

# Fixation of Aluminum by Hide Substance<sup>1,2</sup>

Arthur W. Thomas and Margaret W. Kelly

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

**T**HE use of aluminum salts for tannage dates back to very early times and is still applied to the manufacture of certain kinds of leather and furs. The operation involving the use of egg yolk, oil, flour, and common salt, together with a salt of aluminum, is called tawing.

Ancient history tells us that the Egyptians and Romans tanned with alum and salt and, within the limits of our knowledge of ancient methods, the practice of alum tanning has undergone but negligible changes through the intervening centuries, although, of course, the nature of the final products and degree of perfection have changed markedly. Industrially, tawing was at its height during the nineteenth century in France, the center of the industry where tawed skins were used, not only in the fabrication of gloves, but also in the manufacture of fancy shoes. The discovery of the tanning action of chromium salts was followed by a diminution of alum tawing. Alum tawing is nevertheless still an important industry and is highly perfected in the glove centers of France. While chromium produces a leather that is resistant to the action of boiling water, alum leather decomposes slowly in cold water—i. e., its tanning action is "weak." Alum tannage is readily reversed—i. e., the aluminum extracted—by treatment with decidedly acid or weakly alkaline solutions. Alum tanning must therefore be conducted very differently from chrome tanning.

In practice the skins are tumbled in a solution of basic aluminum sulfate and sodium chloride. It is sometimes desirable to add enough sodium bicarbonate to the liquor after the alum has completely penetrated the skins to bring it to the point at which precipitation of aluminum hydroxide just begins. After a few hours the skins are rubbed with a mixture of egg yolk, fatty oil, and flour, but not washed. They are then allowed to dry thoroughly. Sometimes the egg-yolk mixture is added to the tanning bath. The skins are kept in the dried state for weeks or months to allow the aluminum to become permanently fixed. The skins are then soaked in water to remove the salt and are fat-liquored, colored, and finished according to the kind of leather required. In tanning skins for furs it is customary to work the alum solution into the skin from the flesh side, supplemented with oils to keep the skin soft. Work of this kind is usually done by hand and requires some skill in order to get the best results.

<sup>1</sup> Presented by Margaret W. Kelly under the title "A Study of Tannage by Aluminum Salts" before the Division of Leather and Gelatin Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

<sup>2</sup> Contribution No. 561 from the Chemical Laboratories, Columbia University.

Solutions of aluminum salts are quite acid in reaction, owing to hydrolysis. Since, as in the case of chromium, the basic salts have greater tanning action than the normal salts, it is customary to secure the desired basicity by careful addition of sodium hydroxide, sodium bicarbonate, or sodium carbonate to the solution of the normal aluminum salt. This partial neutralization must, of course, be carefully regulated in order not to increase the pH to the point at which aluminum hydroxide would be precipitated.

While alum was formerly chiefly used in tawing, the sulfate is now generally employed, since it can now be obtained free from iron and furnishes per unit weight a larger amount of aluminum.

In 1858 Knapp<sup>3</sup> compared the amounts of alum, aluminum sulfate, chloride, and acetate removed from solution by hide. While he found that considerable amounts of each salt were taken up by hide, he asserted that serviceable leather was obtained only by use of alum and sodium chloride. Previous to this time the favorable action of sodium chloride upon alum tannage

When hide substance is treated with solutions of the normal chloride or sulfate of aluminum and then washed with water, practically all of the adhering aluminum salt is removed. When, however, the pH values of the solutions are increased an irreversible fixation of aluminum, increasing with the pH value, is obtained. While greater aluminum fixation occurs in solutions of the chloride up to pH = 3.65, beyond this point the sulfate excels as a tanning agent because it can be rendered more basic without precipitation of hydrous aluminum oxide. The maximum degree of aluminum fixation found was 3.5 grams (as  $\text{Al}_2\text{O}_3$ ) per 100 grams hide substance. There is an optimum concentration of the aluminum salt of about 0.2 normal, below and above which the degree of fixation diminishes. The time required for complete tannage is only a few hours. Sodium chloride and sulfate diminish the amounts of aluminum fixed by hide substance, the effect of the former being slight while that of the latter is marked.

was thought to be due to the formation of aluminum chloride through interaction of aluminum sulfate and the salt.<sup>4</sup> Knapp thereby overthrew this old point of view, substituting his belief that the action of sodium chloride was a desiccation thus preventing the adherence of the hide fibers upon drying the tawed hide. Today, however, the action of sodium chloride is ascribed to the fact that salts in general prevent the swelling of hides in the acid solution.<sup>5,6</sup>

It is generally believed that the aluminum-collagen complex is such a weak union that the aluminum can be all washed out by neutral water. In 1906, however, it was shown by Lumière and Seyewitz<sup>7</sup> that gelatin fixes aluminum from an alum solution very tenaciously, since sheets of gelatin tanned in alum solutions and then washed to negative tests for either sulfate or aluminum ions in the wash waters contained fixed aluminum, a maximum quantity of 3.6 grams  $\text{Al}_2\text{O}_3$  being fixed by 100 grams gelatin. The tanned nature of the gelatin was also demonstrated by the fact that the setting temperature of gelatin solutions was raised by the presence of aluminum salts, the maximum value being obtained always at the same concentration of aluminum in solution regardless of whether the chloride, nitrate, or sulfate was employed.

Moreover, Knapp<sup>3</sup> noted that the amount of aluminum

<sup>3</sup> Through *Collegium*, 1919, 133, 166; *J. Am. Leather Chem. Assoc.*, 16, 658 (1921).

<sup>4</sup> Berzelius, "Lehrbuch der Chemie," Arnoldschen Buchhandlung, Dresden and Leipzig, 1840.

<sup>5</sup> Procter and Wilson, *J. Chem. Soc. (London)*, 109, 307 (1916).

<sup>6</sup> Procter, "Principles of Leather Manufacture," p. 242, D. Van Nostrand, New York, 1922.

<sup>7</sup> *Brit. J. Phot.*, 53, 573 (1906).

chloride absorbed from solution by hide was reduced in 3 days' washing from 27.3 per cent to 3.66 per cent of the weight of pelt employed. He stated that this small amount "without doubt would also be removed by continued washing." But it seems more probable that this amount represents an irreversible fixation also. It is interesting to note that Knapp's figure for pelt corresponds quite remarkably with that obtained by Lumière and Seyewitz for gelatin.

Only one methodical investigation of aluminum tannage from a chemist's point of view has been published in recent times—namely, that of Mezey,<sup>8</sup> which was carried out at the French tanning school in Lyons under the direction of Professors Meunier and Chambard. Mezey found that the best tanning action is obtained with basic aluminum sulfate solutions and in the presence of salt. He suggests that the mechanism of the binding of aluminum is chemical in action, common salt favoring alum tannage because "it represses the ionization and prevents the hydrolysis of the basic aluminum salt combined with the substance of the hide fibers."

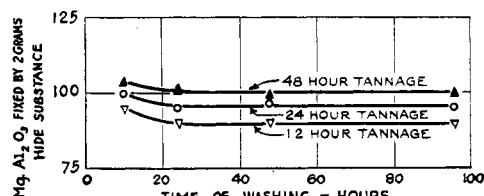


Figure 1—Influence of Washing Tanned Powders with Distilled Water

Mezey's quantitative data were all obtained on pieces of hide by means of the "by-difference" technic; i. e., the amounts of aluminum, etc., fixed by the hide were calculated from the difference in concentrations of the tanning solutions before and after hide had been immersed in them. The change in concentration may give a general idea concerning the amount of aluminum taken up by the hide, but is quantitatively valid only when no water is absorbed. Owing to the variability of water absorption by hide with variation in pH, presence of salts, etc., the "by-difference" technic frequently yields data which are far removed from the true degrees of fixation, as has been shown in the case of chromium fixation.<sup>9,10</sup>

In view of the fact that measurements of the amounts of aluminum irreversibly fixed by hide substances have never been reported in the literature, the experiments recorded in this paper were undertaken. (The authors use the term "fixed" to signify the amount of aluminum retained by the hide substance after prolonged washing with distilled water at room temperature.) Despite the general notion that aluminum is not irreversibly fixed by hide substance, this was deemed feasible on account of the behavior of gelatin-aluminum complexes reported by Lumière and Seyewitz.<sup>7</sup>

### Materials and Method

As sources of aluminum salts, the sulfate and chloride were employed. For determination of the aluminum content of these solutions, Blum's method<sup>11</sup> was used. Stock concentrated solutions of aluminum sulfate were prepared by dissolving the crystals (Merck's highest purity) in water. The solutions were colorless, gave a negative test for iron, and gave no trouble with the hydrogen electrode in measurements of pH and in titration to a definite pH. The anhydrous aluminum chloride, on the other hand, gave a positive test for

ferric ion. Before it was possible to apply the hydrogen electrode to these solutions, it was necessary to free them from traces of iron. This was successfully accomplished by precipitating the ferric ion present with a slight excess of potassium ferrocyanide. This precipitate of Prussian blue, being of colloidal character, cannot be removed completely by filtration. Consequently, after allowing the deep blue precipitate to settle, the clear solution was decanted and traces of colloidal  $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$  removed by two treatments of the warm solution with small amounts of charcoal. On filtering, the resulting solution was colorless, contained no iron, and gave no trouble in electrometric titration.

In all experiments American standard hide powder, defatted by chloroform, was employed. Portions of this hide powder, equivalent to 2.000 grams, dry basis, were treated with 400-cc. portions of tanning solution, this large volume being used to prevent any considerable change in pH during the tanning period. After tanning for the desired length of time, samples were filtered on Wilson and Kern extractors, washed thoroughly to free from tanning solution ("Aluminon" test<sup>12</sup> used on washings), air-dried, and finally ashed in platinum dishes in an electric muffle. The final heating was at high temperature in order to insure the conversion of aluminum compounds to  $\text{Al}_2\text{O}_3$  (begins at  $770^\circ\text{C}$ . and complete at red heat). This weight of ash, corrected for the small ash content of the hide powder, was taken as a measure of the amount of aluminum irreversibly fixed by the hide powder. In determining the ash content of original hide powder, the following method was used: Duplicate samples of hide powder, of weight equivalent to 2.000 grams, dry basis, were treated for several one-hour periods in Wilson and Kern extractors with successive 200-cc. portions of dilute sulfuric acid at  $\text{pH} = 3.45$ , then washed with distilled water, air-dried, and ashed. The weight of ash obtained in each case was 0.0043 gram, which was therefore used as the correction factor throughout the work reported here.

After treatment with aluminum salts the tanned hide powders were white. Preliminary experiments were carried out in order to determine suitable periods for tannage and for washing on the extractors after the tanning period. The results, summarized in Figure 1, show that, for a 24-hour period of tannage, equilibrium was obtained after washing for 24 hours; consequently the amount of aluminum remaining under these conditions can be assumed to be irreversibly fixed. Therefore for all experiments, unless otherwise indicated, tanning was continued for a 24-hour period, and followed by continuous washing for 24 hours on Wilson and Kern extractors before the samples were air-dried and ashed.

### The pH Factor

Since the method adopted for measurement of tannage necessitated the use of a clear tanning solution, considerable

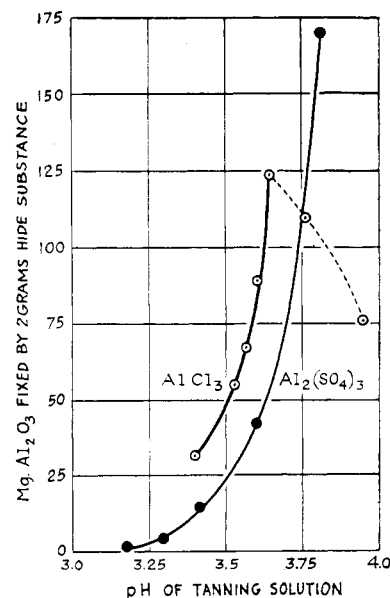


Figure 2—pH Factor

<sup>8</sup> "Contribution à l'Étude du Tannage à l'Alaun," Imprimerie Bosc Frères et Rivu, Lyons, 1925.

<sup>9</sup> Thomas and Kelly, *J. IND. ENG. CHEM.*, **13**, 31 (1921).

<sup>10</sup> Thomas, *J. Am. Leather Chem. Assoc.*, **18**, 423 (1923).

<sup>11</sup> *Bur. Standards, Sci. Paper* **286** (1916).

<sup>12</sup> Hammett and Sottery, *J. Am. Chem. Soc.*, **47**, 142 (1925).

care was exercised in determining suitable concentration and pH ranges of the aluminum salt solutions in which no interfering precipitate of alumina would be formed. In the case of aluminum sulfate it was found that for a concentration of 47.4 grams aluminum sulfate per liter (7.5 grams Al or 0.138 molar) the acidity could be decreased from pH = 3.2 (for solution of the normal salt) by addition of sodium hydroxide solution to pH = 3.8 without precipitation of aluminum hydroxide. Consequently experiments were limited to this range of pH. For aluminum chloride solutions containing 36.95 grams  $\text{AlCl}_3$  per liter (7.5 grams Al or 0.277 molar), it was found possible to vary the pH from 3.4 (for solution of the normal salt) to pH = 4.0, on addition of sodium hydroxide, the final solutions showing a slight

acids to a solution of an aluminum salt is the chief point in favor of their use. Also they are perhaps safer than the stronger alkalies ordinarily employed on account of their buffer action.

### Concentration Factor

In order to study the effect of change in concentration of aluminum sulfate, a concentrated stock solution was titrated to pH 3.6 by means of sodium hydroxide, this pH value having been found to be a convenient basicity for preparation of a concentrated solution. Since a considerable amount of aluminum hydroxide precipitated out from this concentrated solution, the mixture was allowed to stand for 48 hours in order to peptize the precipitated hydroxide as far as possible; then the remaining precipitate was filtered off and the aluminum content of the clear solution determined before use in the experiments described below.

Preliminary experiments showed that dilution of this basic solution with distilled water caused a separation of precipitate; consequently, dilution to the desired concentration was effected by addition of a sulfuric acid solution of pH = 3.65. In this way large changes in pH were avoided as well as complications due to precipitation, except for the three most dilute solutions, in which cases the slight turbidity was neglected. In each case the pH values of a portion of the original solution and of the filtrate were determined electrometrically. The results are given in Table II and Figure 3. The broken-line portion of the curve represents the region of presence of precipitate in the tanning solution and therefore

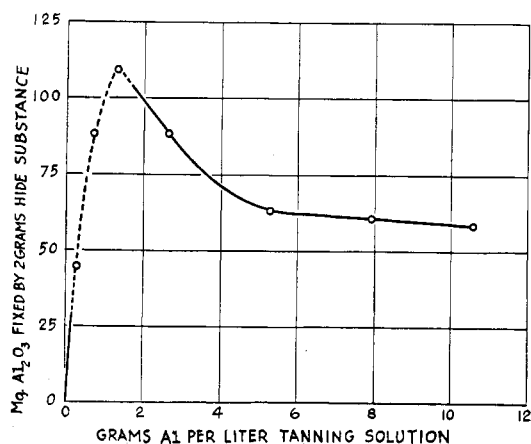


Figure 3—Concentration Factor

turbidity. This latter point, as shown in Table I, was the cause of irregularities in the results obtained with the more basic solutions of aluminum chloride. The pH values of a portion of the original solution and of the filtrate were determined in each case.

Table I—The pH Factor

TANNAGE WITH $\text{Al}_2(\text{SO}_4)_3$ SOLUTION (47.4 GRAMS PER LITER, 0.138 M)			TANNAGE WITH $\text{AlCl}_3$ SOLUTION (36.95 GRAMS PER LITER, 0.277 M)		
pH Before	pH After	$\text{Al}_2\text{O}_3$ fixed Mg.	pH Before	pH After	$\text{Al}_2\text{O}_3$ fixed Mg.
3.18	3.22	2 <sup>a</sup>	3.41	3.53	32 <sup>f</sup>
3.30	3.30	4 <sup>a</sup>	3.53	3.69	56 <sup>f</sup>
3.42	3.43	14 <sup>a</sup>	3.57 <sup>d</sup>	3.73	67 <sup>g</sup>
3.60	3.55	42 <sup>b</sup>	3.61 <sup>d</sup>	3.75	89 <sup>g</sup>
3.81	3.76	170 <sup>c</sup>	3.65 <sup>d</sup>	3.82	124 <sup>h</sup>
			3.77 <sup>e</sup>	3.95	110 <sup>h</sup>
			3.95 <sup>e</sup>	4.10	76 <sup>h</sup>

<sup>a</sup> Sticky while wet; hard when dry.

<sup>b</sup> Softer, somewhat fluffy.

<sup>c</sup> Soft, fluffy, well tanned.

<sup>d</sup> Slight precipitate in original solution, filtered off before using; little change in concentration.

<sup>e</sup> Heavier precipitate in original solution, filtered off before using; slight decrease in concentration.

<sup>f</sup> Slightly sticky.

<sup>g</sup> Poor tannage, only very slightly sticky.

<sup>h</sup> Fluffy, well tanned.

The results, using both aluminum sulfate and aluminum chloride, are summarized in Table I and Figure 2. It is found that, whereas with solutions of the normal salt very little aluminum is irreversibly fixed by hide powder, this amount is enormously increased with increasing basicity of the tanning solution, while at the same time the character of the tanned product, after washing, is greatly improved. This confirms the results of Mezey, using pieces of skin and calculation by the "by-difference" technic. It is interesting to note in this connection that several patents have been taken out involving the use of alkali and alkaline-earth formates, acetates, and pyrophosphates in conjunction with tannage by aluminum salts. It seems probable that the reduction in acidity resulting from the addition of a salt of these weak

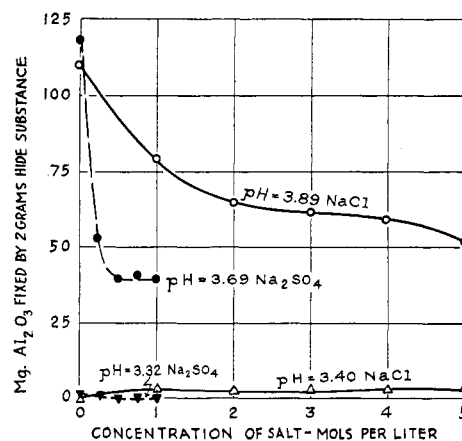


Figure 4—Effect of Neutral Salts

At pH 3.32 the powders were not tanned. At pH 3.69 the powders were well tanned at 0 and at 0.25 molarity of sodium sulfate. At higher concentrations of sodium sulfate the powders were not well tanned.

the "amounts of aluminum fixed" may be in part merely occluded aluminum oxide. It is seen that an optimum is obtained in solutions containing about 2 grams aluminum per liter. The interpretation of these results as a function of concentration is unfortunately complicated by pH changes and requires repetition under more closely controlled pH conditions.

Table II—Concentration Factor— $\text{Al}_2(\text{SO}_4)_3$

Al CONCN. Grams/liter	pH Before Tanning	pH After Tanning	$\text{Al}_2\text{O}_3$ FIXED Mg.
0.35 <sup>a</sup>	4.09	4.00	45 <sup>b</sup>
0.67 <sup>a</sup>	3.95	3.97	88 <sup>c</sup>
1.33 <sup>a</sup>	3.92	3.84	109 <sup>c</sup>
2.65	3.80	3.79	88 <sup>c</sup>
5.30	3.73	3.70	63 <sup>c</sup>
7.95	3.64	3.64	61 <sup>b</sup>
10.6	3.60	3.60	58 <sup>b</sup>

<sup>a</sup> Slight amount of precipitate separated after sample stood for 24 hours.

<sup>b</sup> Fair tannage.

<sup>c</sup> Good tannage.

These results are at variation with those of Mezey, who found an increasing degree of fixation with increasing concentration of aluminum in the tanning solution. It is to be remembered, however, that his method of measurement includes the salt dissolved in the intercellular liquid held in the interstices in the pieces of hide, whereas the data reported here represent only the amount of aluminum retained after complete removal of the intermicellary solution.

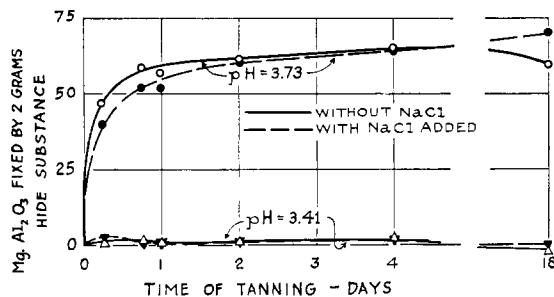


Figure 5—Time Factor

At pH 3.41 the powders were not tanned although traces of aluminum were fixed. At pH 3.73, however, both in the presence and absence of sodium chloride, all powders were well tanned.

#### Effect of Added NaCl and $\text{Na}_2\text{SO}_4$

Since the addition of common salt is recommended in alum tanning, it was deemed advisable to study the effect of adding sodium chloride and sodium sulfate to aluminum sulfate before tanning, both at the pH of the solution of the normal aluminum salt and at the less acid pH values found to be optimum in the study of the pH factor. A concentration of aluminum sulfate of 2.5 grams aluminum per liter was chosen, this being in the range of optimum concentration at the higher pH values. Preliminary experiments showed that such a solution of aluminum sulfate would dissolve sodium chloride in concentrations up to 5 molar, and sodium sulfate up to 1 molar. Figure 4 summarizes the results obtained.

Since the general tannery practice recommends the addition of salt, especially for tanning with solutions of the normal aluminum salt, it was decided to carry out another series of experiments at the lower pH value using sodium chloride in which the concentration intervals were much smaller. In this series the pH of the original solution was taken after the desired amount of sodium chloride had been dissolved.

In the case of the more basic aluminum sulfate solution, fixation was inhibited progressively with increasing concentration of the added salt, the effects produced with sodium sulfate being much greater than with sodium chloride. For solutions of the normal aluminum salt, at a concentration of 2.5 grams aluminum per liter, almost negligible amounts of aluminum are fixed, and it is difficult to attribute any marked action favorable to aluminum fixation by sodium chloride in the case of the tannage of hide powder.

Mezey found a decreased adsorption of aluminum by hide in the presence of these salts, but no means to the marked extent as reported here, again showing marked differences between values found for irreversible fixation and "by-difference" technic. Mezey did find, however, that a better leather is produced in presence of salt, in confirmation of general practical experience. This is easily understood, since salts repress the swelling of the hide, thus preventing a "dead tannage" such as is obtained whenever a swollen hide is tanned. Consequently the favorable effect of salt in practical alum tanning is clearly not due to increased aluminum fixation.

The inhibition of fixation of aluminum by the salts checks with results previously reported for chrome tanning.<sup>13</sup>

<sup>13</sup> Thomas and Foster, *J. IND. ENG. CHEM.*, **14**, 132 (1922).

#### Time Factor

In order to study the rate at which aluminum sulfate is fixed by hide powder, both from solutions of the normal and the basic salt, and likewise both in the presence and absence of sodium chloride, the following experiment was carried out. It seemed especially interesting to discover whether sodium chloride might exert a favorable effect during a longer tanning period than that described above. The method used was that outlined in the earlier experiments, except that the tanning period was varied from 6 hours to 18 days. A concentration of 2.5 grams aluminum per liter in the optimum range for the basic salt was used throughout. The results are summarized in Figure 5.

In the case of the normal sulfate, where very little fixation occurs, equilibrium is reached in a period somewhat less than 6 hours, the shortest period used. All samples were sticky, showing undertannage. The addition of sodium chloride here is practically without effect. After 18 days the hide powder was considerably gelatinized, indicating extensive hydrolysis.

The basic salt requires 18 hours to attain, practically speaking, a state of equilibrium, fixation increasing only slightly with increased time of tannage. The presence of sodium chloride retards the rate of fixation of aluminum, especially during the shorter tanning period. In all cases the basic aluminum salt gives a well-tanned product, no gelatinization taking place even when the hide powder remained in contact with the solution for 18 days, thus confirming general practical usage and Mezey's assertion that better leather is produced in the presence of salt. In studying adsorption of aluminum as a function of time Mezey obtained results practically identical to those reported here.

It is observed that the maximal fixation of aluminum is 3.5 grams  $\text{Al}_2\text{O}_3$  per 100 grams hide substance, a figure closely checking that obtained for hide by Knapp and for gelatin by Lumière and Seyewitz. Taking 750 as the equivalent weight of collagen,<sup>14</sup> 2.27 grams of  $\text{Al}_2\text{O}_3$  would be fixed by 100 grams of collagen if all three valences of aluminum combine with the protein. The value of 3.5 grams, however, is about 50 per cent higher than 2.27, which may mean that only two valences of aluminum enter into combination with the hide substance.

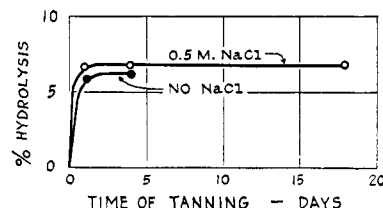


Figure 6—Hydrolysis of Hide Substance in Tanning Solution

#### Hydrolysis Factor

It seemed of interest to determine whether the presence of sodium chloride actually inhibited hydrolysis of hide powder. Experiments were conducted parallel to the preceding work in study of the time factor, using only the basic solutions, since at the lower pH values samples were considerably undertanned. At the end of the tanning period, before filtering, dry sodium chloride of weight required to give 0.5 M solution was added to the sample tanned in absence of sodium chloride, in order to reduce the swelling of samples to an equal degree in each case, thereby minimizing possible errors due to changes in concentration as a result of variations in imbibition by hide powder. The mixture was then filtered through a dry, fluted filter paper, the first portions of filtrate being discarded. The nitrogen content of the filtrate was

<sup>14</sup> Wilson, *J. Am. Leather Chem. Assoc.*, **12**, 108 (1917).

then determined by analysis of an aliquot of the filtrate, using the Kjeldahl method.

The results, summarized in Figure 6, indicate that sodium chloride exerts a slightly positive catalytic effect upon hydrolysis of hide powder in the presence of aluminum sulfate.

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## Fixation of Iron by Hide Substance<sup>1,2</sup>

Arthur W. Thomas and Margaret W. Kelly

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

THE use of salts of iron for tanning hides started in the eighteenth century in attempts to find a tanning operation more rapid in nature than that using vegetable tannins. Patents were taken out as early as 1770 by Johnson and 1794 by Ashton, both Englishmen. In 1794 Robert Lindet reported in France a rapid tanning method using iron, his investigations being prompted by the urgent need for leather by the French army. From the eighteenth century to the present time many patents have been granted for iron tanning methods. Likewise the chemical literature has discussed it from many angles, the first extended attempt to elucidate its nature being made by Prof. Friedrich Knapp, of Brunswick, in 1856, who believed it to be a physical combination in contradistinction to Professor Deyeux, of Paris (1793), who believed tanning phenomena in general to be the formation of salts of gelatin.

The published information shows that ferric salts tan while ferrous salts do not and that basic ferric salts are much better tanning agents than the normal salts. It is interesting to note that the requirements of low acidity and oxidized state of iron for tannage were discovered by the eighteenth century patentees. An excellent summary of the history of iron tannage is to be found in Jettmar's book.<sup>3</sup>

Despite the numerous patents and chemical reports on iron tannage, no investigation of the irreversible combination of ferric iron and hide substance has ever been made. The purpose of this paper is to provide some information on this subject.

Since it is a well-established fact that tannage is due to the ferric, and not the ferrous, salts, the present study was limited to solutions of ferric sulfate, and includes experiments involving variations in tanning power of this salt with change of basicity and concentration of ferric sulfate, time of tannage, and effect of added sodium chloride and sodium sulfate.

In a prior publication it was shown that no aluminum is irreversibly fixed by hide substance unless the solutions of the aluminum tanning salts are rendered basic. It is revealed here that iron is irreversibly fixed by hide substance in solutions of normal ferric sulfate. Increase in basicity, however, results in increased iron fixation. The tanning action is exceedingly rapid. Sodium chloride diminishes the amount of iron fixed by the protein. Sodium sulfate, however, shows less inhibitory effect and, in fact, in solutions of the normal ferric salt actually favors degree of fixation of iron when small amounts of the sodium salt are present. Thus sodium sulfate produces different effects in iron tanning than it does in chromium and aluminum tanning.

#### Materials and Method

Concentrated stock solutions of ferric sulfate were prepared from the anhydrous c. p. salt. While this salt is quite soluble, it has a very low "solution velocity;" consequently considerable time is required to effect complete solution. The method employed was to weigh out 100 grams of the anhydrous salt, make up to 1000 cc. with distilled water, and allow to stand for 3 or 4 days, with frequent shaking. The yellow-white powder dissolved slowly to give a deep red-brown solution, which was filtered off from the undissolved residue and analyzed for iron content by the Zimmerman-Reinhardt method.

Since the Wilson and Kern modified method was to be used as a measure of the fixation of iron from ferric sulfate solution by hide powder, thereby demanding a clear solution, and since, either by dilution or partial neutralization, the hydrolysis of ferric salts is easily promoted to the point at which hydrous ferric oxide precipitates, it was necessary to establish first in what ranges of concentration and basicity it would be possible to work. Preliminary experiments with solutions of the normal salt indicated no precipitation upon dilution of the clear concentrated stock solution from 100 down to 3.5 grams of the salt per liter. In the case of solutions rendered basic by the addition of sodium hydroxide, the range was more limited, as indicated in the experiments described below involving the concentration factor.

In consequence of the ease with which ferric salts are reduced, determination of their pH values by use of the hydrogen electrode is impossible. Attempts to use the quinhydrone electrode likewise were unsatisfactory, even in the acid range of ferric salt solutions. Therefore the following method of expressing the basicity of solutions of the ferric salt, partially neutralized by addition of sodium hydroxide, was adopted:

$$B = \text{basicity} = \frac{\text{equivalents (OH)}^-}{\text{equivalents Fe}^{+++}}$$

in which a solution of the normal salt has a value for  $B = 0.000$ , this value increasing with addition of base until an equivalent amount of base [6 NaOH to 1  $\text{Fe}_2(\text{SO}_4)_3$ ] has been added, in which case  $B = 1.000$ .

<sup>1</sup> Presented by A. W. Thomas under the title "Iron Tannage" before the Division of Leather and Gelatin Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

<sup>2</sup> Contribution No. 562 from the Chemical Laboratories, Columbia University.

<sup>3</sup> "Die Eisengerbung: Ihre Entwicklung und jetziger Zustand," Verlagsbuchhandlung Schulze & Co., Leipzig, 1920.