

## RESEARCH PAPER RP846

*Part of Journal of Research of the National Bureau of Standards, Volume 15,  
November 1935*

## DETERIORATION OF VEGETABLE-TANNED LEATHERS CONTAINING SULPHURIC ACID AND GLUCOSE

By Everett L. Wallace and Joseph R. Kanagy

### ABSTRACT

The influence of glucose on the deterioration of chestnut- and quebracho-tanned leathers containing sulphuric acid was studied. Samples of both kinds of leather, each containing varying amounts of acid, and comparable leathers which contained similar amounts of acid and approximately 5 percent of glucose were examined. Deterioration was measured by determining the change in tensile strength after 0, 12, 18, and 24 months storage under conditions of 70° F and 65-percent relative humidity. The results show that glucose has no measurable influence on the deteriorating effect of the acid. There was no deterioration of the leathers having a pH value of 3 or higher when stored for 2 years at 70° F and 65-percent relative humidity.

### CONTENTS

	Page
I. Introduction.....	523
II. Materials and methods.....	523
III. Results and discussion.....	524
IV. Summary.....	525
V. References.....	527

## I. INTRODUCTION

In the manufacture of commercial sole leather, filling materials such as magnesium sulphate and glucose are commonly used. It is generally agreed that the use of these materials in leather has no harmful effect on the aging quality of the product during storage and that their addition in moderate amounts produces a leather with better selling qualities, having better color and appearance.

The effect of magnesium sulphate on the deterioration of leather by sulphuric acid has been reported in a previous publication [13].<sup>1</sup> This report presents the data on the influence of glucose on the deterioration of leather by sulphuric acid during storage and is the last of a series of published articles relative to the effect of acids on leather and methods of determining harmful acidity [1 to 15, inclusive].

## II. MATERIALS AND METHODS

The leather used in this work consisted of lot 25, tanned with powdered chestnut-wood extract and lot 26, tanned with ordinary solid quebracho-wood extract. The method of preparing these leathers and the procedure followed in making the aging tests have been described in previous reports. [1, 2, 13].

<sup>1</sup> The figures given in brackets in the text correspond to the numbered references at the end of this paper.

The results of the analysis of the leathers before adding the acid and glucose are given in table 1.

TABLE 1.—*The chemical analyses of leather before treatment*

[Results are expressed in percentage of the leather, excepting for degree of tannage and pH]

Items determined	Tannage	
	Chestnut	Quebracho
Water-soluble.....	7.58	11.55
Hide substance.....	49.90	44.17
Grease (petroleum-ether extract).....	3.23	3.52
Moisture.....	11.72	10.79
Insoluble ash.....	0.12	0.07
Combined tannin <sup>1</sup> .....	27.45	29.90
Total.....	100.00	100.00
Degree of tannage <sup>2</sup> .....	55.	68.
Soluble tannins.....	5.54	9.93
Soluble nontannins.....	2.04	1.62
Total ash.....	0.24	0.12
pH <sup>3</sup> (glass electrode).....	3.85	4.00

<sup>1</sup> Determined by difference.

<sup>2</sup> The ratio of combined tannin to hide substance  $\times 100$ .

<sup>3</sup> 5 g of leather in 100 ml of distilled water.

The distribution of the samples relative to hide location, for treatment with acid and glucose was similar to that previously described [13], except that each value of deterioration reported is calculated from the average of 11 samples instead of 42. The amounts of sulphuric acid added to the specimens were approximately 0, 1, 2, and 3 percent. After the acid treatment the leather was allowed to dry at room temperature and one-half of the samples were treated in a solution of glucose. The amount of glucose absorbed by the leather was determined by the official method of the American Leather Chemists Association.

The leather was stored at a temperature of 70° F and a relative humidity of 65 percent. Samples for the determination of the tensile strength were taken 0, 6, 12, 18, and 24 months after treatment.

### III. RESULTS AND DISCUSSION

The percentages of sulphuric acid and glucose added, the original pH values, and the percentage of glucose and the pH values of the samples after 24 months storage are given in table 2. The percentage change in tensile strength after storage is also given in table 2.

These data show that the addition of glucose had no apparent effect on the original pH value of the leather and that the pH of all the samples containing acid increased after 2 years' storage. It is of further interest to note that the percentage of glucose found in the original samples decreased after storage for 2 years and was the least in the samples having the lowest pH values. Apparently below certain pH values the glucose is decomposed into organic acids, which are not determined by the method of analysis used.

TABLE 2.—The analysis of the treated leathers and the percentage change in tensile strength

## CHESTNUT

Acid added	Glucose added	Glucose after 24 months	pH original	pH after 24 months	Percentage change in tensile strength for—				
					Age (months)				
					0	6	12	18	24
0.0	0	-----	3.85	3.97	0.0	0.0	0.0	0.0	0.0
1.18	0	-----	2.99	3.08	-2.4	-5.1	2.3	-2.9	1.1
1.57	0	-----	2.48	2.78	-2.8	-10.4	-8.8	-16.0	-24.8
2.61	0	-----	2.16	2.47	-7.0	-25.6	-28.5	-39.6	-49.0
0.00	5.20	5.14	3.84	4.05	0.0	0.0	0.0	0.0	0.0
1.07	4.80	4.34	2.94	3.15	5.2	3.1	3.5	-2.3	-0.8
1.60	6.00	5.26	2.52	2.81	2.0	-13.6	-0.9	-12.8	-28.1
2.37	5.62	4.02	2.30	2.54	-6.9	-5.9	-38.5	-37.5	-56.3

## QUEBRACHO

0.0	0	-----	4.00	4.28	0.0	0.0	0.0	0.0	0.0
0.83	0	-----	2.99	3.26	1.5	-6.0	-13.4	-4.4	-8.0
1.78	0	-----	2.52	2.73	3.5	-1.7	3.4	5.6	-5.5
2.44	0	-----	2.20	2.44	0.2	-21.3	-26.9	-20.0	-18.4
0.00	5.34	5.34	4.09	4.20	0.0	0.0	0.0	0.0	0.0
0.79	5.40	4.84	2.99	3.27	5.8	1.0	1.5	5.2	-4.7
1.60	6.03	5.08	2.57	2.86	-1.8	-7.8	-2.0	3.2	-0.3
2.32	5.86	4.16	2.23	2.51	-2.2	-15.0	-10.2	-12.3	-25.8

The results for the deterioration of the leathers for the 2-year storage period, as a function of the original pH values, are given in figures 1 and 2. The percentage change in tensile strength has been corrected for the change in strength of the control samples containing no added acid, so that the points in the graphs represent the deterioration caused by the acid. The chestnut leather (fig. 1) shows a decided decrease in tensile strength below a pH value of 3. The quebracho leather, figure 2, shows a much greater resistance to deterioration at the lower pH values (below 3) than the chestnut leather. The variation in tensile strength between the leathers containing acid and glucose, and comparable leathers containing similar amounts of acid and no glucose is no greater than the experimental error of the determinations.

## IV. SUMMARY

The influence of glucose, added to leather containing sulphuric acid, on the deterioration of the leather during storage was determined by comparing the change with age of the tensile strength of the leather with and without added glucose.

The addition of glucose had no apparent influence on the deteriorating effect of the acid.

The chestnut- and quebracho-tanned leathers showed no deterioration after 2 years' storage at 70° F and 65-percent relative humidity when the pH of the leather was 3 or higher.

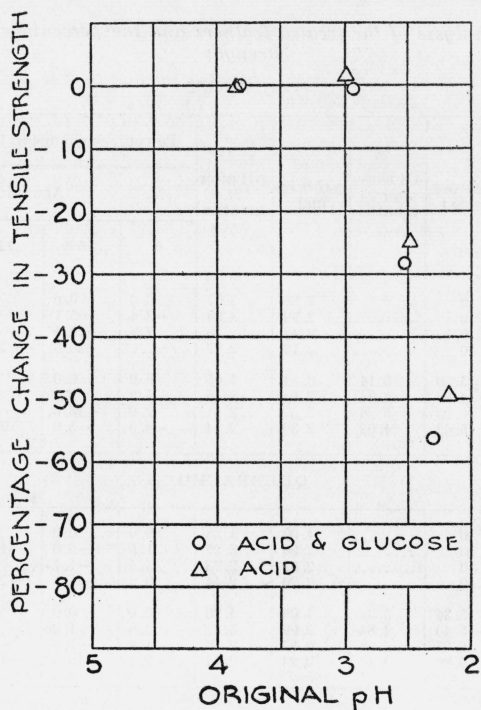


FIGURE 1.—Results of the 24-month aging tests on lot 25, chestnut-tanned leather, plotted against the pH of the leather before aging.

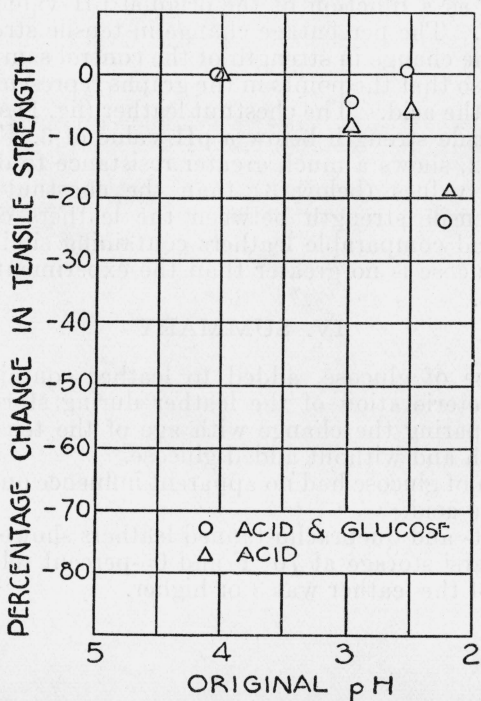


FIGURE 2.—Results of the 24-month aging tests on lot 26, quebracho-tanned leather, plotted against the pH of the leather before aging.

## V. REFERENCES

- [1] R. C. Bowker and E. L. Wallace, Progress Report on the Effects of Acids on Leather, *J. Am. Leather Chem. Assn.* **23**, 82 (1928).
- [2] R. C. Bowker, The Deterioration of Chestnut- and Quebracho-Tanned Leathers by Sulphuric Acid, *J. Am. Leather Chem. Assn.* **26**, 444 (1931).
- [3] E. L. Wallace, The Hydrolysis of Chestnut- and Quebracho-Tanned Leathers by Sulphuric Acid, *J. Am. Leather Chem. Assn.* **26**, 545 (1931); *BS J. Research* **7**, 621 (1931) RP362.
- [4] R. C. Bowker, The Influence of Grease on the Deterioration of Chestnut- and Quebracho-Tanned Leathers by Sulphuric Acid, *J. Am. Leather Chem. Assn.* **26**, 667 (1931).
- [5] R. C. Bowker and W. D. Evans, The Effect of Atmosphere Moisture on the Deterioration of Commercial and Quebracho-Tanned Leathers Containing Sulphuric Acid, *J. Am. Leather Chem. Assn.* **27**, 81 (1932).
- [6] R. C. Bowker and C. L. Critchfield, The Deterioration of Leather by Sulphuric Acid as Influenced by Tanning with Blends of Chestnut and Quebracho Extract, *J. Am. Leather Chem. Assn.* **27**, 158 (1932).
- [7] R. C. Bowker and E. L. Wallace, The Influence of pH on the Deterioration of Vegetable-Tanned Leather, *J. Am. Leather Chem. Assn.* **28**, 125 (1933) and *BS J. Research* **10**, 559 (1933) RP547.
- [8] E. L. Wallace and J. R. Kanagy, The Influence of Sodium Chloride and Magnesium Sulphate on the Hydrolysis of Leather by Sulphuric Acid, *J. Am. Leather Chem. Assn.* **28**, 186 (1933).
- [9] R. C. Bowker and E. L. Wallace, Effect of Temperature on the Deterioration of Leather Containing Sulphuric Acid, *J. Am. Leather Chem. Assn.* **29**, 623 (1934).
- [10] R. C. Bowker and J. R. Kanagy, The Deterioration of Vegetable-Tanned Leathers by Oxalic Acid, *J. Am. Leather Chem. Assn.* **30**, 26 (1935).
- [11] E. L. Wallace, J. Beek, Jr., and C. L. Critchfield, The Effect of Sulphuric Acid on Chrome-Tanned Leather. *J. Am. Leather Chem. Assn.* **30**, 311 (1935); *J. Research NBS* **14**, 771 (1935) RP802.
- [12] E. L. Wallace, Method for Measuring the pH of Leather Using a Simple Glass Electrode Assembly, *J. Am. Leather Chem. Assn.* **30**, 370 (1935) and *J. Research NBS* **15**, 5 (1935) RP805.
- [13] R. C. Bowker, E. L. Wallace, and J. R. Kanagy, Influence of Magnesium Sulphate on the Deterioration of Vegetable-Tanned Leathers by Sulphuric Acid, *J. Am. Leather Chem. Assn.* **30**, 91 (1935); *J. Research NBS* **14**, 121 (1935) RP761.
- [14] E. L. Wallace, C. L. Critchfield, and J. Beek, Jr., Influence of Sulphonated Cod Oil on the Deterioration of Vegetable-Tanned Leather. *J. Am. Leather Chem. Assn.* **30**, 438 (1935), *J. Research NBS* **15**, 73 (1935) RP811.
- [15] E. L. Wallace, J. R. Kanagy, and C. L. Critchfield, Influence of Some Sulphur-Containing Tanning Materials on the Deterioration of Vegetable-Tanned Leathers by Sulphuric Acid, *J. Am. Leather Chem. Assn.*; **30**, (1935) and *J. Research NBS* **15**, 369 (1935) RP835.

WASHINGTON, SEPTEMBER 27, 1935.