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SOLUBLE DECOMPOSITION PRODUCTS IN AGED VEGETABLE-TANNED LEATHERS

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ABSTRACT

Vegetable-tanned leathers, containing 0, 1, 2, 3, and 4 percent of sulphuric acid and aged for 2 to 10 years were examined for soluble nitrogen compounds. The soluble decomposition products were extracted with water and with 0.1 *N* sodium carbonate. Ammonia, amino nitrogen, and nitrogen precipitated with phosphotungstic acid were determined in the extracts.

A comparison is made between the results obtained from acid-treated leathers which had been aged, and those obtained from the direct hydrolysis of leather and hide substance in acid solutions.

The data indicate that most of the physical deterioration results from hydrolytic reactions.

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I. INTRODUCTION

For the past few years a study of the effect of acids on leather [1]¹ has been carried on at the National Bureau of Standards. Leathers of different tannages, containing various leather-making materials and varying amounts of acid were aged under different conditions. It was shown that the governing factor of deterioration was the pH, as determined by making a water extract of the leather. Leathers finished and aged below pH 3 were almost certain to show a loss in tensile strength, while those finished above pH 3 and aged showed practically no deterioration in 2 years. It was also found that the deterioration of leather produced soluble nitrogen compounds.

It has been known for a long time that soluble nitrogen compounds can be extracted from deteriorated leathers. This has been especially noticeable in the case of old bookbinding leathers which have absorbed

¹ Numbers in brackets refer to references at the end of this paper.

large amounts of sulphur dioxide from the atmosphere. Veitch, Frey, and Leinback [2] studied a large number of bookbinding leathers and found that approximately one-third of the total nitrogen was extractable with water. Fifty percent of this nitrogen was in the form of ammonia. Innes [3, 4, 5] used the amount of soluble nitrogen as a criterion in making an extensive study of the various factors influencing deterioration. He analyzed the total soluble nitrogen for ammonia and amino nitrogen. Frey and Beebe [6] determined soluble nitrogen and ammonia in leathers exposed to sulphur dioxide in a gas chamber. They used as the figure for total nitrogen extracted the sum of that extracted with water and then with 0.1 *N* sodium carbonate.

In this investigation a more detailed study has been made of the soluble nitrogen compounds in aged vegetable tanned leathers with the purpose of obtaining some fundamental information for an accelerated aging test, and also, to study the cause of deterioration. The work reported in this paper deals only with the chemical changes produced in collagen.

II. MATERIALS AND METHODS

The leathers used were from the same lots and had undergone the same treatments as those which were used in the study of the effect of acids on the tensile strength of leather. The initial pH values of these leathers ranged from 1.7 to 5.0. After tensile-strength measurements were made the leathers were stored. The storage period varied from 2 to 10 years. Each sample of leather, containing approximately 0, 1, 2, 3, or 4 percent of acid, was ground and mixed to form a uniform sample.

1. WATER EXTRACTIONS

A 10-g sample of leather was extracted with 200 ml of water at 25° C by shaking in a bottle for 3 hours. The mixture was filtered and the total nitrogen extracted was determined by the kjeldahl method on an aliquot of the clear filtrate. The amounts of ammonia, amino nitrogen, and nitrogen precipitated by phosphotungstic acid were then determined in other aliquots of the clear filtrate.

The ammonia was determined as follows: 50 ml of the clear filtrate was placed in a kjeldahl flask and diluted to 200 ml. 25 ml of a 2-percent suspension of magnesium oxide was added and the ammonia distilled over into standard acid as in a kjeldahl distillation.

The amino nitrogen was determined on the residue remaining in the kjeldahl flask after the removal of the ammonia. The residue was made acid to litmus with acetic acid. It was diluted to 200 ml in a volumetric flask and the amino nitrogen determined on an aliquot of this solution by the Van Slyke method [7], which is based on the measurement of the volume of nitrogen evolved by the action of nitrous acid on primary amino groups.

Ten ml of a 5-percent solution of phosphotungstic acid in 2.5-percent solution of hydrochloric acid was added to a third aliquot of the water extract. After standing for 2 hours the mixture was filtered and the total nitrogen determined in the precipitate by the kjeldahl method.

2. SODIUM CARBONATE EXTRACTIONS

Frey and Beebe [6] pointed out that tannins form insoluble substances with gelatin and other partially hydrolyzed proteins, and therefore a complete extraction of the soluble nitrogen compounds in leather cannot be made with water. It is necessary to use a solvent which will dissolve the tannin as well as the protein. Since tannins and proteins are both soluble in alkaline solutions, a few preliminary experiments were made by the adopted procedure using 0.2 *N* sodium bicarbonate, 0.3 *N* disodium phosphate, 0.1 *N* sodium carbonate, and 0.1 *N* sodium hydroxide as solvents. The most nitrogen was extracted from the leather with the 0.1 *N* sodium hydroxide solutions, but subsequent experiments in which standard hide powder instead of leather was extracted, showed that it caused a breakdown in the protein molecule. The results are given in tables 1 and 2, and indicate that 0.1 *N* sodium carbonate solution is the most suitable solvent for this work because it extracts practically no more nitrogen from hide substance than does water.

TABLE 1.—Nitrogen extracted from quebracho leather (lot 1) containing 4 percent of acid

Solvent	Nitrogen extracted
	mg
0.2 <i>N</i> NaHCO ₃	12.4
.3 <i>N</i> Na ₂ HPO ₄	12.1
.1 <i>N</i> Na ₂ CO ₃	60.8
.1 <i>N</i> NaOH.....	103.2

TABLE 2.—Nitrogen extracted from standard hide powder

Solvent	Nitrogen extracted
	mg
Water.....	4.5
0.2 <i>N</i> NaHCO ₃	4.6
.3 <i>N</i> Na ₂ HPO ₄	4.5
.1 <i>N</i> Na ₂ CO ₃	4.8
.1 <i>N</i> NaOH.....	13.8

With 0.1 *N* sodium carbonate as the solvent, the same procedure was adopted in making the extraction as that which was used with water, except that 2 g of leather instead of 10 g was used.

The amount of nitrogen present as ammonia was determined. This was compared with that in the water extract so as to make a correction in the total amount of extracted nitrogen for that lost as ammonia by the alkaline carbonate treatment. An aliquot of the extracted solution was neutralized with hydrochloric acid and the amount of nitrogen precipitated by the excess tannins was determined. Phosphotungstic acid was then added to the filtrate from the tannin precipitate in order to remove all the incompletely hydrolyzed proteins. The sum of these two figures was recorded as the total nitrogen precipitated.

III. EXPERIMENTAL

To determine the effect of tannins on the hydrolysis and on the determination of soluble nitrogen compounds as outlined above, 1-g samples of hide substance and samples of chestnut- and quebracho-tanned hide substance, equivalent to 1 g of hide substance, were hydrolyzed at 60° C in 0.05 *N* solutions of sulphuric acid. At various intervals the solutions were tested for total nitrogen, amino nitrogen, ammonia, and nitrogen precipitated by phosphotungstic acid. The results given in figure 1 and table 3 show that the percentage of total nitrogen in solution as ammonia and amino nitrogen is nearly the same in each of the three cases for each interval, even though the amount of total nitrogen in solution is less for the tanned hide substances. This indicates that the tannins do not prevent the hydrolysis of the protein but retard the rate at which it goes into solution. Experiments have shown that tannins present in protein solutions cause high values for amino nitrogen. The error increases as the amount of tannin is increased. The amount of tannin present in the above experiments was not enough to cause an appreciable error.

TABLE 3.—Soluble nitrogen compounds from hide substance and tanned hide substance hydrolyzed in 0.05 *N* sulfuric acid at 60° C for different periods of time

[Results are given in percentage of total nitrogen in solution]

Material	pH	Time	Total nitrogen in solution	Phosphotungstic acid precipitate	Ammonia	Amino nitrogen
		<i>Hours</i>	<i>mg</i>	<i>%</i>	<i>%</i>	<i>%</i>
Hide substance.....	1.55	18	173.4	99.7	0.30	4.4
Quebracho.....	1.59	18	16.9	98.8	.25	0
Chestnut.....	1.59	18	57.0	97.8	0	5.8
		<i>Days</i>				
Hide substance.....	1.59	2	174.1	97.1	1.0	5.6
Quebracho.....	1.60	2	32.9	96.0	1.4	8.2
Chestnut.....	1.57	2	60.3	95.8	1.1	6.8
Hide substance.....	1.60	4	174.6	92.5	2.5	7.5
Quebracho.....	1.59	4	66.4	92.0	1.8	8.3
Chestnut.....	1.57	4	92.9	90.6	1.8	7.4
Hide substance.....	1.57	7	174.3	89.6	1.5	10.3
Quebracho.....	1.60	7	80.2	89.2	2.0	9.6
Chestnut.....	1.60	7	118.4	85.0	2.2	11.1
Hide substance.....	1.79	14	176.1	80.2	1.8	16.1
Quebracho.....	1.72	14	90.0	82.2	2.2	18.3
Chestnut.....	1.77	14	135.4	79.2	2.6	16.8
Hide substance.....	1.84	21	175.5	79.1	2.0	16.4
Quebracho.....	1.84	21	116.9	76.0	2.6	18.8
Chestnut.....	1.86	21	142.3	71.5	2.6	17.8
Hide substance.....	1.84	28	178.6	72.0	2.2	20.7
Quebracho.....	1.83	28	126.8	72.2	2.3	23.8
Chestnut.....	1.84	28	148.8	68.3	2.2	21.8

As a control experiment to determine the effect of pH on the formation of soluble nitrogen compounds, 2-g samples of standard hide substance were placed in sulphuric acid solutions of various concentrations ranging from 1.0 to 0.005 *N* and heated in an oven at 60° C for 4 weeks. At the end of this time the soluble nitrogen compounds in the solutions were determined using the methods described above. The results shown in figure 2 and table 4 indicate that at first the

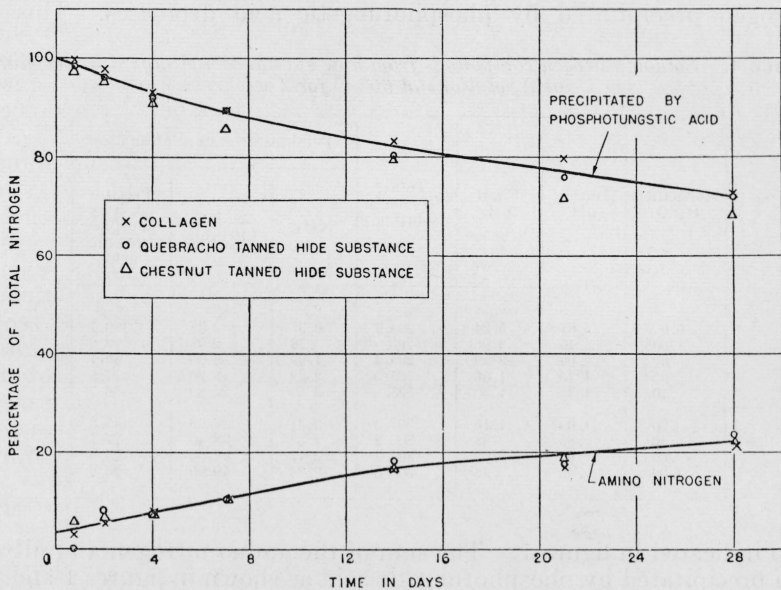


FIGURE 1.—Rate of change of the total soluble nitrogen as amino nitrogen and as nitrogen precipitated by phosphotungstic acid for hide substance and tanned hide substances hydrolyzed in 0.05 N sulphuric acid.

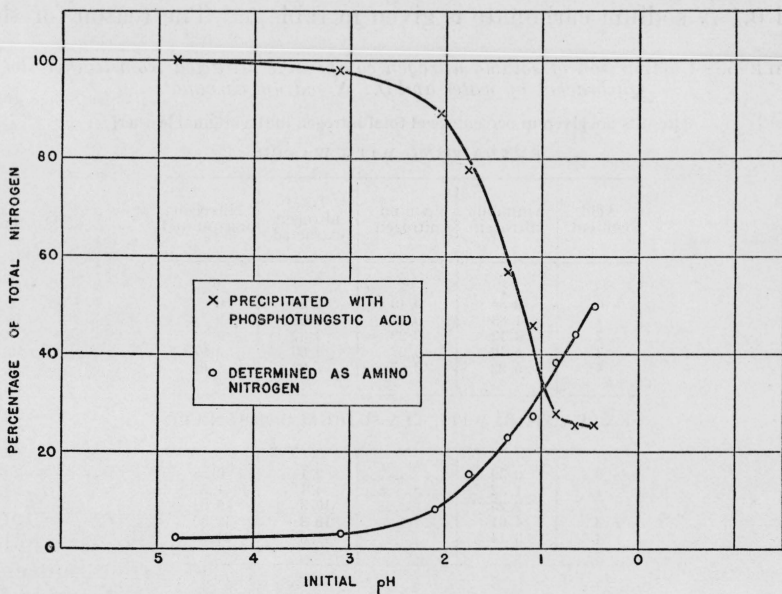


FIGURE 2.—Change with pH of the amino nitrogen and the nitrogen precipitated with phosphotungstic acid for hide substance hydrolyzed in sulphuric acid solutions.

amino nitrogen increases to approximately the same extent as the nitrogen precipitated by phosphotungstic acid decreases. This is

TABLE 4.—*Soluble nitrogen compounds from hide substance hydrolyzed in sulphuric acid solutions at 60° C for 4 weeks*

Normality H ₂ SO ₄	Initial pH	Final pH	Total nitrogen in solution	Total nitrogen in solution as—		
				NH ₃	Amino nitrogen	Precipi- tated by phospho- tungstic acid
			mg	%	%	%
0.0	4.81	5.24	295.4	0.37	2.37	100.7
.005	3.10	3.96	295.9	.78	2.98	98.2
.02	2.09	2.49	295.4	1.99	8.60	89.7
.05	1.75	1.86	305.5	2.32	15.20	77.8
.10	1.36	1.50	308.6	2.30	22.80	56.7
.20	1.09	1.16	307.3	2.31	26.90	45.6
.40	.85	.85	300.2	2.36	38.40	27.7
.60	.66	.68	304.3	2.17	44.00	25.5
1.00	.45	.46	305.0	2.33	49.90	25.6

also indicated in figure 1. The sum of the amino nitrogen and nitrogen precipitated by phosphotungstic acid as shown in figures 1 and 2, slightly exceeds 100 percent because a part of the nitrogen precipitated is free amino nitrogen.

1. EXTRACTIONS

A comparison of the soluble nitrogen compounds extracted by water and 0.1 *N* sodium carbonate is given in table 5. The reason for the

TABLE 5.—*Comparison of soluble nitrogen compounds extracted from leather (lot 1 Quebracho) by water and 0.1 N sodium carbonate*

[Results are given in percentage of total nitrogen in the original leather]

EXTRACTING WITH WATER

Acid content	Ammonia nitrogen	Amino nitrogen	Total nitrogen extracted	Nitrogen precipitated
%	%	%	%	%
0	0.35	0.40	0.65	0
1	1.83	0.51	2.08	0
2	3.12	0.22	3.37	0
3	5.10	0.27	6.00	0.97
4	5.22	0.57	7.22	1.69

EXTRACTING WITH 0.1 N SODIUM CARBONATE

0	0.39	-----	2.1	0.58
1	1.32	-----	4.4	1.67
2	2.25	-----	10.3	6.05
3	4.01	-----	19.3	13.30
4	3.14	-----	41.6	34.50

differences in the soluble nitrogen extracted is obvious on an examination of table 6. Water extracts chiefly ammonia and amino acids. On the other hand the sodium carbonate extracts more tannin and a larger amount of soluble nitrogen because it dissolves the otherwise

insoluble tannin-protein compound. In both cases the residual leathers contained larger percentages of nitrogen than the original samples. The amount of residual leather decreased with increasing acid content, but the percentage of nitrogen remained approximately constant.

TABLE 6.—Ratio of nitrogen to solids in the extract and in the residue of quebracho leather (lot 1) when extracted with water and with 0.1 N sodium carbonate ¹

[Results for 1 g of leather]

EXTRACTING WITH WATER

Acid (approx.)	Tannins extracted	Non-tannins extracted ²	Total solids extracted	Nitrogen in solids	Nitrogen in residual leather	Nitrogen in original leather
%	g	g	g	%	%	%
0	0.046	0.017	0.064	0.83	8.9	8.2
1	.040	.024	.064	2.5	8.9	8.4
2	.041	.028	.069	3.9	9.5	8.9
3	.049	.038	.088	5.6	9.2	8.9
4	.051	.043	.095	5.7	8.9	8.5

EXTRACTING WITH SODIUM CARBONATE

0	-----	-----	³ 0.396	0.41	14.2	8.2
1	-----	-----	.402	.80	14.5	8.4
2	-----	-----	.392	1.76	13.9	8.9
3	-----	-----	.446	3.72	14.0	8.9
4	-----	-----	.584	5.31	13.0	8.5

¹ Determination of total solids, tannins, and non-tannins made by ALCA methods.

² Non-protein, non-tannins.

³ These values are corrected for the sodium carbonate present in the solution.

2. AMMONIA

Table 4 shows that the amount of ammonia formed in the hydrolysis of hide substance in acid solution reaches a maximum of 2.32 percent in 0.05 N sulphuric acid and does not change appreciably beyond this figure in the more concentrated acid solutions. Table 3 shows that the tanned hide powders gave approximately the same percentage of ammonia. In the leathers aged under natural conditions the percentage of the total nitrogen as ammonia is higher. The oxidation in the leathers is probably caused in part by molecular sulphuric acid, therefore the percentage of total nitrogen as ammonia, after making a correction for the nitrogen as ammonia present in leather containing no acid, was plotted against the percentage of acid added. Figures 3 and 4 show that the ammonia content increases with acid content and time. The smaller amounts of ammonia in those leathers aged at high relative humidities are in accord with results obtained by Innes. The figures also show that the presence of grease has a retarding effect on the formation of ammonia.

3. AMINO NITROGEN

The results for amino nitrogen are plotted against the pH rather than the percentage of acid, since hydrolysis is catalyzed by hydrogen ions. The amount of amino nitrogen formed in the leathers is small. The results shown in figure 5 compare well with those obtained by

the direct hydrolysis of hide substance by sulphuric acid solutions, figure 2. Only small amounts of amino nitrogen are formed above a

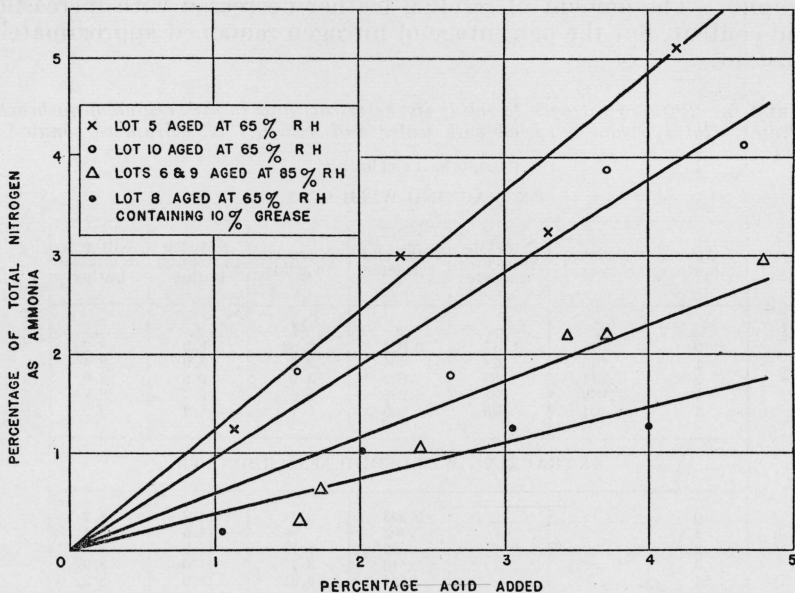


FIGURE 3.—Effect of relative humidity and grease on the ammonia content.

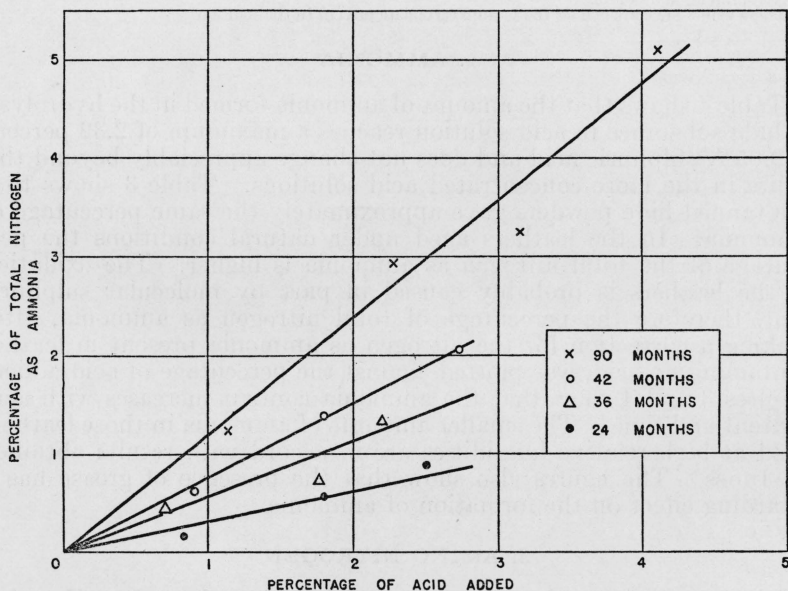


FIGURE 4.—Effect of time and acid content on the ammonia content of quebracho leather.

pH of 2, while below this pH the amount of amino nitrogen formed increased rapidly with decreasing pH. Figures 1 and 5 show that the formation of amino nitrogen is also a function of time.

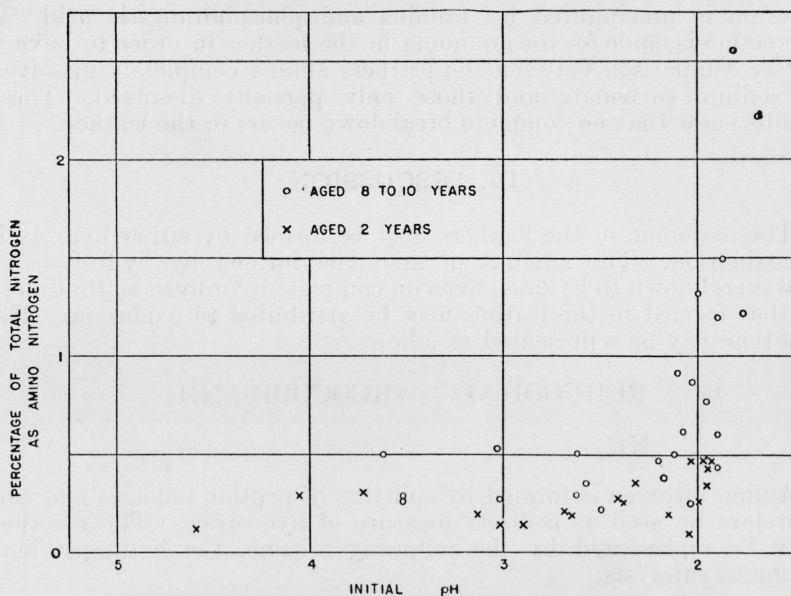


FIGURE 5.—Effect of time and pH on the amino-nitrogen content.

4. NITROGEN PRECIPITATED BY TANNINS AND BY PHOSPHOTUNGSTIC ACID

An examination of table 7 shows that over 90 percent of the total nitrogen extracted from the leather by a 0.1 *N* sodium carbonate

TABLE 7.—Nitrogen compounds soluble in 0.1 *N* solution of sodium carbonate and precipitated by tannins and by phosphotungstic acid

Lot ¹	Acid (approx.)	pH	Total nitrogen extracted	Total nitrogen precipitated	Total nitrogen extracted and precipitated	Total nitrogen extracted and precipitated, correcting for ammonia	
			mg	mg	%	%	
1	%	4	1.94	60.8	53.2	87.5	96.4
2		4	1.70	149.3	134.2	90.0	93.6
3		4	1.95	50.6	39.1	77.6	90.8
4		4	1.76	140.7	126.5	89.8	93.3
5		4	1.86	59.3	49.2	82.8	93.0
6		4	1.80	141.0	139.0	98.2	101.0
7 (10% grease)		4	1.92	149.1	134.8	90.4	91.8
7 (20% grease)		4	1.88	131.7	124.7	94.8	96.0
8 (10% grease)		4	2.03	121.6	119.9	98.5	101.5
8 (20% grease)		4	2.10	108.1	105.2	97.4	100.0
9		4	1.89	41.3	30.3	73.4	83.5
9 (85% RH) ²		4	1.87	106.1	99.4	93.6	95.4
10		4	1.87	139.3	125.9	90.4	93.4
10 (85% RH)		4	1.82	141.8	129.4	91.2	93.5
21		3	1.94	102.2	92.2	90.2	91.7
21 (85% RH)		3	1.94	159.2	151.6	95.2	97.0
22		3	1.98	22.4	20.0	89.4	99.0
22 (85% RH)		3	1.98	52.0	46.3	89.1	94.6
23 (0% cod oil)		3	2.28	38.9	34.3	88.2	91.0
23 (10% cod oil)		3	2.35	34.7	30.5	87.9	91.1
25 (0% glucose)		3	2.16	82.6	77.3	93.6	95.4
25 (8% glucose)		3	2.30	48.7	43.9	90.2	94.6

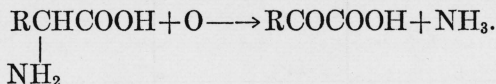
¹ Unless otherwise stated the leathers were conditioned at 65 percent relative humidity for the first 2 years.

² RH=relative humidity.

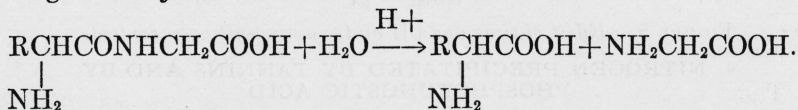
solution is precipitated by tannins and phosphotungstic acid. A correction is made for the ammonia in the leather in order to have a better comparison between the leathers almost completely dissolved in sodium carbonate and those only partially dissolved. These results show that no complete breakdown occurs in the leather.

IV. DISCUSSION

The ammonia in the leathers may be formed by either hydrolysis or oxidation. The amount of ammonia formed by hydrolysis is, however, known to be small even on complete hydrolysis so that most of that formed in the leather may be attributed to oxidation. The reaction may be represented as follows:



Amino nitrogen is formed by splitting of peptide linkages and can therefore be used as a direct measure of hydrolysis. The reaction may be represented by the following scheme, the hydrogen ions acting as catalysts:



Phosphotungstic acid precipitates the basic amino acids, peptones, and other incompletely hydrolyzed proteins. In this work, it may be used as a measure of the incompletely hydrolyzed proteins.

The results indicate that both oxidation and hydrolysis take place in the leather. It is, however, not necessarily true that both of these factors are the causes of physical deterioration. The formation of ammonia and amino nitrogen, which respectively indicate oxidation and hydrolysis, is shown to increase with time. The conditions under which these leathers were aged made both reactions take place slowly.

In table 8 the ammonia content is compared with the total nitrogen extracted and with the loss in tensile strength. The formation of ammonia shows no correlation to the loss in tensile strength, and hence it is probable that ammonia is not formed by the primary reactions which cause the physical deterioration of the leather. It is known that the guanidine nucleus of arginine which is free in the protein molecule is readily oxidized to form ammonia. Ammonia may also be formed from free amino nitrogen or amino nitrogen formed during hydrolysis.

TABLE 8.—Soluble nitrogen compounds formed in leathers aged for different periods of time

Lot ¹	Aging period	Original pH	Total nitrogen extracted	Total nitrogen as amino nitrogen	Total nitrogen as ammonia	Change in tensile strength ²
	Years		%	%	%	%
8 (10% grease)-----	9	2.19	30.3	0.41	2.55	-16.5
3-----	10	2.17	17.3	.38	4.45	-31.8
1-----	10	2.12	18.2	.27	5.10	-20.5
7 (10% grease)-----	9	2.10	91.1	.92	2.23	-52.5
9-----	8	2.07	20.2	.62	5.82	-33.0
9 (85% RH) ³ -----	8	2.02	54.9	.87	2.35	-48.0
10 (85% RH)-----	8	2.00	85.3	1.33	2.69	-58.0
10-----	8	1.98	83.6	.65	4.90	-43.0
6-----	10	1.96	53.0	.77	2.35	-76.5
5-----	10	1.94	27.5	.48	4.12	-44.0
4-----	10	1.90	54.1	.64	4.98	-52.8
2-----	10	1.90	94.6	1.20	2.89	-63.4
29-----	2	2.40	5.5	.28	.93	-25.2
28-----	2	2.38	22.1	.28	1.15	-53.7
27-----	2	2.15	10.0	.21	1.52	-47.2
31-----	2	2.04	7.3	.11	1.31	-43.1
30-----	2	2.03	47.4	.47	1.43	-85.2
22-----	2	1.98	13.1	.26	1.38	-29.0
22 (85% RH)-----	2	1.98	30.5	.47	1.81	-62.0
21-----	2	1.94	57.8	.35	1.49	-61.2
21 (85% RH)-----	2	1.94	90.0	.45	2.09	-75.3

¹ Unless otherwise stated the leathers were conditioned at 65 percent relative humidity for the first 2 years.

² Determined after 2 years of aging.

³ RH=relative humidity.

There is, however, a relation between the amino nitrogen and the total soluble nitrogen. This is shown in figure 6, where the total

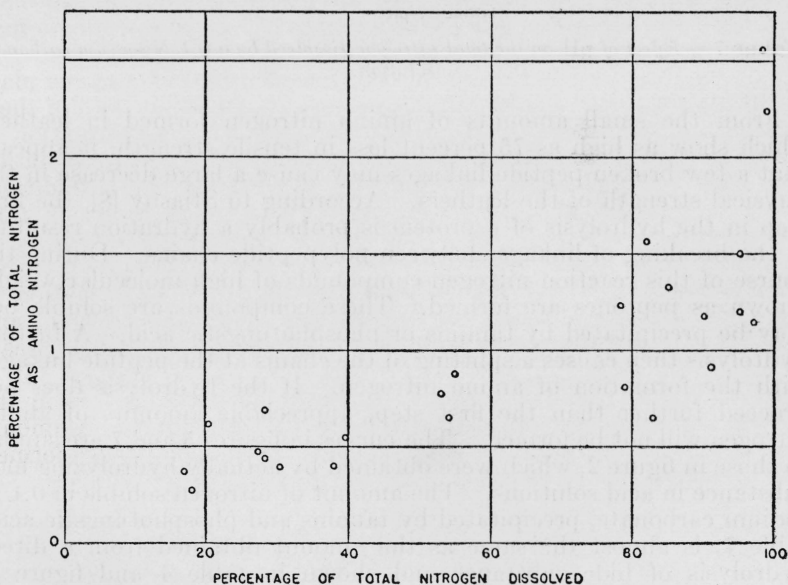


FIGURE 6.—Increase in percentage of total nitrogen as amino nitrogen with the percentage of total nitrogen dissolved by a 0.1 N sodium carbonate solution.

soluble nitrogen is plotted against the amino nitrogen. Previous work [9] has shown that a relationship exists between the total soluble nitrogen and the tensile strength and therefore there must also be a

relation between the tensile strength and the amino nitrogen. Comparing figure 5 with figure 7 shows that the amino nitrogen starts to increase, although to a smaller extent, at the same pH as that at which the amount of soluble nitrogen increases. This indicates that both may result from the same reaction.

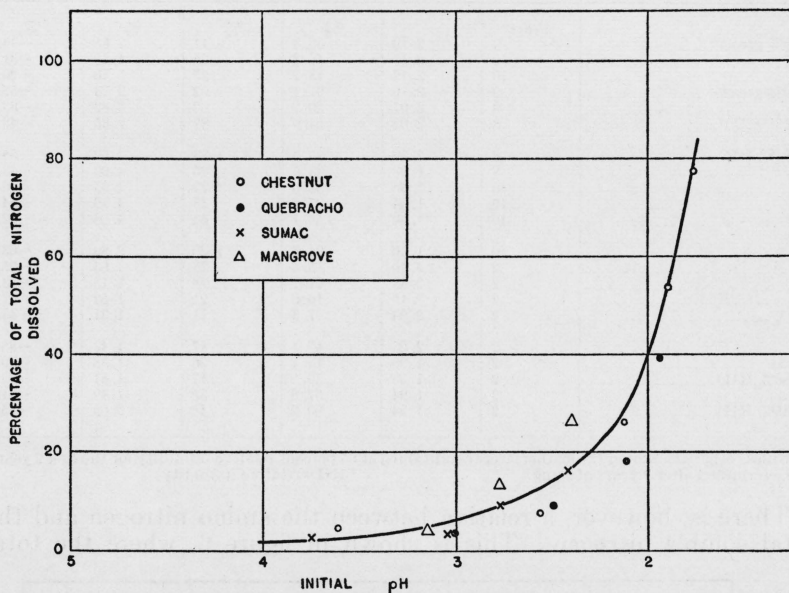


FIGURE 7.—Effect of pH on the total nitrogen dissolved by a 0.1 N sodium carbonate solution.

From the small amounts of amino nitrogen formed in leathers which show as high as 75 percent loss in tensile strength, it appears that a few broken peptide linkages may cause a large decrease in the physical strength of the leathers. According to Stiasny [8], the first step in the hydrolysis of a protein is probably a hydration resulting in the breaking of linkages between polypeptide chains. During the course of this reaction nitrogen compounds of high molecular weight known as peptones are formed. These compounds are soluble but may be precipitated by tannins or phosphotungstic acid. A further hydrolysis then causes a splitting of the chains at the peptide linkages with the formation of amino nitrogen. If the hydrolysis does not proceed further than the first step, appreciable amounts of amino nitrogen will not be formed. The curves in figures 5 and 7 are similar to those in figure 2, which were obtained by actually hydrolyzing hide substance in acid solutions. The amount of nitrogen soluble in 0.1 N sodium carbonate, precipitated by tannins and phosphotungstic acid, table 7, is almost the same as the amount obtained from a direct hydrolysis of hide substance and shown in table 4 and figure 2. These results indicate that most of the physical deterioration in leather is caused by hydrolysis.

V. SUMMARY

1. The deterioration of leather results in the formation of soluble decomposition products containing nitrogen.

2. An average of over 90 percent of the total nitrogen in the decomposition products is precipitated by phosphotungstic acid.

3. Among the decomposition products are ammonia and compounds containing amino nitrogen.

4. The amount of ammonia formed is a function of time and acid concentration, while the amount of amino nitrogen formed is a function of time and hydrogen ion concentration.

5. The data indicate that most of the physical deterioration is caused by hydrolysis.

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