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THE EFFECTS OF ATMOSPHERIC MOISTURE ON THE PHYSICAL PROPERTIES OF VEGETABLE AND CHROME TANNED CALF LEATHERS

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ABSTRACT

Data are presented giving the changes in tensile strength, stretch, load at failure, area, thickness, and moisture content with changes in relative humidity for vegetable and chrome-tanned calf leathers.

The differences between the behaviors of chrome- and vegetable-tanned leathers are accounted for by the difference between the amounts of protein material in the leathers.

The mechanism of the effect of absorbed moisture on the strength of leather is discussed.

CONTENTS

Page
I. Introduction — 147
II. Description of leathers used — 148
III. Methods of tests — 148
  1. Strength and stretch tests — 148
  2. Moisture content — 150
  3. Rate of adsorption — 151
  4. Area change — 151
IV. Results — 153
  1. Strength and stretch tests — 153
  2. Moisture content — 155
  3. Rate of adsorption — 157
  4. Area change — 157
V. Discussion — 159
VI. Summary — 162

I. INTRODUCTION

Water vapor is always present in small amounts in the atmosphere. Usually referred to as "humidity", this water vapor affects the physical properties of materials with which it is in contact. This is particularly noticeable in the case of materials of an organic and fibrous nature, such as wool, cotton, silk, wood, paper, and leather.

For convenience, the water-vapor concentration in the air is usually referred to as a percent of the vapor pressure of pure water at that temperature, or "percent relative humidity." This arbitrary designation has been quite universally adopted, since measurements referred to it are found to be more nearly independent of change with temperature than those referred to the absolute humidity or actual vapor pressure of water.

There are two principal types of tannage—chrome and vegetable. Chrome-tanned leather is tanned with basic chromium salts and usually contains from 5 to 10 parts tanning material (as Cr_2O_3) per

100 parts of hide substance. Vegetable-tanned leather is tanned with extracts of certain vegetable materials and usually contains from 50 to 80 parts tannin per 100 of hide substance.

There is quite a difference between the behavior of these two types of leather as affected by water vapor. Wilson and Kern studied the variations in strength, stretch,[1] and area,[2] for both leathers, but used a limited number of samples. Veitch, Frey, and Leinbach [3] studied the strength and stretch of vegetable tanned calf leather alone at humidities of 35, 55, and 75 percent. In this work a further study has been made of the effects of atmospheric moisture on the properties of both types of leather.

II. DESCRIPTION OF LEATHERS USED

One chrome-tanned and one vegetable-tanned calfskin were used in these tests. The skins were commercially tanned and finished. Their analyses are given in table 1.

The chrome-tanned calfskin was divided into two sides. One of these sides was degreased with petroleum ether. The rest of the leather was used as finished by the manufacturer.

TABLE 1.—*Chemical analyses of leathers used*

[Results expressed in percent, excepting for degree of tannage]

	Vegetable-tanned calf leather	Chrome-tanned calf leather
Moisture	8.04	11.45
Petroleum ether extract	6.83	2.10
Hide substance	42.60	68.30
Total ash	0.85	9.26
Soluble ash	.72	------
Insoluble ash	0.13	------
Water solubles	6.49	------
Soluble tans	2.10	------
Soluble nontans	4.39	------
Cr_2O_3	-------	5.87
Fe_2O_3	-------	.06
Al_2O_3	-------	1.77
Combined tannin [1]	35.91	------
Other organic matter [1]	-------	8.89
Total	100.00	100.00
Degree of tannage [2]	84.30	------

[1] Determined by difference.
[2] Grams combined tannin per 100 g hide substance.

III. METHODS OF TESTS

1. STRENGTH AND STRETCH TESTS

The skins were cut into strips 6 inches long by 1¼ inches wide, parallel to the backbone. The strips were stamped out with a die into standard tensile strength samples [4] (fig. 1). A number was stamped

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[1] Wilson, J. A., and Kern, E. J., Variation in Tensile Strength of Calf Leather with Relative Humidity, J. Am. Leather Chem. Assoc., vol. 21, p. 250, 1926.

[2] Wilson, J. A., and Kern, E. J., Area Change of Shoe Leather with Relative Humidity, J. Am. Leather Chem. Assoc., vol. 21, p. 351, 1926.

[3] Veitch, F. P., Frey, R. W., and Leinbach, L. R., Influence of Atmospheric Humidity on the Strength and Stretch of Leather, J. Am. Leather Chem. Assoc., vol. 17, p. 492, 1922.

[4] Federal specification no. 37.

on each strip to identify it. The strips were marked with gage marks 2 inches apart and the thickness measured in four places. The thickness was estimated to one ten thousandth of an inch on a Randall and Stickney gage reading directly to thousandths of an inch. A constant load of 1 kg was applied to the measuring foot which had an area of 1 cm².

The strips of each skin were divided into three groups according to strength as indicated by Wilson's chart of strength variation over a calfskin.[5] Then each side of skin no. 1 (chrome calf) was divided into 5 lots of 17 strips each, and skin no. 2 (vegetable calf) was divided into 9 lots of 13 strips each. Each strength group was divided evenly among the various lots so that each lot was as nearly as possible representative of the whole skin.

Half-liter bottles were used for conditioning. The corks were paraffined to prevent the passage of moisture and hooks were screwed into the lower ends. Saturated salt solutions with an excess of salt were put in the bottoms of the bottles and the strips suspended in pairs from the hooks.

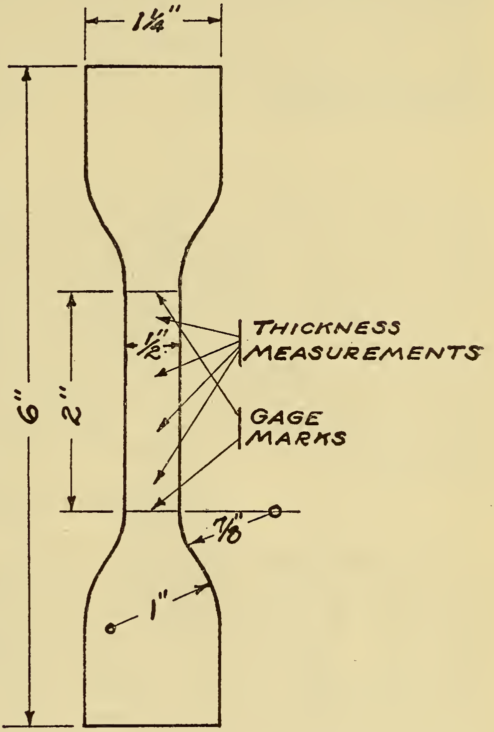

FIGURE 1.—*Diagram showing shape and size of tensile test specimens.*

One lot each of the normal and degreased chrome calf leather from skin no. 1 was placed over dry phosphorus pentoxide for the 0 percent relative humidity conditions. The other 8 lots, 4 each of the normal and degreased leather, were placed over salt solutions maintaining the humidities 32.9, 52, 75.7, and 97.1 percent.

The nine lots of strips from skin no. 2, vegetable-tanned calfskin, were conditioned in a like manner at humidities of 0, 9, 20, 32.9, 52, 75.7, 83.8, and 97.1 percent.

Saturated salt solutions in a closed system at a definite temperature tend to maintain a constant concentration of water vapor in the atmosphere over them. The salt used in these tests and the humidities they maintain are given in table 2. These values were taken from the International Critical Tables.[6] Those salts listed at 20° and 23° were used as being the same at 21°. This introduces but a slight error.

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[5] Wilson, J. A., Chemistry of Leather Manufacture, Am. Chem. Soc. Monograph Series, vol. 2, p. 1063 (2d ed.), 1929.

[6] Int. Crit. Tables, vol. 1, pp. 67–68.

TABLE 2.—*Relative humidities over saturated salt solutions*

	Relative humidity	Temperature
		° *C.*
Phosphoric acid ($H_3PO_4.1/2\ H_2O$)	9	23.5
Potassium acetate (CH_3COOK)	20	20.0
Magnesium chloride ($MgCl_2$)	32.9	21.0
Potassium carbonate (K_2CO_3)	43.5	21.0
Sodium dichromate ($Na_2Cr_2O_7$)	52	20.0
Sodium chloride (NaCl)	75.7 74.3 74.0	21.0 43.0 60.0
Potassium bromide (KBr)	83.8	21.0
Potassium nitrate (KNO_3)	94.2	21.0
Potassium sulphate (K_2SO_4)	97.1	21.0

The bottles and leather were placed in a room kept at a constant temperature of 21° C. At the end of a month the bottles were opened one at a time, and the length, width, and thickness of the strips were again measured. The leather was replaced in the bottles after having been exposed to the outside air less than 1 minute.

After 2 more weeks of conditioning, the bottles were removed a few at a time from the constant temperature room, opened, and the strips broken immediately on a vertical Scott testing machine. The stretch at 2,000 pounds per square inch, the stretch at failure, and the load at failure were noted. From the breaking load and the area and thickness data the tensile strength was calculated in pounds per square inch.

2. MOISTURE CONTENT

The method used to obtain moisture contents was substantially the same as that employed in the strength tests. Leather was suspended in a bottle over a salt solution until equilibrium was obtained. It was put into a weighing bottle and the weight taken. The leather was dried for 24 hours at 100° C. in an electric oven and the loss in weight and dry weight noted. The moisture content was calculated as grams of water per 100 g of dry leather. This method of determining the moisture content was adopted because it is that used by the American Leather Chemists Association. The salts used to maintain humidities were the same as those used in the strength tests. (See table 2.)

For purposes of comparison the moisture contents of several other leathers were measured. Humidities were maintained over sulphuric acid solutions [7] of various concentrations. The leathers used other than the vegetable and chrome tanned calf leathers were:

1. Natural quebracho-tanned steer hide leather.
2. Chestnut-tanned steer hide leather.
3. Degreased alum-tanned cowhide leather.
4. Dehydrated and deashed hide substance (in strips).

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[7] Wilson, R. E., Humidity Control by Means of Sulphuric Acid Solutions, Ind. Engr. Chem., vol. 13, p. 226, 1921.

3. RATE OF ADSORPTION

The rate of adsorption was measured for each leather in a small closed system with no induced circulation of air.

A hole was bored through the cork of a wide-mouthed bottle and a small piece of glass tubing inserted. A piece of fine copper wire was run through a paraffined cork small enough to stopper the glass tubing. The leather was suspended from the wire inside the bottle. Conditioning agents were kept in the bottom of the bottle (fig. 2). When weighings were to be made the bottle was set on a bridge in the balance, the cork removed from the glass tubing, and the cork, wire, and leather weighed together from the balance pan hook. This arrangement permitted keeping a record of the change in weight of the sample without removing it from contact with the conditioning atmosphere.

The suspended sample was placed in a bottle over phosphorus pentoxide until dryness was attained as indicated by constant weight. It was immediately transferred to another bottle in which there was a saturated solution of potassium sulphate (97 percent relative humidity). The sample was weighed at frequent intervals until approximate equilibrium was reached.

The reverse procedure was followed with the chrome-tanned calfskin to obtain a desorption curve. The vegetable-tanned calfskin molded too badly at the high humidity to allow these measurements.

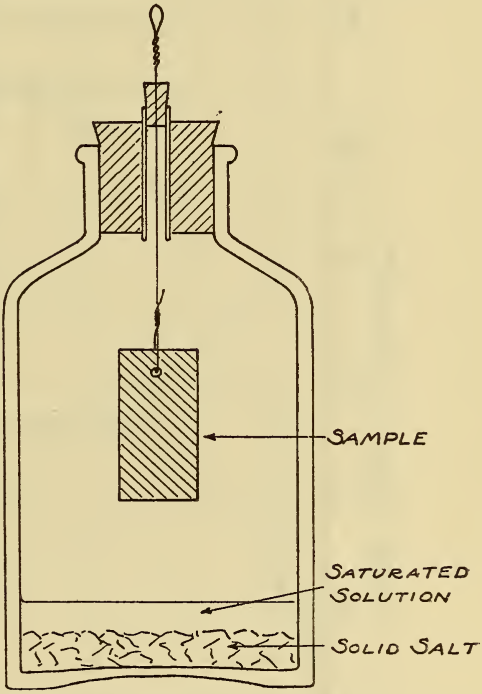

Figure 2.—*Diagram of apparatus used in adsorption-rate measurements.*

4. AREA CHANGE

A flat, horizontal, moisture-proofed box was equipped with a plate-glass cover. An inch and a half below the glass and parallel with it a brass screen was fixed. Three samples of vegetable-tanned calf leather and two samples of chrome-tanned calf leather were cut into circles approximately 10 cm in diameter. Two sets of gage marks were made at right angles to each other on the samples. The leather was put on the brass screen. Humidifying solutions were kept in an enameled pan in the bottom of the box. The removable cover was sealed in place with clamps and stopcock grease.

Measurements were made by means of a movable flat scale and a piece of optical glass 2 inches thick with plane parallel faces. Two lines parallel to each other were etched on opposite faces of the glass identifying a plane perpendicular to the plane of the faces. The glass was placed on the plate-glass cover of the box in such a way that one of the gage marks on a sample and a point on the scale were made to coincide with the line of sight of the etched lines. The glass was moved and sighted on the corresponding gage mark and a scale reading made. From the lengths thus measured the change in area of the leather between different relative humidities was calculated. Readings were taken at humidities of 0, 33, 52, 75, and 94 percent. The samples were conditioned a month or over for each measurement although practically no change in area was observable after 5 days. Concentrated sulphuric acid was used to obtain 0 percent relative humidity. The salts used to maintain the other humidities are given in table 2.

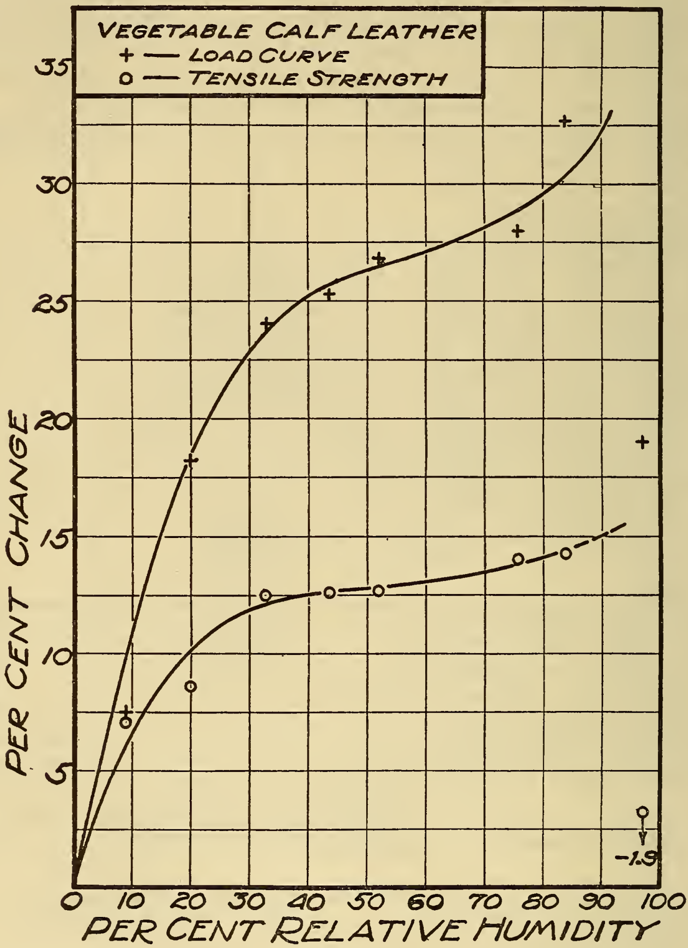

FIGURE 3.—*Percent changes in breaking load and tensile strength with change in relative humidity of vegetable-tanned calf leather.*

This method of procedure allowed a record to be kept of the dimensional changes of a piece of leather over a period of time without rolling, stretching, flexing, or touching it in any way during the course of the experiments.

IV. RESULTS

1. STRENGTH AND STRETCH TESTS

The results of the strength and stretch tests are presented in tables 3 and 4. It will be seen by inspection that the change in properties is much more pronounced for the chrome than for the vegetable-tanned leather.

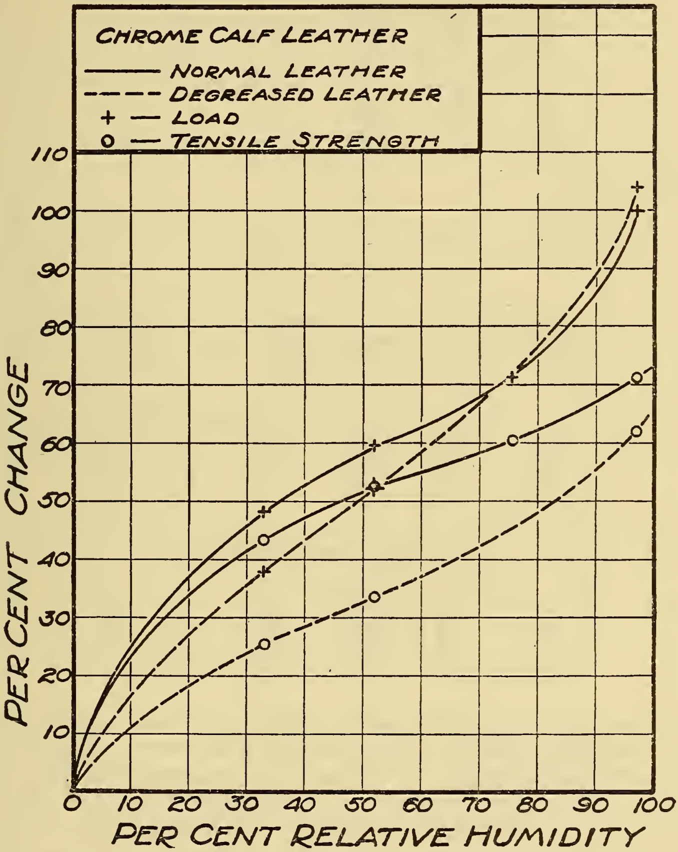

FIGURE 4.—*Percent changes in breaking load and tensile strength with change in relative humidity of chrome-tanned calf leather.*

In figures 3 and 4, the percent changes in load and tensile strength with relative humidity are shown graphically. The percent change in tensile strength is less than the percent change in load, since the change in the former is partly compensated for by the change in cross-sectional area. The load values are the better for the purpose of comparison, since the tensile strength values introduce another variable, cross-sectional area, which for a given sample of leather is not under the control of the observer and may be studied separately.

TABLE 3.—*Physical tests on vegetable-tanned calf leather*

Relative humidity, 21° C.	Load at failure	Tensile strength	Stretch at load of 2,000 lb./in.^{2}	Stretch at failure	Increase in thickness
	Pounds	*Lb./in.^{2}*	*Percent*	*Percent*	*Percent*
0	74.7	4,630	16	30	0.00
9	80.3	4,960	17	32	1.39
20	88.3	5,030	18	38	2.03
32.9	92.7	5,210	19	33	2.30
43.5	93.6	5,215	19	34	2.81
52	94.7	5,220	19	34	2.85
75.7	95.6	5,280	21	36	4.60
83.8	99.1	5,290	20	37	6.01
[1] 97.1	[1] 89.0	[1] 4,540	21	36	9.63

[1] Leather badly molded.

TABLE 4.—*Physical tests on chrome-tanned calf leather*

A. NORMAL LEATHER

Relative humidity, 21° C.	Load at failure	Tensile strength	Stretch at load of 2,000 lb./in.^{2}	Stretch	Increase in thickness
	Pounds	*Lb./in.^{2}*	*Percent*	*Percent*	*Percent*
0	52	3,170	19	34	0.00
32.9	77	4,550	25	46	1.55
52	83	4,840	23	46	1.87
75.7	89	5,080	24	48	4.23
97.1	104	5,420	25	50	14.05
B. DEGREASED LEATHER					
0	53	3,250	16	26	0.00
32.9	73	4,070	22	41	3.95
52	79	4,340	23	43	4.74
97.1	108	5,270	25	54	15.87

Due to an error in conditioning which was not noticed until the samples had been broken, the strength and stretch determinations for the degreased chrome calf leather at 75 percent relative humidity were lost. The other points are not as reliable as those for the normal leather since the individual variations in breaking load were greater. However, it will be noticed that below 50 percent relative humidity the change in load is less for the degreased than for the normal leather, while above this humidity the reverse is true. The change in cross-sectional area was greater for the degreased than for the normal leather; consequently, the tensile strength change is less.

The vegetable calf leather at 97 percent relative humidity molded badly. This resulted in a loss in breaking strength which, in combination with the greatly increased cross-sectional area, was sufficient to give the leather a tensile strength less than that observed at 0 percent relative humidity.

2. MOISTURE CONTENT

The moisture contents of the normal chrome and vegetable-tanned calf leathers at 21° C. at different relative humidities are shown graphically in figure 5. The moisture contents are plotted as grams of water per 100 g of dry leather. The moisture contents of the degreased samples were practically the same as those of the normal leather.

The moisture content of leather dried over phosphorus pentoxide is given as being 0 percent. Actually, such leather upon being heated at 100° C. showed a loss in weight of from 0.3 to 0.8 percent. Wilson [8] reports this as adsorbed water. The authors believe that such is not the case; that this is a permanent loss in weight due to a change in composition of the leather. Phosphorus pentoxide in a closed system maintains over itself a relative humidity below 0.0001 percent, for all practical purposes, 0 percent. Drying at 100° C. is a substitution

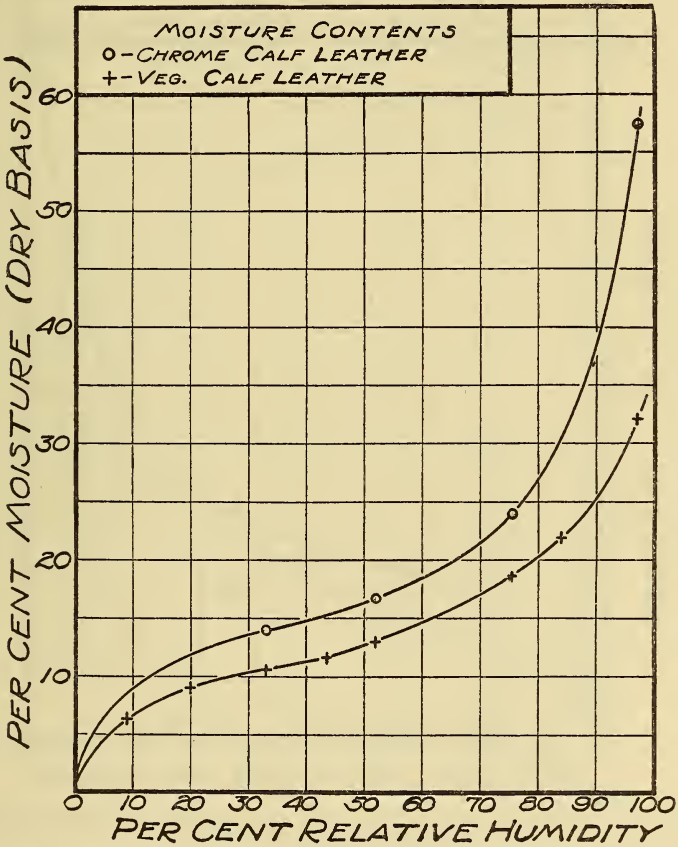

FIGURE 5.—*Change of moisture content with change in relative humidity of chrome- and vegetable-tanned calf leathers.*

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[8] Wilson, J. A., Chemistry of Leather Manufacture, Am. Chem. Soc. Monograph Series, vol. 2, p. 1071, 1929.

for this condition, approximately correct in most cases. This method is to be preferred wherever possible because of its greater convenience and rapidity. However, there are cases where it is inapplicable or only approximately valid. That this is true for leather is shown by the difficulties of the American Leather Chemist's Association Committee [9] and other investigators [10] in providing an accurate or reproducible method for the determination of moisture in leather. Veitch and Jarrell [11] have also shown that vegetable tanned leather heated at 100° loses weight continuously. As evidence that the composition of chrome-tanned leather is changed by heating, the data in figure 6 are presented.

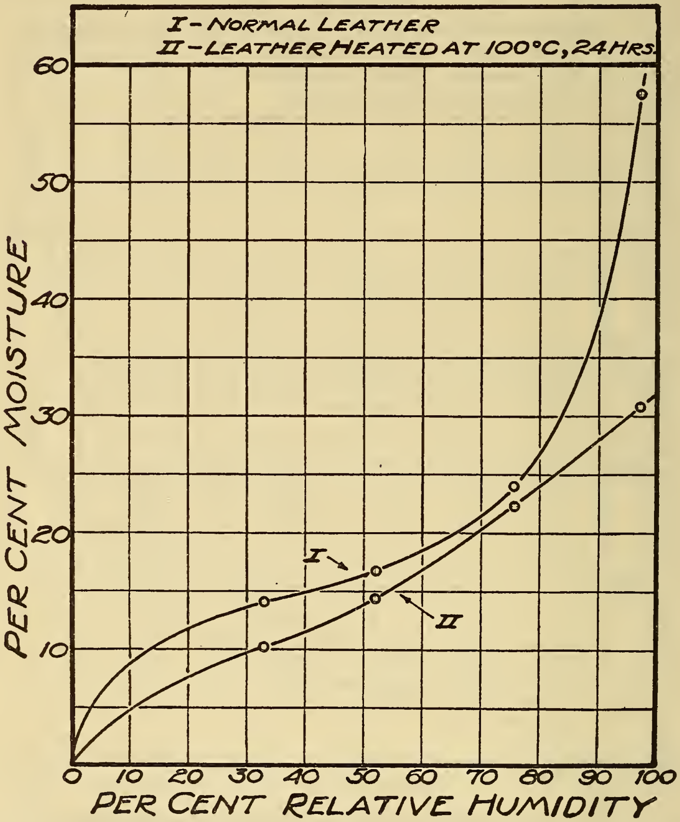

Figure 6.—*Adsorptive capacity of chrome-tanned calf leather before and after being heated for 24 hours at 100° C.*

Chrome-tanned calf leather was conditioned over saturated salt solutions until equilibrium was attained. This leather was then dried at 100° C. for 24 hours and the moisture content calculated on this dry basis (curve 1, fig. 6). The leather was reconditioned over

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[9] American Leather Chemists Association Committee Report on Humidity, J. Am. Leather Chem. Assoc., vol. 15, p. 529; vol. 17, p. 262; vol. 21, p. 435; vol. 22, p. 265.

[10] Veitch, F. P., and Jarrell, T. D., J. Am. Leather Chem. Assoc., vol. 16, p. 547; vol. 19, p. 568; vol. 20, p. 334.

[11] Veitch, F. P., and Jarrell, T. D., J. Am. Leather. Chem. Assoc., vol. 16, p. 547.

the same salt solutions. The new moisture contents are given in curve 2, figure 6. The leather never regained its original weight, the application of heat inhibiting the readsorption of water under the same conditions.

3. RATE OF ADSORPTION

As previously described, leather was dried over phosphorus pentoxide and then exposed to an atmosphere of 97 per cent relative humidity the change in weight being noted at intervals. The results are presented in figure 7. The moisture, as a percent of the total change in weight of the sample, is plotted against the time in hours. Practically no change in weight was observable from 150 to 200 hours. The drying curve for normal chrome tanned calf leather is also shown in figure 7.

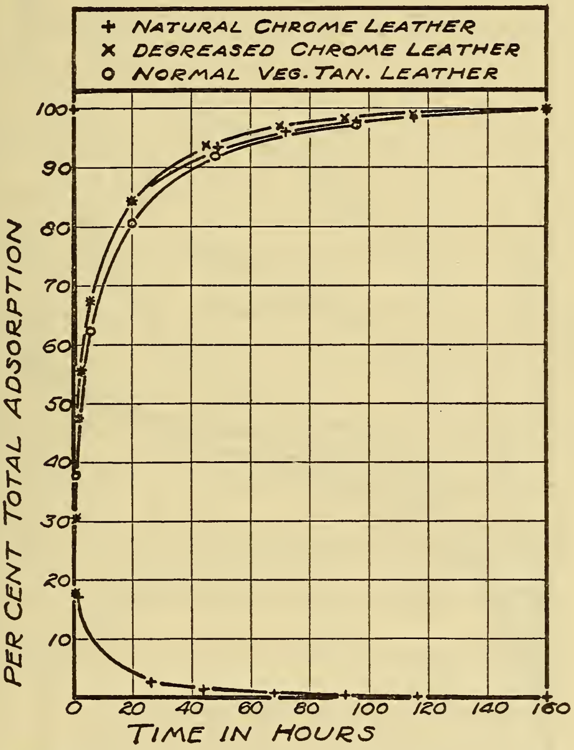

FIGURE 7.—*Rate of adsorption of calf leather in still air.*

4. AREA CHANGE

Change in area is shown as a function of relative humidity in figure 8. The most striking feature of this graph is the large hysteresis effect shown by the chrome calf leather. The small arrow heads show the direction in which conditioning was proceeding. Much less hysteresis was exhibited by the vegetable-tanned calf leather.

No investigator has observed moisture content hysteresis of sufficient extent to account for this effect.[12] It is suggested that when the moisture conditions are changed an internal stress is set up in the leather which does not entirely equalize itself, but will rapidly do so if the leather is bent, handled, or coiled. This would account for the failure of Wilson and Kern[13] to detect this effect since they used strips of leather which were coiled and uncoiled during the course of their experiments. The differences between the behaviors of the chrome- and vegetable-tanned leathers may perhaps be accounted for by the looser structure of the former, the greater range of variation, and the larger percent of protein material.

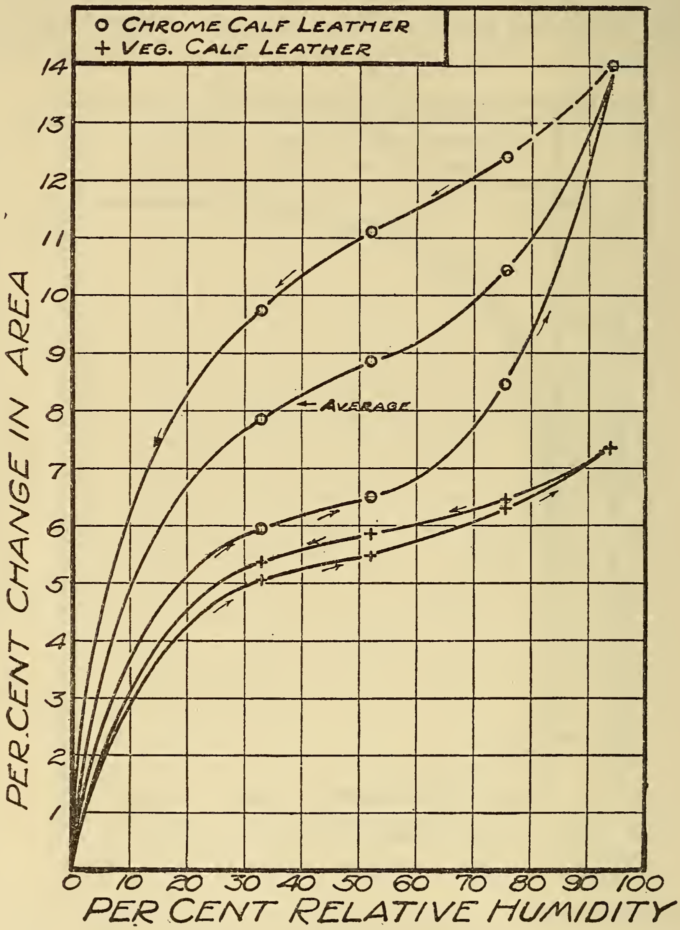

Figure 8.—*Change in surface area with change in relative humidity of vegetable- and chrome-tanned calf leathers.*

Change in cross-sectional area with relative humidity is shown in figure 9. The values for the linear change on the surface which were

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[12] L. Meunier and K. Le Viet, J. Intern. Soc. Leather Trades' Chem., vol. 14, p. 524, 1930.
[13] See footnote 2, p. 148

used in calculation are the averages of those obtained by approaching a humidity from each side of the equilibrium. The thickness changes are the averages of those noted in the strength tests. The change in cross-sectional area is quite different from the change in surface area, due to the greater change in thickness with relative humidity as compared with change in length. Since the fibers are oriented more or less parallel to the grain, the probable explanation for this is the greater swelling of the fibers in a direction perpendicular to their length. This effect would be more noticeable, since the thickness measurements were made with the leather under a compression of 1 kg/cm^2.

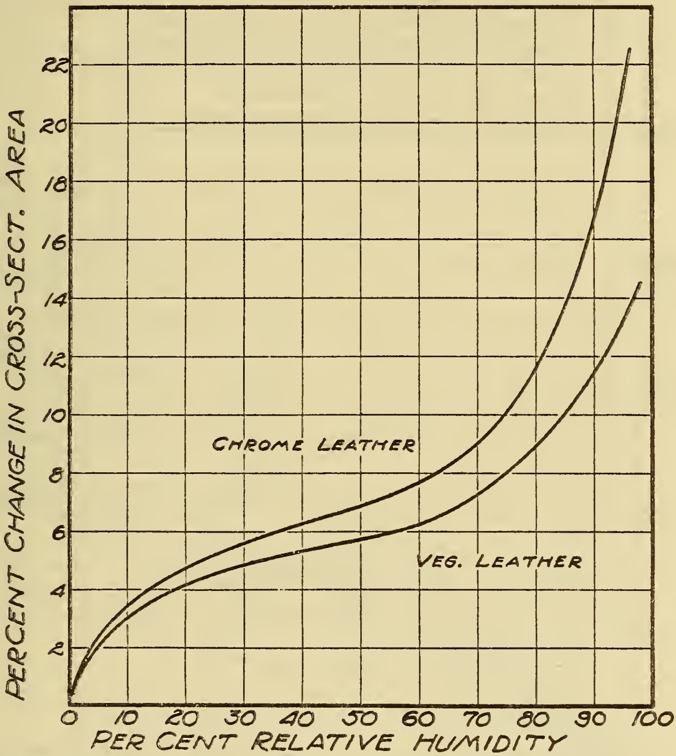

FIGURE 9.—*Change in cross-sectional area with change in relative humidity of vegetable- and chrome-tanned calf leathers.*

V. DISCUSSION

During the previous paragraphs emphasis has been laid principally on the relationships existing between the various properties studied and the relative humidity. It should be remembered that this is a secondary relationship. The variations studied depend upon the moisture content of the leather which in its turn depends upon the relative humidity.

If the moisture content of a sample of leather at a definite temperature is plotted against the corresponding relative humidities, a sigmoid curve characteristic of this material is the result.

The ability of a leather to adsorb water seems to depend principally on the amount of hide substance in the leather. This is augmented or interfered with by the presence of other materials. In figure 10 the percent moisture at 10, 20, 30, 40, 50, and 60 percent relative humidity, 30° C., of six leathers is plotted against the percent hide substance of the leathers. The result is a series of nearly straight lines passing through the origin. This is quite surprising considering that the effects of grease, uncombined tannin, nontans, added salts, etc., have been entirely disregarded. Above 60 percent relative humidity the effect of salts becomes too great to be disregarded, particularly in the case of the alum-tanned leather. As the percent of hide substance decreases the effects of the other materials mentioned are, of course, augmented.

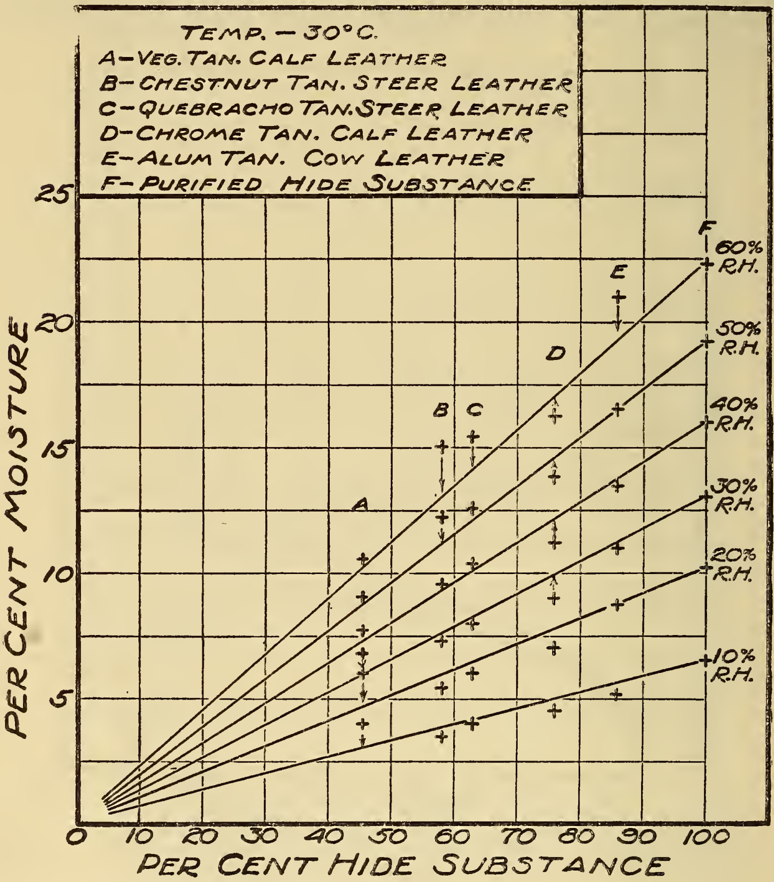

FIGURE 10.—*Relation between adsorptive capacity and constitution of various leathers.*

In figure 11, the percent changes in load and area for the chrome- and vegetable-tanned calf leathers are plotted against the percent changes in moisture content. The points shown represent relative humidities of 10, 20, 30, etc., up to 90 percent. The shape of the corresponding curves is very similar, suggesting merely a change in scale. This change of scale is probably governed by the amount of protein material in the dry leather. It is interesting to notice that lines drawn between the points representing the corresponding relative humidities result in a series of nearly parallel lines.

Wilson and Kern [14] state that the effect of moisture on the strength of leather is due to the lubricating effect of the adsorbed water. However, this curve, shown in figure 11, is a sigmoid, suggesting that the adsorbed water has a compound effect which may be analyzed as in the succeeding paragraphs.

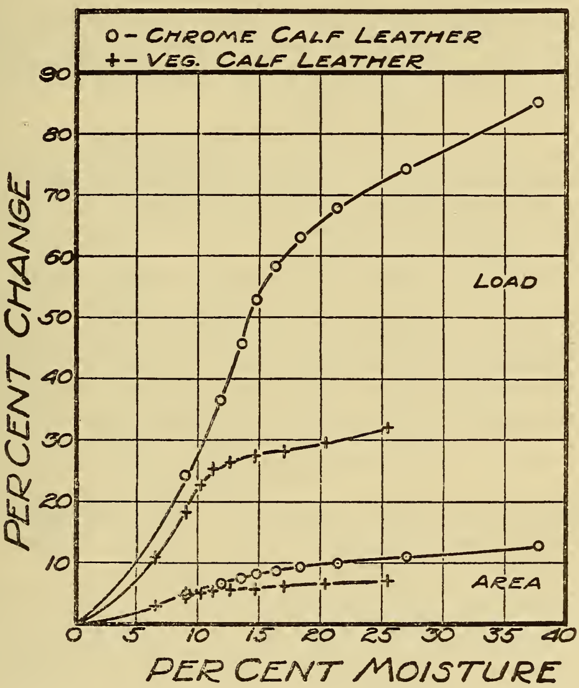

FIGURE 11.—*Changes in breaking load and surface area with change in moisture content of vegetable- and chrome-tanned calf leathers.*

If the stretch of leather at constant load per unit of cross-sectional area is plotted against the moisture content, a rapid increase in ease of stretch is noticed between 0 and 15 percent moisture, after which there is little change. This increase in case of stretch may account for a similar increase in strength.

When a sample of leather is put under tension it does not fail instantaneously. If the sample is held in immovable jaws under a proper tension, the pull of the leather itself will in time be sufficient to break it. First the snapping of individual fibers will be heard, continuing possibly for several minutes. Then the leather will start to tear slowly from one edge. This tearing will increase in speed as

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[14] See footnote 1, p. 148.

more and more tension is placed on fewer and fewer fibers. Finally, when the sample has broken, the torn ends will be seen to consist of a mass of long silky fibers, each pulled from the opposite side of the plane of failure.

The above-described behavior of leather subjected to strain suggests a certain mechanism for the failure of leather as affected by moisture. When a piece of dry leather is put under tension, the stress is not evenly distributed on all the fibers, as witnessed by the snapping of individual fibers as the limit of strength is approached. As the moisture content increases, a more equable distribution of the load between the fibers is obtained due to the greater stretch of the leather. This effect becomes greater the greater the moisture content, giving the first sharp rise in the strength-moisture curve, but approaches a limit when the leather has adsorbed from 10 to 15 percent moisture and the stretch becomes more nearly constant.

Another effect of the moisture is suggested by the fact that failure of the leather consists not only of fiber breakage but also of slippage of the fibers past one another. As the moisture increases in the leather the fibers swell, bringing one fiber more in contact with another. This would tend to increase the friction between them and at the same time increase the strength of the leather.

The two above-mentioned effects, with others, all taken together may account for the complex shape of the strength-moisture curve. If this explanation is valid it means that the strength of the fiber itself may not be increased by the adsorption of moisture. Indeed, in the case of other animal fibers, it has been shown that an increase in moisture content will cause a decrease in the strength of the fiber.[15]

VI. SUMMARY

1. Changes in the relative humidity of the atmosphere result in changes in the tensile strength, load at failure, stretch, area, and moisture content of leather.
2. These variations are more pronounced for chrome-tanned leather than for vegetable-tanned leather.
3. The differences between the behaviors of chrome and vegetable tanned leathers are attributed to the difference between the amounts of protein material in the leathers.
4. A speculation is made concerning the probable mechanism of the effect of adsorbed moisture on the strength of leather.

Washington, May 15, 1933.

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[15] Speakman, J. B., J. Soc. Chem. Ind., vol. 49; T209, 1930.

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