

RESEARCH PAPER RP1128

Part of Journal of Research of the National Bureau of Standards, Volume 21,
August 1938

ACCELERATED AGING OF LEATHER IN THE OXYGEN BOMB AT 100° C

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ABSTRACT

Various tannages of leather and raw hide were exposed to oxygen under pressure in a bomb at 100° C for 7 days. Ammonia, primary amino nitrogen, and the percentages of the total nitrogen dissolved in water and in 0.1 *N* sodium carbonate were determined on the exposed samples and compared with similar data from leather aged under normal conditions. The evolution of carbon dioxide and water from some of the leathers and raw hide was also studied by heating in oxygen at atmospheric pressure at 100° C.

The tannages of leather used were sumac, cutch, copper-free chestnut, and sulfite cellulose pretanned in sulfite cellulose and finished in commercial chestnut, and a blend of chestnut and sulfite cellulose.

The pH values of the vegetable-tanned leathers in most cases drop during exposure in the bomb, while those of raw hide and sulfite cellulose leather rise.

Stability of the leathers under the accelerated conditions at a given pH appears to be dependent upon the type of tanning material.

The vegetable tannins are relatively susceptible to oxidation in oxygen at 100° C, as shown by the percentages of carbon dioxide and water evolved.

A comparison shows that the mechanisms of the deterioration of leather under the normal and the accelerated aging conditions are similar, because the degradation of the hide substance under either condition appears to be hydrolysis, while the breakdown of the tannins under either condition appears to be oxidation.

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I. INTRODUCTION

In a previous investigation [1]¹ at the National Bureau of Standards, quebracho- and chestnut-tanned leathers were exposed in an oxygen bomb under various conditions. The conditions varied were

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

the pressure of oxygen, the temperature in the bomb, the time of exposure, the moisture content of the leather, and the pH of the leather. Samples of these leathers were dried in an oven at 100° C for 24 hours and then exposed in the bomb, containing initially an atmosphere of oxygen at 100 lb/in.², and aged at 100° C for 7 days. The results with respect to the influence of acidity were comparable to those obtained with similar leathers aged under normal aging conditions. The results also definitely indicated that the stability of a leather depends in part upon the type of tanning material used.

This investigation is a continuation of the study of the behavior of leather in the oxygen bomb. A study of the stability of various tannages of leathers and raw hide under these conditions as well as of the comparative rates of evolution of carbon dioxide and water from some of the samples is presented. The latter study was made in order to obtain some data on the mechanism of the deterioration of the tannins.

II. PREPARATION OF LEATHER AND HIDE SAMPLES

The leathers used in this work were prepared in the experimental tannery at the National Bureau of Standards as follows:

1. Leather tanned with a copper-free chestnut-wood extract. The extract was prepared in the laboratory by leaching wood chips in a porcelain-lined container. The leather tanned with the extract was free from copper. This leather was selected for comparison with leather tanned with a commercial extract which was found to contain up to 0.04 percent of copper.

2. Leather tanned with sulfite cellulose extract. The tanning liquors contained 5 percent of sodium chloride by weight. The salt was added to minimize the plumping of the hide.

3. Leather pretanned with sulfite cellulose and finished with commercial chestnut-wood extract. The hides were tanned in a liquor described under 2 for 1 week after which time the tanning was completed in commercial chestnut-wood extract.

4. Leather tanned with a blend of one-third sulfite cellulose extract and two-thirds commercial chestnut extract. The proportions were based on the tannin content of the extract as determined by the ALCA method.

5. Leather tanned with sumac extract.

6. Leather tanned with cutch (mangrove bark) extract.

In the case of the last three tannages, a small amount of acetic acid was added to the initial liquors for the purpose of assisting in neutralizing the residual lime which remained in the hides after bating.

Blocks of the finished leathers 6 by 15 inches, treated with sulfuric acid so as to have pH values ranging from 2.25 to 5, were cut into smaller pieces 1½ by 3 inches, which were used in making the experiments.

The raw hide used in this investigation was prepared from a limed and unhaired steer hide. The hide was washed and bated. It was dehydrated by soaking first in 95-percent ethyl alcohol and finally in petroleum ether. Pieces of the dehydrated hide were then treated with sulfuric acid solutions of different concentrations. After soaking in the acid, the hide was again dehydrated with ethyl alcohol and petroleum ether. Pieces of the hide 1½ by 3 inches, having pH values ranging from 2.25 to 5, were used in the experiments.

III. METHOD OF ACCELERATED AGING

In making the tests, the samples of leather or raw hide were dried in an oven at 100° C for 24 hours. They were then placed in the oxygen bomb, oxygen was added under pressure, and the samples in the bomb were placed in an oven at 100° C and aged under these conditions for 7 days. The initial pressure in the bomb was approximately 100 lb/in² at 25° C. The extent of the deterioration was determined from the percentages of the nitrogenous materials extracted from the aged samples by water and by 0.1 *N* sodium carbonate solution. The details of this method of determining the extent of the deterioration and a description of the oxygen bomb used are given in a previous report [1].

The amount of ammonia in the water extracts was determined [2] by adding an excess of magnesium oxide to an aliquot part of the solution in a Kjeldahl flask and distilling the ammonia into 0.2 *N* sulfuric acid. The amount of primary amino nitrogen was determined [3] on an aliquot part of the water extract by the method of Van Slyke, which is based on the evolution of nitrogen from primary amino groups by a reaction with nitrous acid.

IV. ROLE OF pH IN THE NATURAL AND ACCELERATED AGING OF LEATHER

Since it is known that the deterioration of leathers is influenced by acidity, a knowledge of pH changes occurring during aging is necessary for an accurate interpretation of the results. A discussion of pH changes occurring in chestnut- and quebracho-tanned leathers treated with copper and iron salts and with sulfuric acid was presented in a previous investigation [4]. It was observed that the pH values of these leathers, in most cases, decreased during exposure in the bomb. The extent of the decrease depended upon the initial pH and the salt used in impregnating the leather.

The pH changes for chestnut- and quebracho-tanned leathers are shown in table 1. The greater amount of the pH decrease for these leathers took place within the first 24 hours. For chestnut leather, two of the three samples actually had lower pH values at the end of 24 hours than at the end of 7 days. Raw hide showed a pH increase during exposure in the bomb, as shown in table 2. It may also be observed that this increase in pH was not as rapid as the decrease in pH for the leathers, as practically no change was noticed in the former case at the end of 24 hours. However, at the end of 96 hours' exposure a definite increase in pH had occurred for the raw hide. From these results, it appears that in the case of the leathers the pH after exposure represents most nearly the pH influencing the greater part of the deterioration. However, in the case of the raw hide, where the pH change occurs less rapidly, a value somewhere between the initial and final pH values would most nearly represent that pH value which influences the greater part of the deterioration.

TABLE 1.—*Change of the pH values of samples of quebracho- and chestnut-tanned leathers when exposed under the accelerated conditions*

Leather	Duration of exposure (days)				
	0	1	2	4	7
Quebracho.....	4.34	3.62	3.51	3.47	3.47
Do.....	3.74	3.38	3.28	3.22	3.24
Do.....	2.58	2.60	2.58	2.56	2.39
Chestnut.....	3.47	3.12	3.08	3.12	3.12
Do.....	3.20	2.86	2.86	2.85	2.88
Do.....	2.78	2.52	2.51	2.58	2.64

TABLE 2.—*Change of the pH values of samples of raw hide when exposed under the accelerated conditions*

Sample number	Duration of exposure (days)				
	0	1	2	4	7
1.....	2.62	2.60	-----	-----	2.92
2.....	2.46	2.36	-----	-----	2.52
3.....	2.42	2.42	-----	-----	2.62
4.....	2.59	-----	2.64	-----	2.73
5.....	2.54	-----	2.54	-----	2.74
6.....	2.25	-----	2.25	-----	2.46
7.....	2.76	-----	-----	2.92	2.96
8.....	2.69	-----	-----	2.90	2.83
9.....	2.25	-----	-----	2.38	2.46

V. COMPARATIVE STABILITY OF VARIOUS TANNAGES IN OXYGEN UNDER PRESSURE

Since the pH values of the leather and raw hide samples do not remain constant during exposure, and especially since the pH changes of the two types of samples are opposite in trend, for purposes of comparison the results are presented as a function of the initial pH in figure 1(A) and as a function of the pH after exposure in figure 1(B). Results for quebracho- and commercial chestnut-tanned leathers, which were presented in a study of the effects of copper and iron salts on leather, are also given in these figures. Because of variations in the results obtained for raw hide, a curve indicating only the trend of the increase in deterioration with decrease in pH is shown in this figure. The actual results are given in figure 2, where the percentages of the total nitrogen dissolved are presented as a function of the initial pH.

The results in figure 1 indicate that with the exception of the sulfite cellulose leather, the conclusions as to the comparative stabilities of the leathers would be the same from observations of either graph. The percentages of the total nitrogen dissolved from the leathers presented as a function of the initial pH indicate that the sulfite cellulose leather is comparable with the cutch leather, but when the same results are presented as a function of the pH after exposure it is comparable with the chestnut leathers. Since the pH values of the samples of sulfite cellulose leather rise during exposure, it appears from

a consideration of the results that this leather is less stable than the cutch leather and probably has no greater stability than the chestnut leather prepared from the commercial extract. The order of decrease-

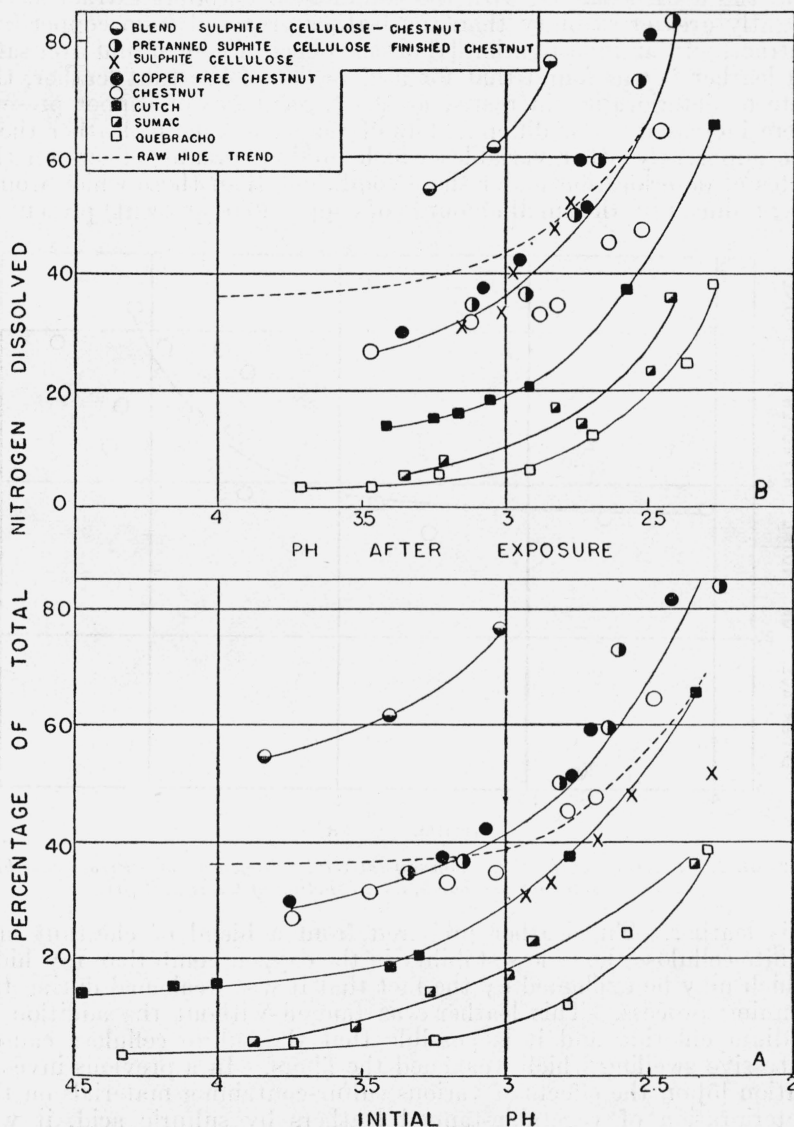


FIGURE 1.—Increase in the percentages of the total nitrogen dissolved from various tannages of leather exposed in the oxygen bomb, as a function of the initial pH and as a function of the pH after exposure.

ing stability of the samples at pH 3 is then, quebracho leather, sumac leather, cutch leather, sulfite cellulose and chestnut leathers, raw hide, and leather prepared from a blend of commercial chestnut and sulfite cellulose.

All leathers of a chestnut tannage except that prepared from a blend of chestnut and sulfite cellulose show approximately equal stabilities at pH 3.25. Below this pH value, however, variations occur and the leather tanned with the commercial chestnut extract shows slightly greater stability than the leather prepared from copper-free extract. In an investigation [4] on the effect of copper and iron salts on leather it was found that for a given lot of chestnut leather, the rate of deterioration increased as the percentages of copper present were increased. For different lots of the same type of leather there are apparently other variables which produce greater effects on the rates of deterioration under these conditions than those which would be produced by the small amounts of copper (0.04 percent) present in

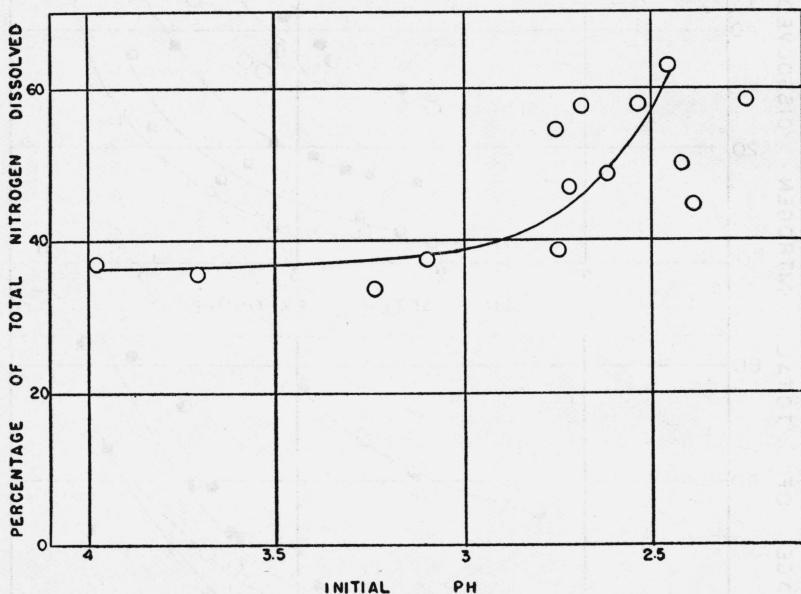


FIGURE 2.—Increase in the percentages of the total nitrogen dissolved from raw hide exposed in the oxygen bomb, as a function of the initial pH.

this leather. The leather prepared from a blend of chestnut and sulfite cellulose shows less stability in the oxygen bomb than raw hide, which may be explained by the fact that it was weakened during the tanning process. This leather was tanned without the addition of sodium chloride and it is possible that the sulfite cellulose caused excessive swelling which weakened the fibers. In a previous investigation [5] on the effects of various sulfur-containing materials on the deterioration of vegetable-tanned leathers by sulfuric acid, it was observed that leathers tanned with a blend of either quebracho or chestnut and sulfite cellulose showed the lowest original tensile strength.

VI. COMPARISON OF NORMAL AND ACCELERATED AGING

In a previous investigation [2] a study was made of the soluble decomposition products formed when leather was aged under normal conditions. These leathers were aged at 70° F and 65-percent relative

humidity for 2 years in the absence of direct sunlight, and then stored from 3 to 8 years longer at room temperature and atmospheric conditions. A comparison may therefore be made of the pH changes that have occurred and the soluble decomposition products formed in these leathers with the same data obtained from leathers treated under the accelerated conditions.

1. pH CHANGES

A comparison of the pH changes occurring during accelerated and normal aging conditions is shown in table 3. Under the accelerated conditions a decrease in pH is shown for all samples except those having the lowest initial pH values where, in some cases, a slight

TABLE 3.—Comparison of pH changes occurring under normal and accelerated aging conditions

Leather	pH of samples after normal aging ¹		pH of samples after accelerated aging in oxygen bomb for 7 days	
	Initial	After exposure	Initial	After exposure
Quebracho.....	5.39	4.79	4.98	3.71
Do.....	3.03	3.54	3.25	2.92
Do.....	2.50	3.19	2.78	2.70
Do.....	2.12	2.88	2.30	2.28
Chestnut.....	3.53	3.41	3.74	3.47
Do.....	2.19	2.56	3.20	2.88
Do.....	1.90	2.24	2.78	2.64
Do.....	1.70	2.07	2.48	2.46
Cutch.....	5.25	4.08	4.16	3.24
Do.....	3.16	3.26	3.30	2.92
Do.....	2.78	3.05	2.78	2.62
Do.....	2.40	2.70	2.34	2.46
Sumac.....	3.75	3.45	3.86	3.35
Do.....	3.05	2.94	3.26	2.73
Do.....	2.77	2.60	2.90	2.49
Do.....	2.42	2.34	2.34	2.42

¹ The normal aging period for the quebracho and chestnut leathers was 10 years, and for cutch and sumac 5 years.

increase in pH occurs. For leathers aged under the normal conditions, only those samples having the highest initial pH values and the samples of sumac leather show a decrease in pH. The decrease in pH is probably caused by organic acids formed by the oxidation of the tannins, while the rise in pH is probably caused by the presence of ammonia and amino nitrogen formed by deteriorating reactions in the hide substance. The pronounced tendency of the pH to decrease during accelerated aging is due to greater oxidizing action and the fact that less ammonia is formed, as shown in table 4.

TABLE 4.—Comparison of the percentages of ammonia formed under normal and accelerated aging conditions

Leather	Initial pH conditions		Percentage of the total nitrogen as ammonia	
	Normal	Accelerated	Normal aging ¹	Accelerated aging in oxygen bomb for 7 days
Quebracho.....	5.39	4.98	0.35	0.32
Do.....	3.03	3.25	1.83	.48
Do.....	2.50	2.78	3.12	.24
Do.....	2.12	2.30	5.10	.48
Chestnut.....	3.53	3.74	0.96	.25
Do.....	2.19	3.20	1.84	.46
Do.....	1.90	2.78	2.90	.53
Do.....	1.70	2.48	4.03	.63
Cutch.....	5.25	4.16	0.20	.24
Do.....	3.16	3.30	.60	.24
Do.....	2.78	2.78	1.55	.49
Do.....	2.40	2.34	2.64	.49
Sumac.....	3.75	3.86	0.34	.22
Do.....	3.05	3.26	.46	.44
Do.....	2.77	2.90	.56	.44
Do.....	2.42	2.34	2.34	.67

¹ The normal aging period for the quebracho and chestnut leathers was 10 years and for cutch and sumac 5 years.

2. FORMATION OF AMMONIA AND PRIMARY AMINO NITROGEN

A study of the soluble decomposition products formed under normal aging conditions indicated that the formation of ammonia increased with both acid concentration and time, and that the percentages of ammonia formed in leathers aged under various conditions showed no correlation with the deterioration of the leathers. The amounts of ammonia formed during accelerated aging are shown in table 4 and figure 3. In figure 3, the ammonia content of leathers treated with copper and iron salts, leathers treated with sulfuric acid, and raw hide treated with sulfuric acid are given as a function of the initial pH values of the samples. The results indicate that in most cases less than 1 percent of ammonia was formed, although the amount of deterioration occurring was in most cases greater than that taking place under normal conditions where the ammonia content was as much as 5 percent for a 10-year aging period, as shown in table 4. The leathers treated with copper and iron salts showed slightly higher ammonia contents than any of the other samples at the same pH values, which indicates that these salts exerted a slightly accelerated oxidizing effect on the hide substance.

The fact that less ammonia is formed during accelerated aging than during normal aging, as shown in table 4, is not thought to have any significance with regard to the mechanisms of deterioration under the two sets of conditions. Since the formation of ammonia has been shown to increase with time of aging and acid content, it is possible that if the time of aging in the oxygen bomb were of greater duration, the amount of ammonia formed would be increased. The small amounts of ammonia formed under the accelerated conditions indicate that gaseous oxygen has little oxidizing effect on the hide substance.

The percentages of the total nitrogen as primary amino nitrogen for copper- and iron-treated leathers, sulfuric acid treated leathers, and sulfuric acid treated raw hide are shown in figure 4. The amounts of primary amino nitrogen formed are extremely small and although they are slightly higher than the amounts for the same pH values obtained under normal aging conditions, they are hardly appreciable. These results indicate little hydrolysis of peptide linkages. The percentages of the total nitrogen as primary amino nitrogen for the three types of samples tend to increase slightly with decrease in pH. There is no indication of a difference in the average amounts formed at a given pH value for any of the three types of samples.

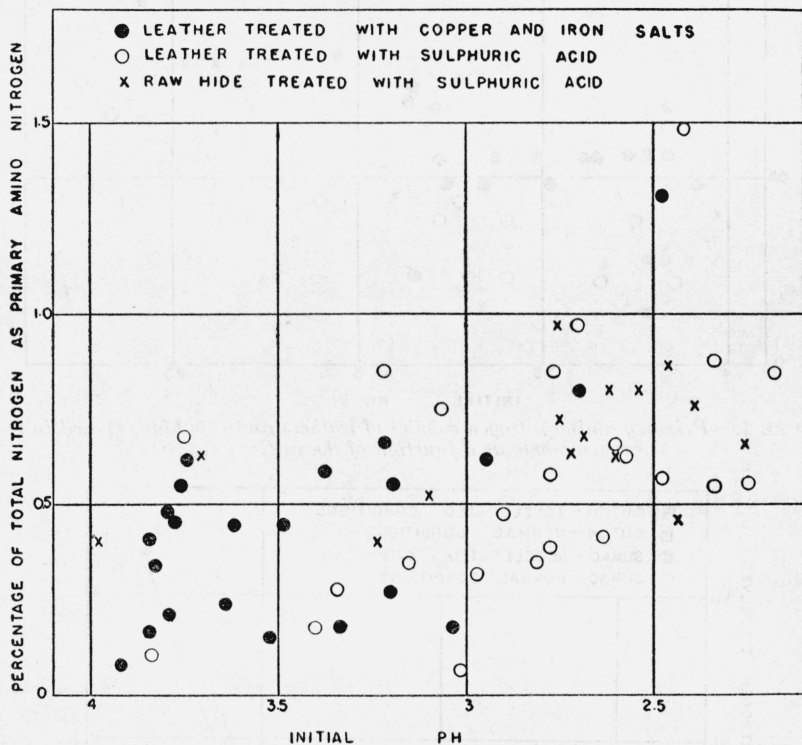


FIGURE 3.—Ammonia contents of leathers and raw hide exposed in the oxygen bomb, as a function of the initial pH.

3. FORMATION OF SOLUBLE NITROGENOUS COMPOUNDS

The percentages of the total nitrogen dissolved from cutch and sumac leathers as a function of the initial pH under normal and accelerated aging conditions are shown in figure 5. Both leathers showed greater percentages of the total nitrogen dissolved at all pH values studied under accelerated conditions. Under either set of conditions sumac leather was more stable than cutch leather. The leathers showed rapidly increasing percentages of the total nitrogen dissolved below pH 3 under either set of conditions. Similar observations in the case of chestnut- and quebracho-tanned leathers were made in a previous

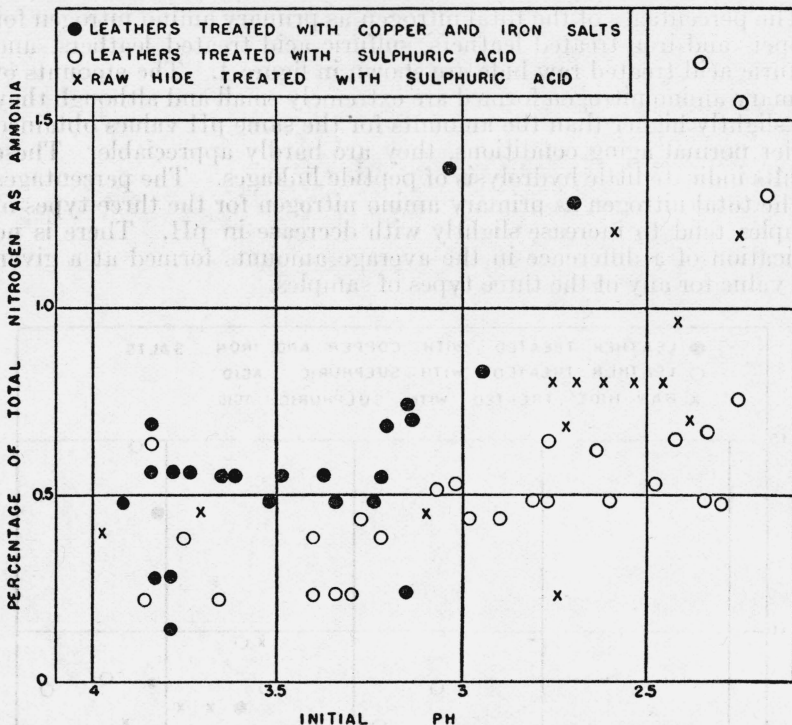


FIGURE 4.—Primary amino nitrogen content of leathers and raw hide exposed in the oxygen bomb, as a function of the initial pH.

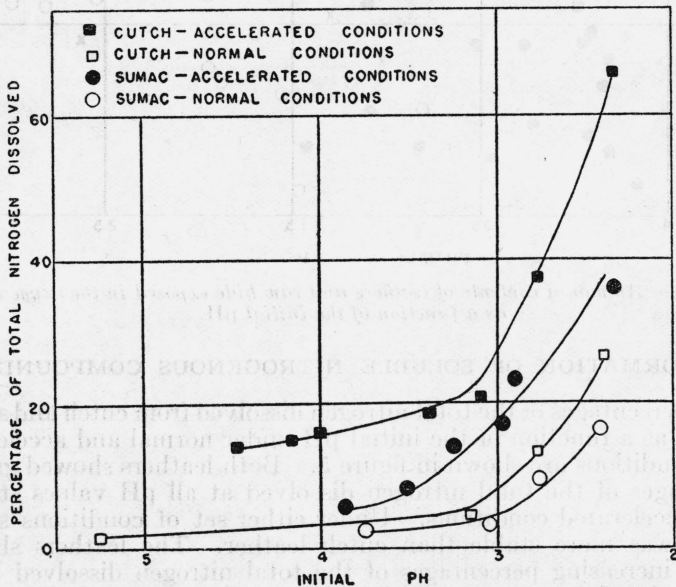


FIGURE 5.—Comparison of the increase in the percentages of the total nitrogen dissolved from sumac and cutch leathers exposed in the oxygen bomb and aged under normal conditions, as a function of the initial pH.

investigation [1]. The nitrogenous compounds dissolved were precipitated almost completely by tannins and phosphotungstic acid, which is a further indication that few peptide linkages are broken during the deteriorating process under these conditions. A similar observation was also made for the leathers aged under normal conditions.

4. MECHANISM OF DETERIORATION

In a discussion of the mechanism of deterioration of leather in the presence of oxygen, the assumption is made that the constituents of leather—hide substance and tannins—behave as in a mixture. Although there is evidence to show that there is some combination

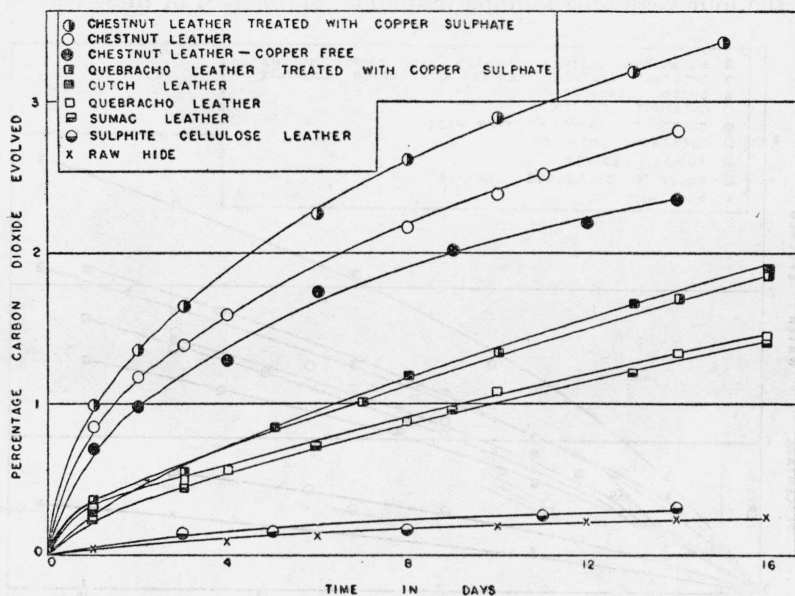


FIGURE 6.—Evolution of carbon dioxide from leathers and raw hide heated in a stream of oxygen at 100° C.

[Percentages based on the original air-dry weight of the samples.]

between hide substance and tannin, these substances have such high molecular weights that they retain most of their original chemical properties in the combined state. The evidence to be presented indicates that the deterioration of leather in the presence of oxygen appears to proceed by two mechanisms, an oxidizing action on the tannins and a hydrolytic action on the hide substance. The mechanism of deterioration under natural and accelerated aging conditions is compared on this basis.

(a) DETERIORATION OF THE TANNINS

In order to obtain some data on the oxidation of the tannins in the presence of oxygen, samples of leather and raw hide in U-tubes were placed in an oven at 100° C. Dry and carbon dioxide-free oxygen was then passed over the samples. Water and carbon dioxide were collected by leading the gases out of the oven and through U-tubes

containing magnesium perchlorate and Ascarite, respectively. The water was absorbed by the magnesium perchlorate and the carbon dioxide by the Ascarite. The rates of evolution were determined by weighing the U-tubes at various intervals of time. Because of the continuous loss of weight by the leathers, the calculated percentages of carbon dioxide or water are based on the original air-dry leather.

The rate of evolution of carbon dioxide from leathers and raw hide in oxygen at atmospheric pressure at 100° C is shown in figure 6. These results show that the rates of evolution of carbon dioxide depend upon the type of tanning material and that for the same tanning material the rate of evolution is increased by the presence of copper (approximately 0.30 percent) in the form of copper sulfate. Of the four vegetable tanning materials represented in these leathers,

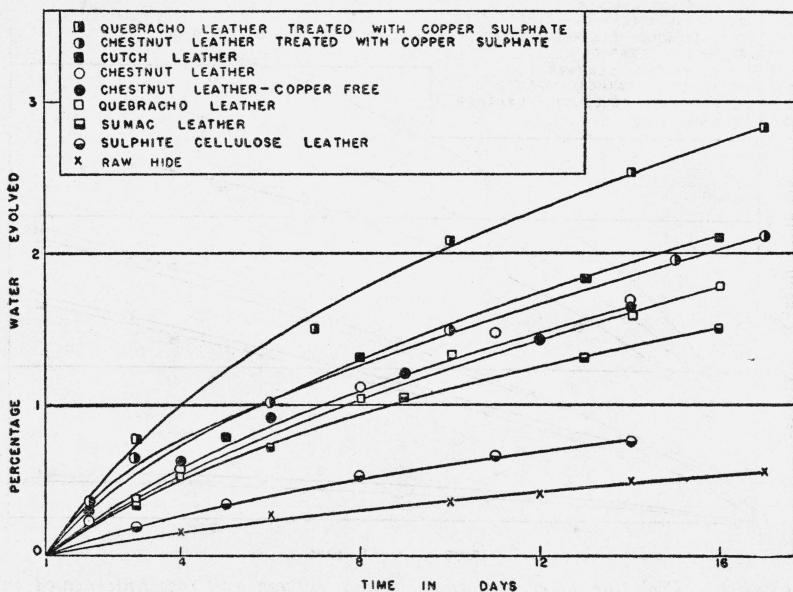


FIGURE 7.—Evolution of water from leathers and raw hide heated in a stream of oxygen at 100° C.

[Percentages based on the original air-dry weight of the samples.]

that containing chestnut tannin gives off carbon dioxide most rapidly, while sumac and quebracho leathers evolve this gas least rapidly. Of all the leathers, the one tanned with sulfite cellulose gives off carbon dioxide at the lowest rate. Raw hide evolves very little carbon dioxide, which indicates that the source of most of that evolved from the leathers is the tanning materials.

The rate of evolution of water from the raw hide and leather samples starting after the first 24 hours of exposure is shown in figure 7. During the first 24 hours of heating most of the adsorbed water in the leather is evolved and the principal source of water thereafter is from oxidation and dehydration reactions. A better comparison of the stability of the leathers with respect to the evolution of water may therefore be given by showing its rate of evolution after the adsorbed water, which also varies for each leather, has been removed.

Of the untreated vegetable-tanned leathers, cutch leather gives off water at the greatest rate, while sumac leather evolves water at the lowest rate. Chestnut- and quebracho-tanned leathers give off water at practically the same rate. The addition of approximately 0.30 percent of copper as copper sulfate has greatly increased the rate of evolution of water from quebracho leather but has only slightly increased it from chestnut leather. Sulfite cellulose leather gives off water at a lower rate than any of the other leathers, and the rate of evolution from raw hide is the lowest for all the samples. This was also the case where carbon dioxide was evolved and gives a further indication that the action of oxygen on leather is confined principally to the tanning materials.

Under either normal or accelerated conditions the tannins are oxidized to a certain extent, as shown by the decrease in the pH values during aging. This oxidizing action is, however, much more drastic under the accelerated conditions, as shown by larger decreases in the pH values and by the amounts of carbon dioxide and water evolved under conditions similar to those used in accelerated aging

(b) DETERIORATION OF THE HIDE SUBSTANCE

There is no indication of any significant difference between the mechanisms of the degradation of the hide substance of leather under accelerated or normal aging conditions. Definitely more ammonia was found for the leathers aged under normal conditions but, as mentioned before, this is not thought to be a significant factor in the actual deterioration. The degradation in the hide substance under both sets of conditions appears to consist principally in the separation of polypeptide chains rather than any extensive hydrolysis or oxidation of these chains. This is shown by the small amounts of amino nitrogen formed and by the fact that most of the dissolved nitrogen compounds may be precipitated by tannins and phosphotungstic acid. By such a mechanism the leather loses its physical strength without much measurable chemical change occurring in the hide substance, in regard to the formation of ammonia or primary amino nitrogen. The greatest measurable change in the hide substance is an increase in solubility; the chemical reaction bringing about this change is probably hydrolytic. Deterioration under the accelerated conditions may, therefore, be considered similar in mechanism to that occurring under normal conditions, with the action on the tannins increased in a greater proportion than the action on the hide substance. The hydrolytic deterioration of the hide substance is probably accelerated principally by the increase in temperature, while the deterioration of the tannins is accelerated by the increased concentration of oxygen as well as the elevated temperature.

VII. CORRELATION OF ACCELERATED TESTS WITH THE STABILITY OF LEATHER

The tannins in leather may be considered as protective agents for the raw hide and, therefore, the resistance to oxidation of the tanning material under any set of aging conditions is one factor influencing the stability of the leather. This influence of the tannins may be observed in figure 1, where the percentages of the total nitrogen dissolved from the leathers and raw hide are presented as a function of

pH. In this figure raw hide shows more deterioration than any of the leathers with the exception of that tanned with a blend of commercial chestnut and sulfite cellulose. The comparative instability of the raw hide under the accelerated conditions was expected since it contained no protective material. The order of decreasing stability for the leathers tanned with the vegetable tannins alone is quebracho, sumac, catch, and chestnut. The comparative rates of evolution of carbon dioxide and water from these leathers, as shown in figures 6 and 7, correlate with their comparative stabilities in the oxygen bomb. The chestnut leathers are the least stable of these, and the amounts of carbon dioxide evolved are greatest. Quebracho and sumac leathers are most stable and they evolve smaller quantities of either carbon dioxide or water than any of the other vegetable-tanned leathers. Catch leather evolves more water than any of the untreated vegetable-tanned leathers but less carbon dioxide than any of the chestnut-tanned leathers. In the oxygen bomb, it shows more stability than chestnut leather but less than sumac or quebracho. Quebracho and chestnut leathers treated with copper sulfate give increased rates of evolution of both carbon dioxide and water (figs. 6 and 7). In a previous investigation [4] it was shown that these leathers when treated with copper sulfate had less stability in the oxygen bomb than the corresponding untreated ones. This indicates further that the stability of the tannins is an important factor in determining the stability of a leather.

Sulfite cellulose leather evolves less carbon dioxide and water than any of the other leathers, yet when it is exposed in the oxygen bomb it shows no greater stability than chestnut leather. It is known that leathers prepared from sulfite cellulose alone have strongly hydrophilic characteristics and in practice this tanning material is never used alone for making leather. The hydrophilic character of this leather causes it to have properties similar to those of raw hide and it is questioned whether the sulfite cellulose extract actually has good tanning properties.

As mentioned above, the leather prepared from a blend of commercial chestnut and sulfite cellulose shows less stability in the bomb than raw hide, possibly because the hide substance was weakened in the tanning process.

Thus, under the accelerated conditions in the oxygen bomb, such factors as stability of the tannins to oxidation, condition of the hide substance, and actual tanning properties of the tanning materials appear to be reflected in the results obtained. This and a previous investigation [1] have shown that deterioration of the leathers under these conditions is comparable to that obtained for similar leathers under normal conditions. The mechanism of deterioration under these accelerated conditions also appears to be similar to that occurring under normal conditions. For these reasons, tests made under the accelerated conditions described in this report should give valuable indications as to the aging quality of a leather.

VIII. SUMMARY

1. The results obtained after aging leathers at 100° C for 7 days in the oxygen bomb containing an atmosphere of oxygen initially at 100 lb/in² should give valuable indications as to their aging properties for the following reasons:

The influence of the type of tanning material and changes in pH on the deterioration of the leathers under these conditions is similar to that occurring under normal conditions.

The mechanism of the deterioration occurring under the accelerated aging conditions is similar to that occurring under the normal aging conditions.

2. The order of decreasing stability at pH 3 under the accelerated conditions in the oxygen bomb for the various tannages of leather studied is quebracho, sumac, cutch, sulfite cellulose, the leathers containing chestnut, and a blend of commercial chestnut and sulfite cellulose.

3. The comparative rates of evolution of carbon dioxide and water from the vegetable-tanned leathers when heated in a stream of oxygen at 100° C are related to their stability in the oxygen bomb.

4. Sulfite cellulose leather is comparatively stable in the presence of oxygen at 100° C. Its instability in the oxygen bomb is an indication that the sulfite cellulose extract has poor tanning properties.

5. The evolution of both carbon dioxide and water is increased in the case of either chestnut or quebracho leathers by the presence of small amounts of copper in the form of copper sulfate.

6. Raw hide evolves comparatively small amounts of either carbon dioxide or water when heated in a stream of oxygen at 100° C, which indicates that the source of the greater part of either of these compounds from the leathers is the tannins.

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