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INFLUENCE OF SOME SULPHUR-CONTAINING TANNING MATERIALS ON THE DETERIORATION OF VEGETABLE-TANNED LEATHERS BY SULPHURIC ACID

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ABSTRACT

The influence of a synthetic tanning material, sulphite cellulose, and sulphited extracts on the deterioration of leather, when used with chestnut and quebracho extracts for tanning, was studied. Leathers tanned with the aid of these materials were treated with varying amounts of sulphuric acid and aged under controlled conditions of temperature and relative humidity. Deterioration was determined by measuring the change in tensile strength after 6, 12, 18, and 24 months. The amount of extractable nitrogen was also determined for the samples aged for 24 months. The results show that deterioration as measured by tensile strength and chemical decomposition of the hide substance is a function of the pH value of a water extract of the sample rather than the acid content of the leather as measured by the total sulphur or the Procter and Searle method.

CONTENTS

I. INTRODUCTION

The development and increased use of materials containing sulphur in the production of vegetable-tanned leather has logically led to an investigation of the effects of these materials on the deterioration of the leather, as a function of the acidity, during storage.

Any of the direct analytical methods in use for evaluating the acidity are of doubtful value when applied to leather tanned with materials containing organic sulphur compounds.

In previous work [1] at the National Bureau of Standards on the effect of acid on different leathers during storage, the deterioration has been expressed both as functions of the added sulphuric acid and of the pH value of an aqueous extract of the leather. It was also shown [2] that the amount of added sulphuric acid which would cause serious deterioration in 2 years varied from 0.3 to 1.8 percent for the different leathers, and that the pH of the leather extract had a more definite relation to the loss in strength than did the acid content.

The sulphur-containing substances selected for study in this report were synthetic tanning materials, sulphited quebracho extract, and

[1] BS J. Research **10**, 559 (1933) RP548; J. Am. Leather Chem. Assn. **28**, 125 (1933).
[2] J. Research NBS **14**, 121 (1935) RP761; J. Am. Leather Chem. Assn. **30**, 91 (1935).

sulphite cellulose extract. These products are commonly used in the manufacture of both heavy and light leathers.

II. MATERIALS AND METHODS

The leather used in this work was prepared in the experimental tannery at the National Bureau of Standards from green-salted steer hides and consisted of the following lots; lot 21 (chestnut extract and syntan); lot 22 (quebracho extract and syntan); lot 27 (sulphited quebracho extract); lot 28 (chestnut extract and syntan); lot 29 quebracho extract and syntan); lot 30 (chestnut extract and sulphite cellulose); and lot 31 (quebracho extract and sulphite cellulose). Lots 21 and 22 were tanned with a blend consisting of 25 lb of syntan of 21° Be to 75 lb of the liquid vegetable extracts containing 25 percent of tannin. This is a larger proportion of syntan than is normally used in the production of heavy leather, but was used to assure a high Procter and Searle value. Lot 27 was tanned with sulphited quebracho extract and the pH of the liquors was maintained at approximately 4 by the use of acetic acid. Lots 28 and 29 were tanned with a blend similar to that used for lots 21 and 22, except that the proportion was 10 lb of syntan to 90 lb of liquid vegetable extract. Lot 30 was tanned with a blend consisting of 75 percent of chestnut extract and 25 percent of sulphite-cellulose extract. Lot 31 was similar to lot 30, except that quebracho was used instead of the chestnut extract. The chemical analyses of these leathers before aging are given in table 1.

TABLE 1.—*Chemical Analyses of Leather*

[Results expressed in percentage, excepting for degree of tannage and pH value]

Items determined	Leather lot number and tanning material						
	21—Chestnut syntan	22—Quebracho syntan	27—Quebracho sulphited	28—Chestnut syntan	29—Quebracho syntan	30—Chestnut sulphite cellulose	31—Quebracho sulphite cellulose
Water-soluble	9.19	8.93	8.28	8.40	11.53	10.26	11.04
Hide substance	49.68	47.93	48.95	48.16	45.69	47.22	45.06
Grease (petroleum-ether extract)	3.23	3.89	4.37	3.69	4.73	4.26	2.92
Moisture	11.96	9.97	9.40	11.26	9.91	10.86	9.80
Insoluble ash	.20	.21	.10	.11	.09	.12	.10
Combined tannin [1]	25.74	29.07	28.90	28.38	28.06	27.28	31.08
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Degree of tannage [2]	52.00	61.00	59.00	59.00	61.00	58.00	69.00
Soluble tans	7.87	7.73	6.71	7.10	9.91	8.76	9.56
Soluble nontans	1.32	1.20	1.57	1.30	1.62	1.50	1.48
Total ash	.34	.42	.18	.31	.16	.31	.27
Acid (Procter and Searle)	1.70	1.61	.80	.35	.41	.62	.70
pH value [3]	3.62	4.36	3.90	4.07	4.58	3.72	4.04

[1] Determined by difference.
[2] Ratio of combined tannin to hide substance.
[3] 5 g of leather in 100 ml of distilled water.

The different lots of leather were divided into 4 groups for acid treatment and aging. The original tensile strength of the leather was determined by the average of 2 specimens cut from each block. The leather was then treated with acid, air dried, and after conditioning at 65-percent relative humidity, and tensile strengths of

2 more specimens from each block were measured to determine the immediate effect of the treatment. The blocks containing no added acid, used for determining the normal aging of the leather, were treated with water. The method of sampling was similar to that described by Bowker, Wallace, and Kanagy in their report on the influence of magnesium sulphate on the deterioration of vegetable-tanned leather by sulphuric acid.[3]

The original pH values and sulphuric-acid content of the different lots of leathers are given in table 2.

TABLE 2.—*Original* pH *Values and Sulphuric-Acid Content of the Leathers*

Leather lot number and tanning material	Sample number	Original pH	Percentage of sulphuric acid in dry leather					
			Method					
			Procter and Searle		Oxygen bomb		Nitric acid bromine	
			Total	Added	Total [1]	Added [2]	Total [1]	Added [2]
21—Chestnut syntan	0	3.62	1.70	0.00	----------	----------	0.72	0.00
	1	2.64	2.30	0.60	----------	----------	1.68	0.96
	2	2.18	3.20	1.50	----------	----------	2.48	1.76
	3	1.94	4.20	2.50	----------	----------	3.50	2.78
22—Quebracho syntan	0	4.36	1.61	0.00	----------	----------	0.65	0.00
	1	2.94	2.21	0.60	----------	----------	1.49	0.84
	2	2.28	3.28	1.67	----------	----------	2.57	1.92
	3	1.98	4.11	2.50	----------	----------	3.44	2.79
27—Sulphited quebracho	0	3.90	0.80	0.00	2.30	0.00	1.65	0.00
	1	2.76	1.59	0.79	3.10	0.80	2.54	0.89
	2	2.35	2.34	1.54	3.86	1.56	3.18	1.53
	3	2.15	3.06	2.26	4.62	2.32	3.94	2.29
28—Chestnut syntan	0	4.07	0.35	0.00	1.02	0.00	0.10	0.00
	1	3.01	1.08	0.73	1.82	0.80	0.88	0.78
	2	2.65	1.74	1.39	2.60	1.58	1.62	1.52
	3	2.38	2.40	2.05	3.50	2.48	2.48	2.38
29—Quebracho syntan	0	4.58	0.41	0.00	0.89	0.00	0.28	0.00
	1	3.13	0.96	0.55	1.66	0.77	1.03	0.75
	2	2.64	1.77	1.36	2.45	1.56	1.83	1.57
	3	2.40	2.25	1.84	3.07	2.18	2.47	2.19
30—Chestnut sulphite cellulose	0	3.72	0.62	0.00	2.44	0.00	1.74	0.00
	1	2.67	1.20	0.58	3.16	0.72	2.35	0.61
	2	2.33	1.88	1.26	3.94	1.50	3.12	1.38
	3	2.03	2.80	2.18	4.59	2.15	3.68	1.94
31—Quebracho sulphite cellulose	0	4.04	0.70	0.00	2.48	0.00	1.57	0.00
	1	2.89	1.23	0.53	3.19	0.71	2.35	0.78
	2	2.33	2.27	1.57	3.90	1.42	3.13	1.56
	3	2.04	2.80	2.10	4.68	2.20	3.87	2.30

[1] Sulphuric acid calculated from the total sulphur in the sample.
[2] Sulphuric acid added, calculated from the difference in acid content of the sample before and after treatment.

The amount of acid added was determined by the difference between the calculated amount of acid in the original sample and in the sample after treatment. The acid was determined by the following methods: Modified Procter and Searle; complete combustion of the sample in an oxygen bomb and a subsequent gravimetric determination of the sulphates in the bomb washings; and by oxidation of the sample with nitric acid and a gravimetric determination of the sulphates formed.

[3] J. Research NBS **14**, 121 (1935) RP761; J. Am. Leather Chem. Assn. **30**, 91 (1935).

It is shown in table 2 that the agreement between the bomb and the nitric-acid methods is close for the calculated amount of acid added to the samples, but that the acid calculated from the total sulphur in the sample before treatment is much higher by the bomb method. This indicates that certain sulphur compounds in these leathers are resistant to oxidation by the nitric-acid treatment.

III. RESULTS AND DISCUSSION

The results for the tensile strength determinations for the different leathers and aging periods are given in table 3.

TABLE 3.—*Results of tensile strength determinations of leathers aged at 70° F, calculated in pounds per square inch*

Sample number	Untreated	Age of treated samples in months				
		0	6	12	18	24
Lot 21 Aged at 65-Percent Relative Humidity						
0	3872	[a] 3739	3615	3550	3556	3522
1	4218	3572	3378	3546	3172	3270
2	4058	3273	2964	2848	2616	2295
3	4270	3111	2101	1516	1221	1271
Lot 21 Aged at 85-Percent Relative Humidity						
0	3670	[a] 3769	3322	3422	3232	3210
1	4188	3504	3045	2838	2531	2390
2	4158	3280	2658	1826	1528	1363
3	3980	3057	1162	631	515	488
Lot 22 Aged at 65-Percent Relative Humidity						
0	4718	[a] 4560	4698	4588	4233	4652
1	4850	4748	4491	4476	4438	4688
2	4791	4202	4078	4366	3990	4217
3	5146	4293	3841	3162	2796	3560
Lot 22 Aged at 85-Percent Relative Humidity						
0	4848	[a] 4837	4445	4692	4323	4520
1	4659	4612	4192	4006	3835	4170
2	5014	4762	4264	3695	3642	3387
3	4738	4095	3065	1877	1500	1457
Lot 27 Aged at 65-Percent Relative Humidity						
0	3467	[a] 3637	3325	3469	3310	3700
1	3130	3381	3209	3280	3060	3410
2	3430	3424	3138	3162	2915	3211
3	3512	3162	2513	2370	2169	2078
Lot 28 Aged at 65-Percent Relative Humidity						
0	3446	[a] 3458	3359	3498	3002	3410
1	3415	3246	2851	2973	2762	2826
2	3270	3029	2640	2330	2010	2072
3	3315	2982	2240	1862	1465	1500
Lot 29 Aged at 65-Percent Relative Humidity						
0	3795	[a] 4090	3970	4102	3661	3940
1	3797	3850	3622	3890	3670	3768
2	3961	3706	3610	3532	3437	3430
3	3822	3545	3285	3290	3113	3002

TABLE 3.—*Results of tensile strength determinations of leathers aged at 70° F, calculated in pounds per square inch*—Continued

Lot 30 Aged at 65-Percent Relative Humidity

Sample number	Untreated	Age of treated samples in months				
		0	6	12	18	24
0	3079	[a] 3279	3161	3520	2975	3312
1	3121	3094	2902	2972	2706	2836
2	3138	2769	2394	2280	2021	1925
3	3148	2811	1717	1196	872	700

Lot 31 Aged at 65-Percent Relative Humidity

0	3071	[a] 3250	3360	3389	3338	3360
1	3010	3082	2920	3198	3290	3225
2	3450	3170	3166	3112	3020	3350
3	3313	3138	2689	2360	2240	2190

[a] Treated with water for control.

Lots 21 and 22 were aged at 70° F and at 65- and 85-percent relative humidities. The remaining lots were aged at 70° F and 65-percent relative humidity.

The normal aging for the leathers containing no added acid is shown for the different leathers and aging periods in table 3. The average loss in tensile strength for lot 21, chestnut-syntan leather, containing no added acid is, for the 2-year aging period, approximately 9 percent. The average loss in tensile strength for a 2-year aging period of 3 lots of straight chesnut-tanned leather previously reported,[4] [5] [6] was approximately 9 percent. This indicates that the large percentage of syntan used in the tanning liquors and the resulting high Procter and Searle value of 1.70 percent had no appreciable influence on the loss in tensile strength of the leather containing no added acid over an aging period of 2 years. The chestnut-syntan leather in lot 28, containing no added acid, showed less than a normal deterioration in strength, and the chestnut-sulphite cellulose leathers in lot 30 were stronger at the end of the 2-year period. The quebracho leathers containing syntan and sulphite cellulose and the sulphited quebracho leathers appear to have aged normally when compared with previous lots of these leathers tanned without the use of sulphur-containing materials. As shown in table 3, in all cases there was a loss in tensile strength immediately after treatment of the samples with acid when compared with the samples treated with water for control. This loss in strength is considered in the final results as a part of the total deterioration.

The results for the deterioration of the leathers for the 2-year aging period as a function of the original pH are given in figures 1 to 3, inclusive. The percentage change in tensile strength has been corrected for the loss in strength of the control samples containing no added acid, so that the points in the graphs represent the deterioration caused by the acid.

[4] J. Am. Leather Chem. Assn. **29,** 623 (1934).
[5] J. Am. Leather Chem. Assn. **30,** 91 (1935).
[6] J. Research NBS **15,** 73 (1935) RP811.

Figure 1 shows the effect of humidity on the deterioration of these samples during storage. The leather stored at 85-percent relative humidity showed a larger percentage loss in tensile strength than

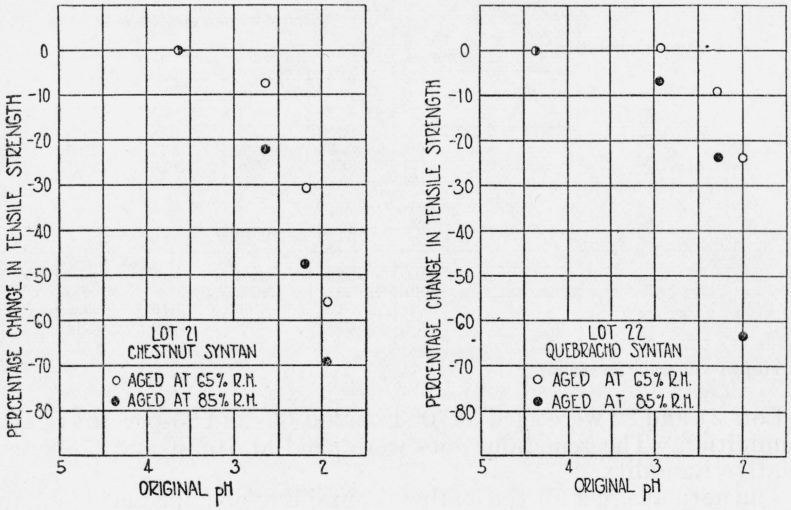


FIGURE 1.—*Effect of* pH *on the change in tensile strength of leathers aged for 2 years.*

similar leathers stored at 65-percent relative humidity. This is particularly noticeable with the leathers having a low pH value.

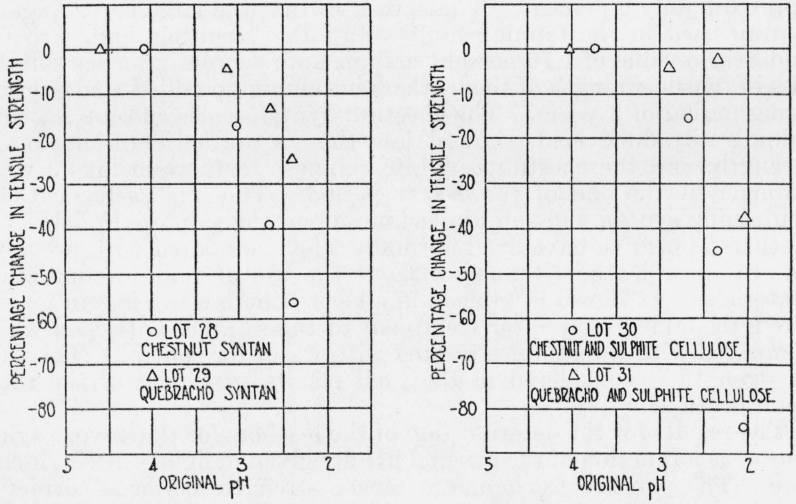


FIGURE 2.—*Effect of* pH *on the change in tensile strength of leathers aged for 2 years.*

The chestnut leathers at the lower pH values show a much greater deterioration than the quebracho leathers at the same pH.

In figure 2, lot 31, the point representing the percentage loss in tensile strength for the quebracho leather having a pH value of 2.3 is

doubtful, probably because of a variation in the uniformity of this group of samples, since it is shown in table 2 that there was a much greater loss in strength for the 18-month period than for the 24-month period.

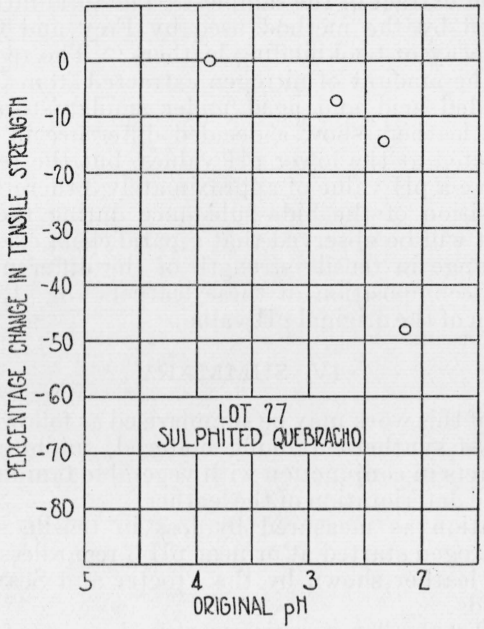
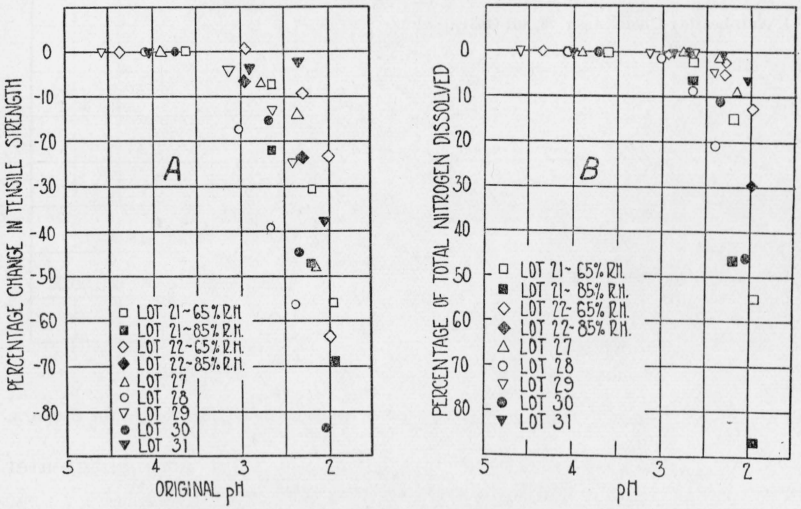


FIGURE 3.—*Effect of* pH *on the change in tensile strength of leather aged for 2 years.*

The results for the 7 lots of leather are shown plotted on the same graph in figure 4. With the exception of 1 lot of leather, the percent-



Graph A.—Effect of pH on the change in tensile strength.

Graph B.—Effect of pH on the total nitrogen dissolved.

FIGURE 4.—*Results for the 7 lots of leather showing physical and chemical deterioration after 2-year aging period, as a function of the original* pH.

age change in tensile strength of the samples having an original pH of 3 or higher, was less than 10 over the 2-year aging period.

The chemical change in the leather, shown by the amount of soluble nitrogen, is also presented in figure 4 as a function of the pH value of a water extract of the samples. The total nitrogen extracted was determined by the method used by Frey and Clarke in their work on the decay of bookbinding leathers.[7] The results have been corrected for the amount of nitrogen extracted from the leather containing no added acid and aged under similar storage conditions. Some of these leathers show a decided difference in the amount of nitrogen extracted at the lower pH values, but the results definitely show that above a pH value of approximately 3 there was no appreciable decomposition of the hide substance during the 2-year period of the test. It will be observed that a parallelism exists between the percentage change in tensile strength of the different leathers, and the chemical decomposition of these leathers (fig. 4, graphs A and B) as a function of the original pH value.

IV. SUMMARY

The results of this work may be summarized as follows:

1. The use of synthetic tanning material, sulphite cellulose, and sulphited extracts in conjunction with vegetable tannins did not cause any appreciable deterioration of the leather.

2. Deterioration as measured by loss in tensile strength or by extractable nitrogen started at or near pH 3 regardless of the amount of acid in the leather shown by the Procter and Searle or the total sulphur methods.

3. Below pH 3 the deterioration was much greater for leathers containing chestnut extract than for leathers containing quebracho extract.

WASHINGTON, August 6, 1935.

[7] J. Am. Leather Chem. Assn. **26**, 461 (1931).