

RESEARCH PAPER RP1566

Part of *Journal of Research of the National Bureau of Standards*, Volume 31,
November 1943

IRON AS A TANNING AGENT

By Joseph R. Kanagy and Ruth A. Kronstadt

ABSTRACT

Lactic, citric, hydroxyacetic, and gluconic acids were found satisfactory for stabilizing iron solutions to be used for tanning leather. The influence of pH and concentration on the combination of iron (Fe_2O_3) with standard hide powder was investigated. The maximum fixation of 23 to 25 percent of ferric oxide occurs in the pH range 3.5 to 4.0. Practical tanning experiments were made with goat- and calf-skins. The shrinkage temperatures of the iron-tanned leathers are lower than those of well-tanned chrome leathers. The results of accelerated aging tests indicate that all of the iron-tanned leathers tested had at least fair aging qualities except where gluconic acid was used. The use of iron salts for replacing those of chromium in the tanning of leather shows most promise where citric acid is used for stabilizing the solutions.

CONTENTS

| | Page |
|---|------|
| I. Introduction..... | 279 |
| II. Review of previous work..... | 280 |
| III. Materials..... | 281 |
| IV. Results and discussion..... | 282 |
| 1. Studies of the iron tanning solutions..... | 282 |
| 2. Effect of pH on the fixation of iron (Fe_2O_3) by hide powder..... | 286 |
| 3. Effect of concentrations on the fixation of iron (Fe_2O_3) by hide powder..... | 287 |
| 4. Tanning experiments..... | 287 |
| 5. Properties of the leathers..... | 288 |
| V. References..... | 289 |

I. INTRODUCTION

This report gives the results of a study of the use of iron salts for tanning light leathers used in the manufacture of shoes and garments for military and civilian use. The investigation includes a study of the properties of the iron tanning solutions, an improved method for tanning the leather, and a determination of the resistance of the leather to an accelerated aging test. This test was developed recently and consists in heating the leathers at 100°C . in the presence of moisture.

The investigation was undertaken at this time of national emergency because of the shortage in the domestic supply of tanning materials. The effect of this shortage is intensified by the demands of industries other than the leather industry, on material which is used in tanning. This is well illustrated in the case of chromium, which has extremely important uses in the manufacture of metal alloys for war industries and in the case of phenols, used for synthetic tanning materials, which are necessary to produce an increasing amount of synthetic resins and plastics.

The possible replacement of chromium by iron in tanning is shown by the results of past investigations. There are plentiful domestic supplies of iron. These facts suggested advantages to be gained by further studies in tanning with iron. The results given in this report show considerable promise for the use of iron salts in place of those of chromium in leather manufacture.

Literature references and a discussion of the work of others on the use of iron salts for tanning are included as a guide for those who may wish to review previous work. Tests of the properties of the iron tanning solutions are described. Experimental data are given on these tests and also on those applied to prepared leathers.

II. REVIEW OF PREVIOUS WORK

As early as the eighteenth century, attempts were made to develop methods of tanning with iron salts. A history of iron tanning is given in a book by J. Jettmar [1].¹ The first recorded patent on iron tanning was that taken out by Johnson, an Englishman, in 1770. Twenty-four years later another English patent was given to Ashton. The ferric salt was prepared either by dissolving iron oxide in acetic acid or by oxidizing ferrous sulfate. Hermbstadt in 1805 studied Ashton's patent and found that the best tannage resulted from the use of iron oxide in acetic acid. This fact is interesting in the light of our present knowledge of the formation of complex ions of organic acids with iron salts.

In 1842 Jules Bordier took out an English patent involving the use of basic ferric sulfate prepared by the treatment of a solution of ferrous sulfate with manganese dioxide or nitric acid, followed by the addition of ferric oxide. Knapp obtained a number of patents on iron tanning, but the use of his methods has failed to produce good leathers. The leather produced was brittle and deteriorated quite rapidly with age. He [2] mentioned also that while the tanning properties of iron were well known, no one as yet had produced a serviceable leather with iron salts.

Several explanations were given for the failures to produce successful iron tannages. Procter [3] suggested that the iron salts were oxygen carriers, and acted as oxidation catalysts to destroy the leather. Casaburi [4] believed that the poor results obtained with iron tannages were due to the failure to remove uncombined ferric salts from the leather. He obtained a complete tannage with a 67-percent acid ferric sulfate, and a less satisfactory result when some ferric chloride was present. With basic ferric chloride the skins became swollen and gelatinized. A better result obtained with basic ferric sulfate may have been due to the fact that it permits less swelling of the skin.

Jettmar [5] found the greatest difficulty in iron tanning to be the proper neutralization of the acid formed in the leather. For comparison, if chrome leather contains too high a proportion of sulfuric acid, it becomes very brittle on drying and assumes a dark-green color. The proper degree of neutralization for chrome leather is easy to achieve, since chromium hydroxide does not precipitate at a low pH value. In neutralizing iron-tanned leather, however, Jettmar found that the iron salts were colloiddally dispersed and were washed out of the leather.

¹ Numbers in brackets indicate the literature references at end of this paper.

Jackson and Hou [6] made an extended study of the various factors involved in the iron tanning of sheep skins, including the best method of oxidizing ferrous to ferric salts and the relation of basicity or acidity of the ferric salt to its stability and tanning properties. They prepared an iron-tanned leather which they were convinced compared favorably with other mineral-tanned leathers. It would not stand the boiling test, but shrank in water at temperatures greater than 75° C. They claimed that the chief cause of brittleness in iron-tanned leather was not the oxidizing action of the ferric salts, but rather an improper method of tanning, resulting in the precipitation of hydrated ferric oxide.

Thomas and Kelly [7] made a theoretical study of the factors involved in iron tanning, applying principles such as those used in alum and chrome tanning. They studied the effect of basicity on the amount of iron fixed by hide substance at different concentrations for different lengths of time. The influence of the neutral salts, sodium chloride and sodium sulfate were also considered.

From our present-day knowledge it is not expected that any of the above methods could be successful in preparing a satisfactory leather with fair aging characteristics, because the pH of the leather they produce is too low. The difficulty which was most likely encountered by the investigators was the precipitation of the iron salt on neutralization. Jettmar [5] was probably the first to attempt to make the iron solutions more stable by adding a strong solution of a neutral salt. Reinich in 1892 [4] suggested the addition of salt to iron chloride and afterward (1912) used an iron tanning solution made with iron chloride, magnesium carbonate, and aluminum chloride.

A number of [8] patents have been issued in which polycarboxylic acids, hydroxy acids, and amino acids are used to stabilize the iron solutions by complex ion formation. Other patents [9] cover the use of phosphates of aluminum, chrome and iron, albuminous substances, such as protalbumic acid and urea, and substitution products of ammonia.

Casaburi followed his use of ferric acetate with that of organic acids. He made extensive studies [10, 11, 12] with citric and tartaric acids and claimed the preparation of an iron-tanned leather with citric acid which withstood the boiling test.

The success of other investigators, although somewhat limited, showed the likelihood that better methods for tanning with iron could be developed. It suggested in a large part the course of the present investigation.

III. MATERIALS

A reagent grade ferric sulfate $\text{Fe}_2(\text{SO}_4)_3 \times \text{H}_2\text{O}$ was used. It contained approximately 29.5 percent of iron determined as Fe_2O_3 and about 56.6 percent of sulfate calculated as H_2SO_4 . The composition of the batches of materials varied slightly.

The acetic and citric acids used were chemically pure grades. The lactic, hydroxyacetic, and gluconic acids were technical grades of 85, 70, and 50-percent strength, respectively.

The sodium carbonate was an anhydrous chemically pure material. Standard hide powder prepared according to the specifications of the American Leather Chemists Association was ground to pass through a 2-mm sieve in a Wiley mill and used in the fixation experiments.

IV. RESULTS AND DISCUSSION

1. STUDIES OF THE IRON TANNING SOLUTIONS

Ferric hydroxide will be precipitated from solutions of ferric sulfate if a base such as sodium hydroxide or sodium carbonate is added, at a pH of about 2.5. Ferric hydroxide cannot be used for tanning. If, however, an organic acid is added to prevent this precipitation, the resulting solution can be used satisfactorily. The amount of the organic acid required to stabilize the solutions or prevent the precipitation of ferric hydroxide was determined by varying the concentration of the acid in increments of 0.05 and 0.1 of a mole per 1,000 ml of solution.

Tanning solutions were prepared by dissolving 40 g of the reagent grade ferric sulfate and the different amounts of the organic acid in 1,000 ml of solution. One-hundred-milliliter portions of the solutions were treated with different amounts of a 5-percent solution of sodium carbonate and made up to 200 ml. The resulting pH values were within the range 1.5 to 6.0.

It was considered that a sufficient quantity of the organic acid had been added if a slight precipitate of ferric hydroxide remained after 48 hours. The absence of a precipitate usually meant that more than the necessary amount of acid had been added, whereas the presence of a large precipitate obviously meant that too little had been added. By this method the amount of acetic, lactic, citric, hydroxy-acetic, or gluconic acid required to stabilize the tanning solutions were determined and are recorded in table 1. Citric acid is required in the lowest concentration of all the acids listed, whereas acetic is required in the highest concentration.

TABLE 1.—Amounts of organic acids required to stabilize the iron tanning solutions at all pH values in the range 2 to 6

| Acid | Acid per 40 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot x \cdot \text{H}_2\text{O}$ in 1,000 ml of solution | |
|--------------------|--|------------------------------|
| | Grams | Concentration Moles/liter |
| Acetic..... | 60 | 1.0 |
| Lactic..... | 9 | 0.1 |
| Citric..... | 6.4 | .033 |
| Hydroxyacetic..... | 15.2 | .2 |
| Gluconic..... | 19.6 | .1 |

The tanning properties of the solutions prepared in this way were determined by placing in them small pieces of steer hide, which were later examined for tannage. Steer hide was used so that the rate of penetration of the iron salt into the skin could be observed. The degree of tanning found by visual inspection indicated that the optimum pH range for tanning was 2.5 to 4.5. Some tanning action occurred throughout the range 1.75 to 5.5. Above or below these limits the hide remained soft and flabby, little combination having occurred. The addition of too much of the organic acid will prevent complete tanning action at any pH.

The changes in the pH on storage of the tanning solutions prepared in this way were determined. These experiments are analogous to others that have been applied to chrome tanning solutions. Iron tanning solutions containing 8 g of ferric sulfate and different amounts

TABLE 2.—Changes in the pH of the iron tanning solutions with time of storage

[Iron tanning solutions containing 8 g of ferric sulfate and different amounts of the organic acid in 100 ml were treated with varying amounts of sodium carbonate or sodium hydroxide and made up to 200 ml. The pH values of the solutions were determined immediately after preparation and after 24 hours and 48 hours.]

| Acid | Initial concentration of organic acid | 1.2 g of sodium carbonate added | | | 2.0 of sodium carbonate added | | | 2.8 g of sodium carbonate added | | | 3.6 g of sodium carbonate added | | | 4.4 g of sodium carbonate added | | |
|--------------------|---------------------------------------|---------------------------------|-------|-------|-------------------------------|-------|-------|---------------------------------|-------|-------|---------------------------------|-------|-------|---------------------------------|-------|-------|
| | | pH | | | pH | | | pH | | | pH | | | pH | | |
| | | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr |
| | <i>g/200 ml</i> | | | | | | | | | | | | | | | |
| Lactic..... | 2.1 | 2.05 | 2.00 | 2.00 | 2.50 | 2.40 | 2.40 | 2.65 | 2.40 | 2.40 | 2.75 | 2.55 | 2.55 | 3.40 | 3.15 | 3.15 |
| Do..... | 4.2 | 1.85 | 1.80 | 1.80 | 2.15 | 2.15 | 2.15 | 2.50 | 2.50 | 2.50 | 3.05 | 2.85 | 2.80 | 3.45 | 3.10 | 3.15 |
| Citric..... | 1.3 | 1.85 | 1.75 | 1.75 | 2.40 | 2.40 | 2.35 | 2.80 | 2.40 | 2.35 | 2.85 | 2.60 | 2.55 | 3.40 | 3.10 | 3.05 |
| Do..... | 2.6 | 1.50 | 1.45 | 1.50 | 1.80 | 1.80 | 1.85 | 2.20 | 2.20 | 2.20 | 2.75 | 2.75 | 2.75 | 3.70 | 3.25 | 3.20 |
| Hydroxyacetic..... | 4.3 | 1.90 | 1.80 | 1.85 | 2.35 | 2.10 | 2.10 | 2.50 | 2.45 | 2.40 | 2.70 | 2.70 | 2.65 | 3.80 | 3.25 | 3.15 |
| Gluconic..... | 3.6 | 1.75 | 1.75 | 1.75 | 2.10 | 2.10 | 2.05 | 2.40 | 2.30 | 2.30 | 3.15 | 2.75 | 2.70 | 3.70 | 3.30 | 3.30 |
| | | 1.0 g of sodium hydroxide added | | | 1.6 of sodium hydroxide added | | | 2.2 g of sodium hydroxide added | | | 2.9 g of sodium hydroxide added | | | 3.5 g of sodium hydroxide added | | |
| | | pH | | | pH | | | pH | | | pH | | | pH | | |
| | | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr | Initial | 24 hr | 48 hr |
| Lactic..... | 2.1 | 2.10 | 2.10 | 2.10 | 2.55 | 2.45 | 2.40 | 2.80 | 2.70 | 2.60 | 3.20 | 3.05 | 3.05 | 4.30 | 4.20 | 4.10 |
| Citric..... | 1.3 | 1.95 | 1.95 | 2.00 | 2.40 | 2.40 | 2.40 | 2.70 | 2.60 | 2.55 | 2.90 | 2.85 | 2.70 | 3.45 | 4.35 | 4.35 |
| Do..... | 2.6 | 1.20 | ----- | 1.30 | 1.45 | ----- | 1.45 | 2.30 | ----- | 2.35 | 3.00 | ----- | 3.00 | 3.50 | ----- | 7.15 |

of the organic acid in 100 ml were treated with varying amounts of sodium carbonate or sodium hydroxide and made up to 200 ml. The pH values of these solutions were determined immediately after preparation and after 24 and 48 hours of storage. The acidity of most of the solutions increased slightly on aging. Little change was noted after 24 hours. The results are shown in table 2.

A range of minimum stability of the tanning solutions containing an organic acid is shown at about pH 3 to 4.5. This is observed in the presence of the smaller concentrations of the organic acids if either sodium hydroxide or sodium carbonate is added. The solutions are stable at pH values above 4.5 or below 3, a behavior which resembles that of an amphoteric compound. This range becomes narrower on increasing the concentration of the organic acid and disappears entirely if sufficient acid is added. Results illustrating observations on gluconic acid are given in table 3.

TABLE 3.—*Ferric hydroxide, expressed as ferric oxide, precipitated from iron tanning solutions at various pH values obtained by the addition of different amounts of sodium carbonate or sodium hydroxide.*

The iron tanning solutions contained 40 g of ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$] and the noted amounts of gluconic acid in 1,000 ml of solution

| 0.05 mole of gluconic acid and Na_2CO_3 | | 0.075 mole of gluconic acid and Na_2CO_3 | | 0.075 mole of gluconic acid and NaOH | |
|---|-------------------------|--|-------------------------|--------------------------------------|-------------------------|
| pH | Fe_2O_3 | pH | Fe_2O_3 | pH | Fe_2O_3 |
| | <i>g</i> | | <i>g</i> | | <i>g</i> |
| 1.5 | 0 | 1.5 | 0 | 1.7 | 0 |
| 2.7 | .04 | 2.6 | 0 | 2.5 | 0 |
| 3.3 | 1.04 | 2.8 | 0.48 | 3.4 | 0.84 |
| 4.6 | 2.40 | 4.0 | 1.24 | 4.0 | .06 |
| 5.8 | 1.16 | 5.7 | 0 | 5.3 | 0 |
| 6.3 | 0.26 | 6.0 | 0 | 10.3 | 0 |

The tanning solutions were also studied by means of electrometric titration curves. Fifty-milliliter aliquots of solutions containing 40 g of ferric sulfate in 1,000 ml or this concentration of ferric sulfate and a definite amount of the organic acid in 1,000 ml were titrated with 1.0 *N* sodium carbonate solution.

The titration curves for the experimental iron tanning solutions, and for solutions of the separate constituents are given in figure 1. The titration curve for sulfuric acid solution equal in sulfate ion content to that of the tanning solutions is also shown.

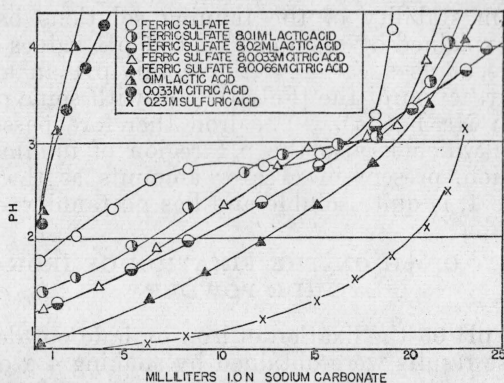
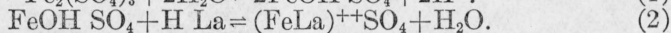
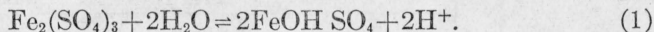


FIGURE 1.—Comparison of the titration curves.

The curves represent the materials at the following concentrations: 40 g of ferric sulfate in 1,000 ml; 40 g of ferric sulfate and 10.6 g of technical lactic acid (0.1M) in 1,000 ml; 40 g of ferric sulfate and 21.2 g of technical lactic acid (0.2M) in 1,000 ml; 40 g of ferric sulfate and 6.4 g of citric acid (0.033M) in 1,000 ml; 40 g of ferric sulfate and 12.8 g of citric acid (0.066M) in 1,000 ml; 10.6 g of technical lactic acid (0.1M) in 1,000 ml; 6.4 g of citric acid (0.033M) in 1,000 ml; 22.5 g of sulfuric acid (0.46N) in 1,000 ml.

The addition of lactic or citric acid apparently increases the amount of highly ionized acid in the solutions, for, as the concentrations of these acids are increased, the curves approach more nearly that of the sulfuric acid. The citric acid is more effective in this respect than the lactic acid. The curve for the ferric sulfate alone has a slope of zero at a pH of about 2.8. At this pH the iron is completely precipitated. This does not occur in the other solutions, where the iron is not completely precipitated.

A probable explanation of the increase in the amount of titratable acid in the regions of pH less than 3 can be given on the basis of a change in the hydrolysis equilibrium of the ferric sulfate solution through the formation of a complex ion. This equilibrium may be represented by the following equations where La represents lactic acid:



Equation 1 represents a partial hydrolysis of the ferric sulfate to form a basic salt and hydrogen ions. The FeOH SO_4 is unstable and slowly hydrolyzes further to form ferric hydroxide which is precipitated. It can then be assumed that the addition of an organic acid, such as lactic (La), will form a complex ion $[\text{FeLa}]^{++}$, which is soluble (eq 2), and the reaction represented by equation 1 will be driven further to the right and more hydrogen ions will be formed. This would explain the increase in hydrogen-ion concentration shown by the titration curves.

The addition of too much of the organic acid will decrease the tanning action at low pH values because reaction (2) will be shifted to the right, and little of the iron salt will be left in the form FeOH SO_4 , which is assumed to be the active tanning agent. The formation of a complex ion that results in an increase in acidity also gives a probable explanation for the increase in hydrogen-ion concentration of the solutions on storage, as shown by the results in table 2.

The minimum stability of the tanning solutions between pH 3 and 4 may be explained by assuming that at pH values lower than 4, the iron is present as a cation. Above this pH an anion may be formed by the reaction of the $[\text{FeLa}]^{++}$ ion with some of the sodium lactate to form $\text{Na Fe}(\text{La})_4$. The iron therefore passes through a transition state which is also the pH region of minimum stability. The $\text{Fe}(\text{La})_4^-$ ion, present in greater amounts as the pH value is increased above 4, is quite soluble and has no tanning effect.

2. EFFECT OF pH ON THE FIXATION OF IRON (Fe_2O_3) BY HIDE POWDER

The effect of pH on the fixation of iron by hide powder is shown in figure 2. These results were obtained by shaking 4 g of the powder for 4 hours in a bottle containing 24 g of ferric sulfate and 6.3 g of lactic acid or 3.9 g citric acid in 600 ml of the solution. The pH was varied by the addition of sodium carbonate. The concentration of ferric sulfate selected was that which gave maximum fixation in simultaneous experiments reported in section IV, 3, where the effect of concentration on the fixation of iron by hide powder is reported.

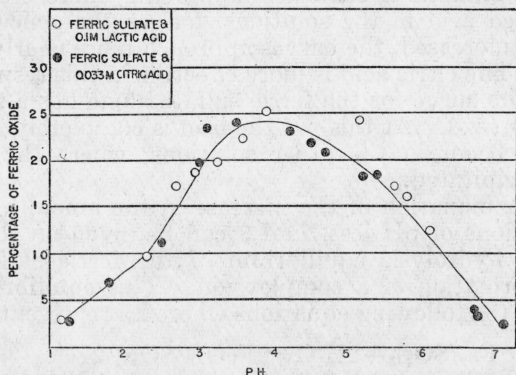


FIGURE 2.—Variation of the percentage of iron determined as ferric oxide fixed by hide powder, with change in pH of the tanning solutions.

Maximum fixation occurs in the pH range 3.5 to 4.25, where the basicity² varies from approximately 0.66 at 3 to 1.0 at 4. The greatest amounts of ferric oxide combined in this region vary from 23 to 25 percent, which is 3 times greater than the results obtained by Thomas and Kelly [7], who made studies at basicities less than 0.33. The smallest amounts of ferric oxide combine at pH 1 and again at pH 7. The results at pH 1 may be attributed to low basicity. The low results at pH 7 are possibly due to the formation of a complex ion that has little tanning action. Similar results were observed when sodium oxalate, which also forms complex ions, was added to chrome liquors [13].

² In leather chemistry the term "basicity" is used to express the ratio of the equivalents of base to equivalents of the metallic tanning element. In this case, it is the ratio of equivalents of sodium carbonate to the equivalents of iron.

3. EFFECT OF CONCENTRATIONS ON THE FIXATION OF IRON (Fe_2O_3) BY HIDE POWDER

The results of the studies on the effect of concentration on the fixation of iron by hide powder are shown in figure 3. In these studies, 4 g of the powder was shaken for 4 hours in a bottle containing 4 to 36 g of the reagent grade ferric sulfate and 1.06 g of the technical grade lactic acid or 0.64 g of citric acid for each 4 g of ferric sulfate in 600 ml of solution at a pH of 3.5 to 4.25. The pH values of the solutions were adjusted with sodium carbonate. The pH range for the determinations was selected from a simultaneous study on the effect of pH on the fixation of iron by hide substance (see this section, part 2).

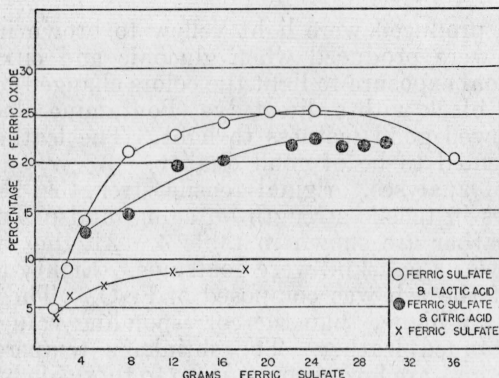


FIGURE 3.—Variation of the percentage of iron determined as ferric oxide fixed by hide powder at pH 3.5 to 4.25, with change in concentration of the tanning solutions.

0.265 g of lactic acid or 0.16 g of citric acid was added for each gram of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$)

Slightly higher percentages of ferric oxide are fixed by hide powder in the presence of lactic acid than in the presence of citric acid. These percentages show a tendency to decrease at the highest concentrations of ferric sulfate.

The curve representing the effect of ferric sulfate alone is presented to show that increased amounts of iron may be fixed in solutions having higher pH values if precipitation of ferric hydroxide is prevented by the addition of an organic acid. This solution of ferric sulfate prior to being used for tanning was adjusted to the point where a slight precipitate failed to dissolve on mixing. The pH was approximately 2.2 and the basicity 0.125.

4. TANNING EXPERIMENTS

Tanning experiments were made with pickled goatskins and one calfskin. The experiments were usually made with half of a skin, the wet pickled weight being about 300 g. This was drummed in 6 liters of a 5-percent solution of sodium chloride for 24 hours. To this was added 120 g of ferric sulfate and the amounts of the organic acid indicated in table 1 for each 40 g of the ferric sulfate, except in the case of citric acid, where 9.6 g was used. Sufficient anhydrous sodium carbonate, usually about 50 g, was then added to bring the pH to approximately 2.5.

The drum was rotated for about 6 hours, and then the solutions were made more basic by the addition of sodium carbonate. The hide remained in the solution in the drum overnight, and the next day the solutions were brought to a pH of 3.75 to 4 by the addition of more sodium carbonate. After drumming for about 6 hours longer, the hide was washed thoroughly. It was then fat-liquored³ with a mixture of sulfonated castor oil, sulfonated neat's-foot oil, and neat's-foot oil in the proportions of 15, 35, and 50 percent, respectively. The amount of fat liquor used was 5 percent of the wet pickled weight. The hide was then tacked on a board and dried. It was then removed from the board, sammied,⁴ and staked.⁵

5. PROPERTIES OF THE LEATHERS

The leathers produced were light yellow to brown in color. The lightest colors were produced when gluconic and citric acids were used. On normal exposure to light the colors changed to deep brown. A sample dyed black with a direct dye (Pontamine black EX, Color Index 581) showed good fastness to light. The leathers were very flexible and seemed to be of good quality.

The chemical analyses, original tensile strengths, shrinkage temperatures, losses in tensile strength on aging, and pH of a water extract of the leather are shown in table 4. All the samples except No. 21, which was a calfskin, were goatskins. Eighty-five to ninety-nine percent of the ash was composed of Fe_2O_3 . These percentages of ferric oxide are higher than the corresponding values for chromic oxide in well-tanned leather. The shrinkage temperatures of the iron-tanned leathers are low in comparison to those of chrome leathers. The calfskin leather gave the highest value for shrinkage temperature. However, this leather was thicker than the goatskin leathers, which may have had some influence on the result.

TABLE 4.—*Analysis of the iron-tanned leather and the results of the accelerated aging tests*

| Hide number | Organic acid | Hide substance | Grease | Ash | Moisture | pH | Shrinkage temperature | Original tensile strength | Loss in tensile strength on aging |
|-----------------------|--------------------|----------------|--------|------|----------|-----|-----------------------|---------------------------|-----------------------------------|
| | | % | % | % | % | | ° C | lb./in. ² | % |
| 1..... | Citric..... | 59.9 | 5.9 | 11.7 | 11.7 | 3.3 | 80 | 1,850 | 20.5 |
| 2..... | Lactic..... | 57.3 | 4.7 | 19.5 | 9.2 | 3.7 | 74 | 1,640 | 37.2 |
| 4..... | Citric..... | 58.5 | 1.0 | 15.4 | 9.6 | 3.9 | 84 | 2,165 | 11.8 |
| 5..... | do..... | 61.5 | 1.3 | 13.8 | 9.3 | 4.8 | 80 | 2,925 | 19.7 |
| 10..... | do..... | 58.2 | 7.7 | 13.4 | 7.0 | 3.4 | 76 | 2,850 | 18.8 |
| 11..... | do..... | 60.2 | 5.7 | 12.0 | 9.1 | 3.6 | 84 | 3,620 | 27.8 |
| 12..... | Hydroxyacetic..... | 54.1 | 9.0 | 15.4 | 7.9 | 3.6 | 75 | 3,875 | 35.2 |
| 13..... | Citric..... | 59.0 | 6.7 | 10.4 | 7.6 | 4.6 | 77 | 4,895 | 31.3 |
| 15 ¹ | do..... | 47.7 | 21.3 | 10.1 | 7.1 | 4.5 | 80 | 4,425 | 31.2 |
| 19..... | Gluconic..... | 55.7 | 11.6 | 14.5 | 10.4 | 3.6 | ----- | 2,905 | 50.1 |
| 20..... | do..... | 55.5 | 12.7 | 7.6 | 10.7 | 3.4 | 77 | 3,695 | 54.4 |
| 21 ² | do..... | 48.9 | 4.7 | 12.5 | 12.4 | 3.0 | 90 | 2,980 | 55.2 |

¹ Dyed black.

² Calfskins.

³ Treated with an oil-water emulsion, from which oil is absorbed by the tanned hide.

⁴ Treated to increase its moisture content by slow absorption from damp sawdust or from a similar material.

⁵ Stretched by pulling it over the edge of a board or similar device.

The best iron-tanned leathers were exposed to accelerated aging conditions. Six control and six tensile-strength test specimens were cut from each sample of leather. Each control was cut adjacent to a test specimen. After the samples had been conditioned at 70° F and 65-percent relative humidity for 48 hours, they were placed in an exposure chamber maintained at $100^{\circ} \pm 2^{\circ}$ C. Air saturated with moisture at 45° C was passed over the samples at a rate of 8 to 12 ml per minute. The air saturated at this temperature contained sufficient moisture to give a relative humidity of 9 to 11 percent in the chamber at 100° C.

The specimens were heated under these conditions for 7 days. They were then reconditioned at 70° F and 65-percent relative humidity and tested with the control samples which had remained in the conditioning room under the same conditions. The percentage loss in tensile strength of the aged samples was calculated from the difference between their average tensile strength and that of the control samples. The results are shown in table 4.

It is considered, from previous experience, that leather showing no more than a 20-percent loss in tensile strength has good resistance to aging; above 20 percent but no more than 35 percent is considered fair.

V. REFERENCES

- [1] J. Jettmar, *Iron Tanning*, (Verlagsbuchhandlung Schulze, Leipzig, 1920).
- [2] F. Knapp, *J. Am. Leather Chem. Assn.* **16**, 658 (1921).
- [3] H. R. Procter, *The Principles of Leather Manufacture*, second edition (D. Van Nostrand Co., Inc., New York, N. Y., 1922).
- [4] V. Casaburi, *J. Soc. Leather Trades Chem.* **3**, 61-74 (1919).
- [5] J. Jettmar, *Cuir Tech.* **8**, 74, 106 (1919).
- [6] D. D. Jackson and Te Pang Hou, *J. Am. Leather Chem. Assn.* **16**, 63, 139, 202, 229 (1921).
- [7] A. W. Thomas and M. W. Kelly, *Ind. Eng. Chem.* **20**, 632 (1928).
- [8] British patent 495,638. Italian patent 339,954. U. S. patent 2,127,297. British patent 461,685. British patent 495,638. British patent 470,536.
- [9] German patents 639787, 645389, French patent 807985, U. S. patent 2,141,276, Danish patent 56228, Norwegian patent 59278, British patent 292,501, U. S. patent 1,892,410.
- [10] V. Casaburi, *Cuir Tech.* **23**, 192 (1934).
- [11] V. Casaburi, *Boll. staz. sper. ind. pelli mat. concianti Napoli-Torino* **12**, 73 (1934); **12**, 169 (1934).
- [12] V. Casaburi, *Boll. staz. sper. ind. pelli mat. concianti Napoli-Torino*, **16**, 34, 79, 126 (1938).
- [13] John Arthur Wilson, *Modern Practice in Leather Manufacture*, p. 403. (Reinhold Publishing Corporation, New York, N. Y., 1941).

WASHINGTON, September 3, 1943.



NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

Send me the Mathematical Tables marked X below. I enclose remittance ¹ to cover the cost.

| Mark X | Title of publication | United States and its possessions, and countries extending franking privilege | Other countries | Amount enclosed |
|--------|---|---|-----------------|-----------------|
| | MT2. Tables of the exponential function e^x | \$2.00 | \$2.50 | |
| | MT3. Tables of circular and hyperbolic sines and cosines for radian arguments | 2.00 | 2.50 | |
| | MT4. Tables of sines and cosines for radian arguments | 2.00 | 2.50 | |
| | MT5. Tables of sine, cosine, and exponential integrals, volume I | 2.00 | 2.50 | |
| | MT6. Tables of sine, cosine, and exponential integrals, volume II | 2.00 | 2.50 | |
| | MT7. Table of natural logarithms, volume I | 2.00 | 2.50 | |
| | MT8. Tables of probability functions, volume I | 2.00 | 2.50 | |
| | MT9. Table of natural logarithms, volume II | 2.00 | 2.50 | |
| | MT10. Table of natural logarithms, volume III | 2.00 | 2.50 | |
| | MT11. Tables of moments of inertia and section moduli | 2.00 | 2.50 | |
| | MT12. Table of natural logarithms, volume IV | 2.00 | 2.50 | |
| | MT13. Table of sine and cosine integrals for arguments from 10 to 100 | 2.00 | 2.50 | |
| | MT14. Tables of probability functions, volume II | 2.00 | 2.50 | |
| | MT15. The hypergeometric and Legendre functions with applications to integral equations of potential theory | 2.00 | 2.50 | |
| | MT16. Table of arc tan x | 2.00 | 2.50 | |
| | MT17. Miscellaneous physical tables—Planck's radiation functions; electronic functions | 1.50 | 1.75 | |
| | MT18. Table of the zeros of the Legendre polynomials of order 1-16 and the weight coefficients for Gauss' mechanical quadrature formula | .25 | .30 | |
| | MT19. On the function $H(m,a,x) = \exp(-ix)F(m+1-ia, 2m+2; ix)$ | .25 | .30 | |
| | Total remittance | | | |

¹ Remittance should be in form of post-office money order, or check, and made payable to the order of the "National Bureau of Standards" in United States currency.

Send to _____
 Number and street _____ City and State _____

(Cut here)

MATHEMATICAL TABLES

Attention is invited to a series of publications prepared by the *Project for the Computation of Mathematical Tables* conducted by the Federal Works Agency, Work Projects Administration for the City of New York, under the sponsorship of the National Bureau of Standards. The tables which have been made available through the National Bureau of Standards are listed below.

There is included in this list a publication on the hypergeometric and Legendre functions (MT15), prepared by the Bureau.

MT1. TABLE OF THE FIRST TEN POWERS OF THE INTEGERS FROM 1 TO 1000:

(1938) VIII+80 pages; heavy paper cover. Out of print.

MT2. TABLES OF THE EXPONENTIAL FUNCTION e^x .

The ranges and intervals of the argument and the number of decimal places in the entries are given below:

| Range of x | Interval of x | Decimals given |
|-------------------|-----------------|----------------|
| -2.5000 to 1.0000 | 0.0001 | 18 |
| 1.0000 to 2.5000 | .0001 | 15 |
| 2.500 to 5.000 | .001 | 15 |
| 5.00 to 10.00 | .01 | 12 |

(1939) XV+535 pages; bound in buckram, \$2.00.

MT3. TABLES OF CIRCULAR AND HYPERBOLIC SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 9 decimal place values of $\sin x$, $\cos x$, $\sinh x$ and $\cosh x$ for x (in radians) ranging from 0 to 2 at intervals of 0.0001.

(1939) XVII+405 pages; bound in buckram, \$2.00.

MT4. TABLES OF SINES AND COSINES FOR RADIAN ARGUMENTS:

Contains 8 decimal place values of sines and cosines for radian arguments ranging from 0 to 35 at intervals of 0.001.

(1940) XXIX+275 pages; bound in buckram, \$2.00.

MT5. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME I:

Values of these functions to 9 places of decimals from 0 to 2 at intervals of 0.0001.

(1940) XXVI+444 pages; bound in buckram, \$2.00.

MT6. TABLES OF SINE, COSINE, AND EXPONENTIAL INTEGRALS, VOLUME II:

Values of these functions to 9, 10, or 11 significant figures from 0 to 10 at intervals of 0.001, with auxiliary tables.

(1940) XXXVII+225 pages; bound in buckram, \$2.00.

MT7. TABLE OF NATURAL LOGARITHMS, VOLUME I:

Logarithms of the integers from 1 to 50,000 to 16 places of decimals.

(1941) XVIII+501 pages; bound in buckram, \$2.00.

MT8. TABLES OF PROBABILITY FUNCTIONS, VOLUME I:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 5.6 at intervals of 0.001.

(1941) XXVIII+302 pages; bound in buckram, \$2.00.

[Continued on p. 4 of cover]

MT9. TABLE OF NATURAL LOGARITHMS, VOLUME II:

Logarithms of the integers from 50,000 to 100,000 to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, \$2.00.

MT10. TABLE OF NATURAL LOGARITHMS, VOLUME III:

Logarithms of the decimal numbers from 0.0001 to 5.0000, to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, \$2.00.

MT11. TABLES OF THE MOMENTS OF INERTIA AND SECTION MODULI OF ORDINARY ANGLES, CHANNELS, AND BULB ANGLES WITH CERTAIN PLATE COMBINATIONS:

(1941) XIII+197 pages; bound in green cloth, \$2.00.

MT12. TABLE OF NATURAL LOGARITHMS, VOLUME IV:

Logarithms of the decimal numbers from 5.0000 to 10.0000, to 16 places of decimals.
(1941) XXII+506 pages; bound in buckram, \$2.00.

MT13. TABLE OF SINE AND COSINE INTEGRALS FOR ARGUMENTS FROM 10 TO 100:

(1942) XXXII+185 pages; bound in buckram, \$2.00.

MT14. TABLES OF PROBABILITY FUNCTIONS, VOLUME II:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 7.8 at intervals of 0.001.

(1942) XXI+344 pages; bound in buckram, \$2.00.

MT15. The hypergeometric and Legendre functions with applications to integral equations of potential theory. By Chester Snow, National Bureau of Standards. Reproduced from original handwritten manuscript.

(1942) VII+319 pages; bound in heavy paper cover, \$2.00.

MT16. TABLE OF ARC TAN X:

Table of inverse tangents for positive values of the angle in radians. Second central differences are included for all entries.

| Range of x | Interval between successive arguments |
|-----------------|---------------------------------------|
| 0 to 7 | 0.001 |
| 7 to 50 | .01 |
| 50 to 300 | .1 |
| 300 to 2,000 | 1 |
| 2,000 to 10,000 | 10 |

(1942) XXV+169 pages; bound in buckram, \$2.00.

MT17. Miscellaneous Physical Tables:

Planck's radiation functions (Originally published in the Journal of the Optical Society of America, February 1940); and Electronic functions.

(1941) VII+58 pages; bound in buckram, \$1.50.

MT18. Table of the Zeros of the Legendre Polynomials of Order 1-16 and the Weight Coefficients for Gauss' Mechanical Quadrature Formula.

(Reprinted from Bull. Amer. Mathematical Society, October 1942.)

5 pages with cover. 25 cents.

MT19. On the Function $H(m, a, x) = \exp(-ix) F(m+1-ia, 2m+2; ix)$; with table of the confluent hypergeometric function and its first derivative.

(Reprinted from Journal of Mathematics and Physics, December 1942.) 20 pages, with cover. 25 cents.

Payment is required in advance. Make remittance payable to the "National Bureau of Standards," and send with order, using the blank form facing page of the cover.

The prices are for delivery in the United States and its possessions and in countries extending the franking privilege. To other countries the price of MT2 to MT16, inclusive, is \$2.50 each; M117, \$1.75; MT18 and MT19, 30 cents each; remittance to be made payable in United States currency.

Copies of these publications have been sent to various Government depositories throughout the country, such as public libraries in large cities, and colleges and universities, where they may be consulted.

A mailing list is maintained for those who desire to receive announcements regarding new tables as they become available.