was wrong and that there is no definite chemical compound formed when cotton is mercerized. It is true, of course, that mercerized cotton does adsorb basic and substantive dyes more strongly than ordinary cotton does² and it is apparently true that mercerized cotton takes up basic mordants³ rather more completely from concentrated solutions than ordinary cotton does; but there is no reason to suppose that this is anything more than an increased adsorption due to a change in structure.

The general results of this paper are:

1. All aluminum salts hydrolyze more or less in aqueous solution and the amount of the hydrolysis increases with rising temperature.
2. The actual hydrolysis is greater with weaker acids; but the apparent hydrolysis may be abnormally large in sulphate solutions owing to the coagulating effect of the sulphate ions on the colloidal alumina.
3. The different fibers adsorb alumina to different degrees, wool having a much greater adsorbing power than cotton, and silk being probably slightly inferior to wool.
4. Owing to this difference in specific adsorption, wool decomposes aluminum salt solutions which are distinctly acid while cotton is effective only in more basic solutions.

¹ Jour. Phys. Chem., **20**, 188 (1916).

² Matthews: "Application of Dyestuffs," 165, 278 (1920).

³ Schaposchnikoff and Minajeff: Zeit, Farben-Ind., **3**, 165 (1904); **4**, 81 (1905).

5. What is taken up and held firmly is the colloidal alumina. While coagulated alumina may be adsorbed to some extent, it rubs off easily.

6. It is probable that in all cases alumina is adsorbed and not a basic salt. The phenomena may be complicated by the fact that the alumina itself will adsorb some sulphuric acid, for instance, and that the wool may, and probably does, adsorb some sulphuric acid also.

7. Since alumina is adsorbed less strongly by cotton than by wool, it is also held less strongly by cotton than by wool.

8. If we add to cotton some substance like tannin which adsorbs alumina strongly, the cotton mordanted with tannin will be able to take alumina out of aluminum salt solutions which are not decomposed by cotton alone. A corollary from this is that alumina will be held more strongly by cotton mordanted with tannin than by cotton alone.

9. The increase in adsorbing power shown by mercerized cotton is undoubtedly due to structural difference in the cotton fibre; but we are not yet able to predict this change.

10. There is no evidence of the formation of any definite chemical compound between alumina and either wool, silk, or cotton.

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