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EVALUATION OF THE RELATIVE SERVICEABILITY OF VEGETABLE- AND CHROME-TANNED LEATHERS FOR BOOKBINDING*

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ABSTRACT

Durability of various bookbinding leathers has been evaluated after 34 years of natural exposure. Five vegetable- and five chrome-tanned calfskins of specific dimensions were used to cover 60 volumes of Chemical Abstracts. In addition, the test was designed to evaluate four different treatments as preservatives for each leather. The degree of chemical deterioration was measured by the liberation of water-soluble nitrogen, the accumulation of sulfates, and changes in pH. Changes in physical properties were determined by measuring residual tensile strength. The results of the physical and chemical tests are correlated and their significance to the evaluation of bookbinding leathers discussed.

INTRODUCTION

The deterioration of bookbinding leather has been a serious problem for more than a century. In 1842, Michael Faraday (1) and others in the first investigation into the cause attributed decomposition to the sulfur products resulting from the incomplete combustion of illuminating gas aggravated by poor ventilation. Subsequent work by Church (2), Davis (3), and Nichols (4) confirmed this and showed that decayed leather had a relatively high sulfuric acid content. They limited the corrosive atmosphere to the area lighted by gas. Calvert (5), Gibbs (6), and Cockerell (7) objected to this. They found significant amounts of sulfuric acid in leathers not stored in illuminated rooms. Calvert contended that sulfuric acid could originate from polluted atmosphere and from the use of sulfuric acid during the tanning process. He considered the latter the real cause of advancing decay.

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The deterioration of leathers became so serious that a committee was appointed by the Royal Society in 1900 to study the causes. A report published in 1905 by the Committee on "Leather for Bookbinding" (8) laid down fundamental requirements for durable bookbinding. They recommended that not more than 0.2 percent sulfuric acid be used in processing and tanning with pyrogallol tannins. Even this could not be relied upon to give durable bookbinding leather, partly because the recommendations were disregarded. In 1926 Veitch, Frey and Leinbach (9) examined books, obtained from a number of United States libraries, exposed only to natural and electric light. They demonstrated that leather in different sections of a deteriorated binding was different in physical and chemical composition. The part most exposed to the atmosphere was most deteriorated. They suggested coatings or dressings to delay the effects of atmospheric corrosion. In 1930, Innes (10) published data on deteriorated bookbindings, ranging in age from 40 to 120 years, collected from libraries in rural and industrial areas in England, confirming the findings of Veitch, Frey and Leinbach. In 1931, Frey and Clarke (11) published on bookbindings aged under known conditions. A strip of leather adjacent to that taken for exposure was put into a sealed envelope, thus giving the investigators an accurate comparison between exposed and nonexposed leather after eight years. They made suggestions for serviceable bookbinding leather, such as the development of leathers of a high natural tolerance to sulfuric acid or made permanently impervious to the gases of the atmosphere or containing material quantities of suitable anti-acid agents.

Innes (12, 13, 14) in a series of bookbinding experiments in 1930–1931 discovered that Nigerian goat held up better than the best English leather. On examination he found the cause to be the presence of water-soluble material in the tanning extracts. He concluded that the leather could be impregnated with various buffer salts to give the protection needed against atmospheric corrosion, which led to the use of potassium lactate. He devised the PIRA‡ test now used to certify English bookbinding leather.

In 1908 Lamb (17) conducted the first accelerated aging experiment. He demonstrated that chrome-tanned leather was more resistant to decay than vegetable-tanned leather. In 1934 Frey and Beebe (18) confirmed these results in accelerated aging experiments and in a later publication (19) showed that buffer salts gave considerable protection to leathers aged in the gas chamber. In 1956, Beebe, et al. (20) published the results of an experiment on the comparison of gas chamber tests of bookbinding leather with natural aging.

The data presented here are the culmination of work initiated by Veitch, Frey and Clarke in 1929. They wished to determine the effect of various surface treatments or dressings on the natural aging characteristics of vegetable- and chrome-tanned leathers.

‡Printing Industry Research Association.

EXPERIMENTAL

Five vegetable-tanned black calfskins and five chrome-tanned black calfskins with glazed finish, one and one half to two ounces and seven to nine square feet, not made specifically for bookbinding leather, were obtained from five different tanners. These were used to cover 20 volumes of Chemical Abstracts, three books to each volume called A, B, and C. Book C always contained the index to the volume. Six bindings were cut from each skin in groups of three to each side (Fig. 1). Bindings cut from the left side were applied to volumes 1–10, and those

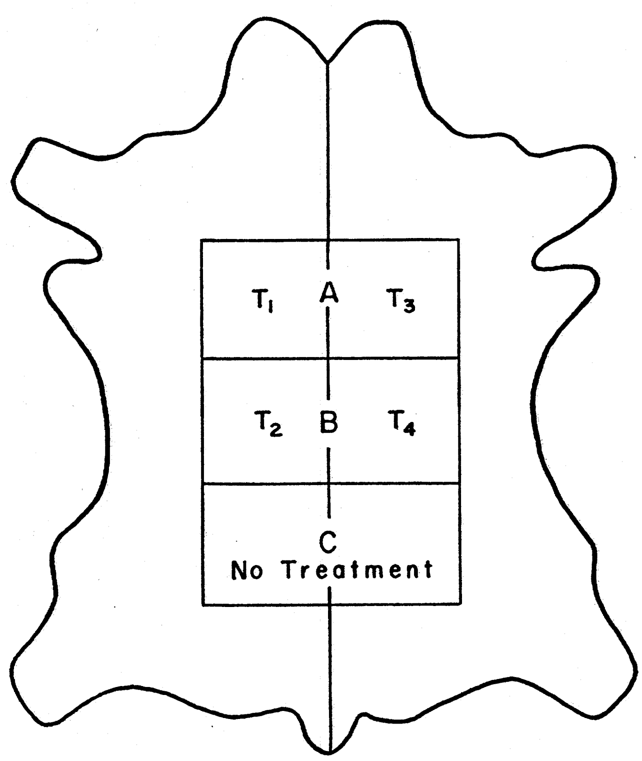

FIGURE 1.—Location of bindings with respect to skin area and scheme for assignment of dressing treatments and controls.

from the right side to volumes 11–20. The vegetable-tanned leathers were identified as Vegetable 1 to Vegetable 5 and the chrome-tanned leathers Chrome 1 to Chrome 5. Alternate volumes were bound in vegetable- and chrome-tanned leathers. Corresponding A, B, and C books were bound with leather cut from the same location on left and right sides starting at the head end of the skin. Since books "C" always contained the index to the volume, greater usage of these books by the reader can be assumed. To what extent the increased handling of the index books and the later editions of Chemical Abstracts contributed to the chemical decomposition of the bindings is not known.

The books were three-quarter bound to give more leather for examination (Fig. 2). The corners were cut as close to the sides and backs as possible. The

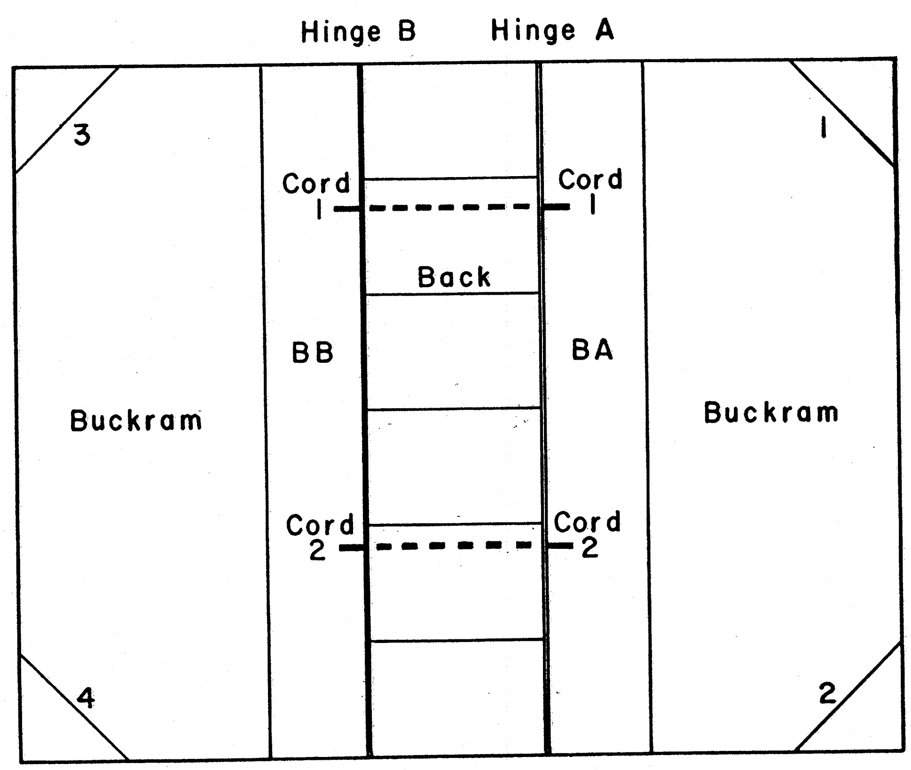

FIGURE 2.—Scheme for three-quarter leather binding of experimental volumes with leather corners.

books were bound at the Government Printing Office at approximately the same time. They had been hand sewn, marbled and the covers laced on with two cords per cover before the leather backs were pasted on**. A gum arabic jelly was rubbed into the backs, sides and corners. A glair†† was applied to the backs only prior to gold lettering. Four dressings (T) were applied to each leather, as shown in Table I. T_1 was applied to all A books, volumes 1–10; T_2 to all B

**Paste:	Flour (soft winter wheat)	19.60%
	Water	79.94%
	Phenol Solution (15%)	0.11%
	Ammonium Alum	0.35%
††Glair:	Pure egg albumin	12.50%
	Water to volume	

books, volumes 1–10; T_3 to all A books, volumes 11–20; T_4 to all B books, volumes 11–20. All C books were untreated. The dressings were to be applied at least every two years during service. The books were put into service October 1929 in the Library of the Bureau of Chemistry and Soils in Washington, D. C., where they were exposed frequently to large amounts of sulfur dioxide from smoke from a railroad two blocks away. After five years the books were moved to a new building where exposure to sulfur dioxide fumes was less severe. Dressings were applied and observations made periodically until 1940. They were brought to Wyndmoor, Pennsylvania, to an air-conditioned library, when the laboratories were relocated in October 1941. Since that time, observations only

TABLE I

FORMULAS FOR DRESSINGS

T_1	40% Anhydrous Lanolin 60% Neatsfoot Oil	T_2	Petrolatum U.S.P.
T_3	3% Castile Soap 12% Beef Tallow 25% Neatsfoot Oil 60% Distilled Water	T_4	30% Anhydrous Lanolin 5% Japan Wax 12% Castor Oil 3% Sodium Stearate 50% Distilled Water

have been made occasionally until 1963. The 60 books of Chemical Abstracts had been exposed to exactly the same varied conditions from October 1929 until January 1963. The books were inspected prior to removal of bindings. After the bindings were removed and cleaned free of the lining material, they were grouped according to the leather from which they were cut. Specimens were prepared for physical tests and conditioned at 50 percent humidity and 73.4°F. temperature. After the physical tests were completed, the test samples were ground for analysis. Because of the nature of the experiment, each binding had to be analyzed separately. Each binding was divided into two sections, back and sides. The leather corners were included with the sides.

RESULTS AND DISCUSSION

Figure 3 shows four books selected by appearance at the end of the experiment, which illustrate (a) the best vegetable-tanned binding, (b) the worst vegetable-tanned binding available, (c) the best chrome-tanned binding, and (d) the worst chrome-tanned binding.

Vegetable-tanned leathers.—Quantitative measurements of tensile strength and slit tear have been made on the exposed leathers according to ASTM methods (15, 16). The original analyses for tensile strength and slit tear were made using procedures current in 1929.

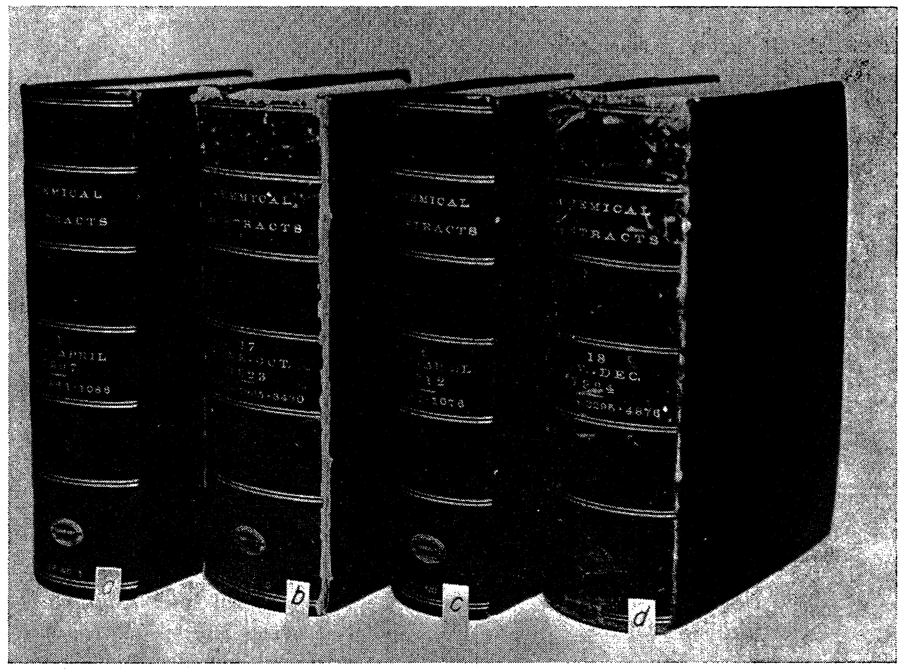

FIGURE 3.—Photograph of representative bookbindings (left to right):
(a) Best vegetable-tanned binding
(b) Worst vegetable-tanned binding
(c) Best chrome-tanned binding
(d) Worst chrome-tanned binding

Tensile strength and slit tear determinations show extensive deterioration (Table II). The sides exhibited less deterioration than the backs with the exception of vegetable-tanned leather No. 3, which was almost completely disintegrated. If the experiment had been terminated at the first indication of deterioration, more significant differences might have been shown. Actually it was noted, during the periodic examinations, that the bindings on volumes bound with vegetable-tanned leather No. 2, 4 and 5 had positive indications of deterioration as early as 1936. Several volumes bound with vegetable-tanned leather No. 3 showed first evidence of deterioration in 1937. The first evidence of deterioration appeared as loss of substance at the corners, as cracking of the surface in the hinges; and as excessive wear on the surface across the cords. On the other hand, bindings made from vegetable-tanned leather No. 1 appeared exceptionally well preserved even at the conclusion of the test although there was considerable deterioration as determined by physical tests.

Chemical analyses were conducted to determine soluble nitrogen, soluble sulfate, total sulfur as sulfuric acid, pH and moisture. All results were reported on a moisture-free basis (Table III). There was a large increase in soluble nitrogen

TABLE II

EFFECT OF DRESSINGS ON THE LOSS OF STRENGTH BY VEGETABLE-TANNED BOOKBINDINGS

		Loss After Aging									
		Untreated†		T_1		T_2		T_3		T_4	
Leather No.	Original* Strength	Back %	Side %	Back %	Side %	Back %	Side %	Back %	Side %	Back %	Side %
					Tensile						
1	4320	88	58	76	38	87	48	77	57	83	46
2	4150	91	65	81	31	94	67	85	52	88	39
3	4420	93	89	93	91	93	91	92	91	95	88
4	4570	89	58	83	21	93	53	85	50	88	37
5	4380	95	82	91	68	93	80	91	74	94	69
					Slit Tear						
1	20	88	75	75	70	85	65	80	65	90	80
2	12	87	79	75	58	83	76	83	66	83	66
3	13	92	88	85	92	92	92	92	92	92	85
4	15	87	77	74	48	81	61	81	68	87	74
5	18	95	86	83	67	95	83	89	83	89	78

*Tensile, PSI; Slit Tear, load to tear, lb.
†Untreated controls — data are averages of results from both volumes.

TABLE III

CHEMICAL ANALYSIS OF TREATED AND UNTREATED VEGETABLE-TANNED LEATHERS*

(Analytical results on moisture-free basis)

		Soluble Nitrogen		Free Sulfuric Acid		Total Accumulated Sulfur as Sulfuric Acid		pH	
Leather	Dressing	Back %	Side %	Back %	Side %	Back %	Side %	Back	Side
1	T_1	0.7	0.4	1.8	1.4	4.1	3.5	2.8	2.8
	T_2	1.6	0.7	3.6	1.2	5.4	3.7	3.0	3.2
	T_3	1.0	0.6	2.7	1.0	4.9	3.7	3.0	3.3
	T_4	2.2	0.6	3.6	1.2	5.5	3.8	3.0	3.3
	none*	3.5	1.8	4.7	1.2	6.6	4.4	2.7	2.8
2	T_1	1.0	0.5	2.4	1.3	3.4	2.4	2.8	3.0
	T_2	1.5	0.7	3.7	2.1	4.5	3.3	2.7	2.8
	T_3	1.6	0.7	3.2	1.6	4.5	2.7	2.8	2.9
	T_4	1.9	0.9	4.2	1.9	4.7	3.5	2.7	2.8
	none*	1.9	0.9	4.6	2.3	5.4	3.8	2.7	2.8
3	T_1	1.8	1.7	0.6	0.4	3.2	2.8	3.0	3.1
	T_2	2.6	2.0	1.4	0.4	3.7	2.8	3.0	3.1
	T_3	2.2	1.9	0.5	0.3	3.1	2.6	3.0	3.1
	T_4	2.4	1.8	1.1	0.03	3.5	2.5	3.0	3.1
	none*	2.8	2.7	1.3	0.4	4.1	2.8	3.0	3.1
4	T_1	1.1	0.5	2.4	0.7	4.9	3.9	2.8	3.2
	T_2	1.8	0.7	4.1	1.7	7.2	4.5	2.7	2.9
	T_3	1.5	0.1	3.6	1.0	5.8	4.5	2.7	3.0
	T_4	2.0	1.0	4.0	1.7	5.9	4.7	2.8	2.9
	none*	2.1	1.0	4.9	2.0	7.4	4.8	2.8	2.9
5	T_1	1.4	0.7	1.3	0.5	5.2	4.0	2.8	2.9
	T_2	1.9	1.5	1.1	1.0	5.4	4.5	2.8	2.9
	T_3	2.0	1.0	1.4	0.5	5.2	4.0	2.7	2.9
	T_4	1.4	0.8	1.0	0.7	6.4	4.9	2.7	2.9
	none*	2.8	1.5	2.9	1.5	7.1	5.6	2.6	2.7
	Original analyses	0.1 to	0.3	0.0 to	0.4	1.3 to	4.6	3.2 to	3.5

*Untreated controls — data are averages of results from both volumes.

and free sulfuric acid in comparison with the original amounts shown at the bottom of the table. With one exception, the backs contained more soluble nitrogen than the sides. The free sulfuric acid was substantially higher in the backs than in the sides in all cases. Total sulfur expressed as sulfuric acid quadrupled in some bindings. The pH of the leathers decreased. The increase in soluble nitrogen with a corresponding decrease of nitrogen in the residual leathers indicated a hydrolytic breakdown of the protein.

Effect of dressing on vegetable-tanned leathers.—The results of both physical analyses (Table II) and chemical analyses (Table III) showed that dressings provided some protection against atmospheric pollution when compared with the untreated bindings. There was a smaller increase in soluble nitrogen and free sulfuric acid and less accumulated total sulfur as sulfuric acid than for the untreated leathers. Again, the backs showed much greater deterioration than the sides.

After 34 years of exposure the backs of the vegetable-tanned leathers showed extensive deterioration. The sides, with the exception of leather No. 3, have been fairly well preserved. Table IV briefly describes the type of tannins used, the

TABLE IV

NATURE OF VEGETABLE TANNINS USED AND APPEARANCE OF AGED BINDINGS

Leather Number	Type Tannins Used	Degree of Tannage	Condition of Bindings	First Indication of Deterioration
1	Pyrogallol	51	Very Good	None
2	Catechol	79	Red Rot	1936
3	Catechol	51	Fair	1937
4	Catechol	81	Red Rot	1936
5	Pyrogallol	40	Poor	1936

degree of tannage, and condition of the bindings after exposure. Vegetable-tanned leather No. 1 showed the least evidence of wear, whereas leather No. 5 was almost completely rotted. It gelatinized at 50°C. (122°F.) during the analysis. The back was 94 percent deteriorated. Leather No. 3 looked better than it actually was. It picked up less acid than the other four vegetable-tanned leathers, but it had lost 90 percent of its strength on both sides and back. Leathers No. 2 and No. 4 showed great amounts of red rot. The sides of all the leathers except one book of leather No. 3 were better than the backs. The backs in every binding were deteriorated from 87 percent to 94 percent as determined by tensile strength.

Chrome-tanned leathers.—Physical measurements of tensile strength and slit tear are presented in Table V. Comparison of these results with original

TABLE V

EFFECT OF DRESSINGS ON THE LOSS OF STRENTH BY CHROME-TANNED BOOKBINDINGS

		Loss After Aging									
		Untreated†		T_1		T_2		T_3		T_4	
Leather No.	Original* Strength	Back %	Side %	Back %	Side %	Back %	Side %	Back %	Side %	Back %	Side %
					Tensile						
1	5300	83	47	70	34	71	51	72	36	75	38
2	7040	60	43	53	50	62	50	67	53	63	29
3	4870	67	41	80	28	62	68	63	62	71	64
4	5230	71	50	71	25	59	52	68	52	63	40
5	4530	70	43	78	46	75	57	69	49	83	59
					Slit Tear						
1	27	93	78	78	48	85	59	78	51	85	55
2	18	78	72	72	61	67	67	79	72	67	61
3	20	83	78	70	65	70	75	70	65	65	70
4	20	78	70	65	41	65	45	65	50	70	45
5	20	85	75	70	54	80	70	75	64	75	54

*Tensile, PSI; Slit Tear, load to tear, lb.
†Untreated controls — data are averages of results from both volumes.

values showed that the trend of percent deterioration was similar whether measured by tensile strength or slit tear. The backs consistently showed a greater loss in strength than the sides with the exception of one treated back of chrome-tanned leather No. 3.

Results of chemical analyses of untreated chrome-tanned leathers are shown in Table VI. All results were reported on moisture-free basis. The increase in soluble nitrogen was small. The total accumulated sulfur calculated as sulfuric acid increased as much as 80 percent.

Effect of dressing on chrome-tanned leathers.—Analytical results of the treated chrome-tanned leathers are shown in Table VI. The pH is above 3. The sides showed a smaller increase in soluble nitrogen and free sulfuric acid than the backs. There was a greater difference between the treated and untreated bindings than among the treated bindings, as indicated in the table.

Comparison of vegetable- and chrome-tanned leather.—The chrome-tanned leathers resisted the deleterious effects of the atmosphere better than the vegetable-tanned leathers. The tensile strength test is considered to be the best measure of deterioration. Comparison of the data in Table II and V show that the loss in tensile strength for the vegetable-tanned backs ranged from 76 percent to 95 percent (avg. 88.7), whereas, the loss for the chrome-tanned backs varied from 53 percent to 83 percent (avg. 69.8). Loss in slit tear strength of the backs averaged about 10 percent less for the chrome-tanned leathers than for the vegetable-tanned leathers.

Chemical tests also indicated greater deterioration for the vegetable-tanned leathers, with the increase in total sulfur being about twice that for the chrome-tanned leathers and the increase in soluble nitrogen being markedly greater in the vegetable-tanned leathers.

CONCLUSION

In conclusion, it can be stated that chrome-tanned leather is more durable than vegetable-tanned leather when both are used for binding books. Although the dressings described in this work provided some protection to all leathers, their use was not adequate to prolong the life of the vegetable-tanned leather effectively, as shown by physical measurements and chemical analysis. Confirming the findings of previous investigators, it can be stated that deterioration is a hydrolytic process caused by the absorption of acid-producing compounds from the atmosphere.

ACKNOWLEDGMENTS

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TABLE VI

CHEMICAL ANALYSIS OF TREATED AND UNTREATED CHROME-TANNED LEATHERS*

(Analytical results on moisture-free basis)

Leather No.	Dressing	Soluble Nitrogen Back %	Soluble Nitrogen Side %	Free Sulfuric Acid Back %	Free Sulfuric Acid Side %	Total Accumulated Sulfur as Sulfuric Acid Back %	Total Accumulated Sulfur as Sulfuric Acid Side %	pH Back	pH Side
1	T_1	0.4	0.2	0.3	0.0	5.0	4.7	3.0	3.2
	T_2	0.4	0.1	0.6	0.2	6.2	5.0	3.0	3.2
	T_3	0.3	0.2	0.1	0.0	5.3	4.9	3.0	3.3
	T_4	0.4	0.1	0.4	0.1	5.9	5.0	3.0	3.3
	none*	0.8	0.2	1.2	0.4	6.7	5.6	2.8	3.1
2	T_1	0.2	0.2	0.3	0.1	6.2	5.9	3.3	3.5
	T_2	0.4	0.2	1.0	0.3	7.4	6.7	3.2	3.3
	T_3	0.3	0.1	0.7	0.1	7.4	6.4	3.2	3.5
	T_4	0.4	0.2	0.9	0.7	7.0	6.2	3.0	3.3
	none*	0.5	0.4	1.2	0.6	8.1	7.3	3.1	3.3
3	T_1	0.4	0.3	0.1	0.1	3.8	3.4	3.5	3.6
	T_2	0.7	0.3	0.7	0.4	5.1	4.1	3.2	3.5
	T_3	0.6	0.3	0.3	0.1	4.2	3.7	3.3	3.5
	T_4	0.6	0.2	0.3	0.4	4.5	3.8	3.2	3.6
	none*	1.0	0.5	1.0	0.5	5.5	4.6	3.1	3.3
4	T_1	0.4	0.1	0.3	0.1	5.9	5.7	3.0	3.2
	T_2	0.5	0.2	0.7	0.2	7.1	6.5	3.0	3.2
	T_3	0.4	0.2	0.6	0.0	7.0	6.2	3.0	3.2
	T_4	0.3	0.3	0.5	0.0	7.1	6.4	3.0	3.2
	none*	0.5	0.2	0.9	0.4	7.5	6.8	3.0	3.1
5	T_1	0.3	0.1	0.5	0.0	6.1	5.2	3.3	3.6
	T_2	0.4	0.2	0.8	0.2	6.9	5.9	3.3	3.5
	T_3	0.4	0.1	0.4	0.1	6.6	5.6	3.3	3.5
	T_4	0.5	0.1	0.9	0.2	7.1	5.8	3.2	3.5
	none*	0.6	0.2	1.0	0.3	7.4	6.3	3.2	3.5
	Original analyses	0.06 to	0.11	0.04 to	0.14	2.97 to	5.8	4.0 to	5.2

*Untreated controls — data are averages of results from both volumes.

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