Adsorption of Water Vapor by Untanned Hide and Various Leathers at 100° F

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Adsorption of water vapor by untanned hide and various tannages of leather was determined at relative humidities ranging from 0 to 96 percent at 100° F. The Brunauer, Emmett, and Teller equations for adsorption of gases in multimolecular layers were applied to the data. Adsorption for all of the samples below a relative humidity of 75 percent is a function of the available surface. Above 75-percent relative humidity, other factors exert an influence, the most important of which is probably size of the capillaries. Untanned hide and chrome-tanned leather adsorb the most water vapor except at relative humidities above 75 percent, at which sole leather adsorbs more. The behavior of the sole leather in this region is ascribed to the presence of deliquescent materials used in the finishing process. The other vegetable-tanned leathers adsorb less moisture than either hide or chrome leather. Calculated heats of adsorption indicate that the affinity of groups for water is not appreciably altered by tanning and that the adsorption is physical in nature. Methods by which the data may be applied to practical processes, such as fat-liquoring and tanning, are pointed out.

I. Introduction [1]

The amount of moisture that leather adsorbs or loses is determined by temperature, relative humidity, degree of porosity, and the size of the pores. Moisture has great practical significance because its amount affects the durability of leather, and in articles such as shoes, gloves, and other garments, the comfort of the wearer. High moisture content accelerates deterioration and promotes mildew action. On the other hand, a minimum amount of moisture is required to keep leather properly lubricated and thus prevent cracking. The adsorption of moisture affects comfort by its influence on weight, area, and insulation. Insulation is a function of the amount of water adsorbed, water vapor transmission, rate of condensation, and evaporation.

From data obtained in the study of the moisture adsorption by leather and untanned hide at various relative humidities, theoretical concepts as to the nature and magnitude of the surfaces may be obtained. Such concepts may be of value in determining the nature of tanning and in studying other processes, such as fatliquoring and dyeing.

The effect of relative humidity on strength and stretch of leather has long been known, and it is now customary to make all such tests under controlled conditions of temperature and humidity. Veitch, Frey, and Leinbach [1] [2] studied the strength and stretch of vegetable-tanned calf leather at relative humidities of 35, 55, and 75 percent. Wilson and Kern [2, 3] determined the

[2] Figures in brackets indicate the literature references at the end of this paper.

variations in strength, stretch and area for both vegetable and chrome-tanned leathers. Evans and Critchfield [4] made an investigation of the amounts of moisture adsorbed by chrome and vegetable-tanned calf leathers at different percentages of relative humidity at a temperature of 21° C. Recently Green [5] determined the moisture content of chrome leather under different percentages of relative humidity at 25° C. These studies have all been somewhat limited in scope and, in general, the results were obtained where static methods for obtaining the relative humidity conditions were used.

Work on the determination of the internal surface area of hide and formaldehyde-tanned hide has recently been done by Zettlemoyer, Schweitzer, and Walker [6]. These determinations were made by studying the adsorption of nitrogen. Bull [7] studied the adsorption of water vapor by a number of different proteins, one of which was collagen.

This paper gives results of an investigation on the moisture relations of collagen and of leather. This is part of a study that is intended to cover a wide range of temperatures and relative humidities. The results given were obtained with collagen (commercial hide powder) and various tannages of leather at 100° F and at relative humidities ranging from 0 to 96 percent.

II. Description of Samples Used

The collagen used was a sample of commercially prepared hide powder. A more highly purified collagen has been prepared since this work was started and will be compared with the commercial hide powder in future work.

Six different samples of leather were used. As there was no precedent to determine the exact nature of the data that would be obtained, the selection of samples was made somewhat arbitrarily, but included leathers which differed from each other in properties and represented some of those most important commercially. Sole leather was used because of its importance and the fact that the addition of salts and glucose in the finishing exerts an influence on the moisture adsorbed. This was compared with a similar tannage of leather from which the grease had been removed, and glucose and salts were removed by washing. Water-soluble material in the leather is mostly vegetable tannin, which it is almost impossible to remove completely by washing. Chrome hydraulic-packing leather was used to represent a mineral tannage. Chrome-retanned leather represents the combination of the mineral and vegetable tannage. Calfskin and belting leather were selected to represent two types of finished vegetable-tanned leathers. The analyses of the leathers are given in table 1.

TABLE 1.—*Chemical analysis of the leathers used in the water-vapor-adsorption measurements, based on moisture-free weight*

Leather	Ash	Grease	Water solubles	Hide substance	Degree of tannage	Acidity	Cr_2O_3
	Percent	Percent	Percent	Percent		pH	Percent
Sole	5.6	6.0	36.5	33.0	74	3.3	---
Sole, degreased and washed	0.8	0.4	10.8	52.3	70	3.2	---
Chrome, hydraulic-packing	5.7	7.9	---	76.3	--	3.1	4.6
Chrome-retanned upper, degreased	3.7	2.5	---	52.5	--	3.1	3.0
Calfskin, vegetable-tanned	1.0	16.9	7.8	42.1	78	3.8	---
Belting	0.4	12.8	9.2	45.0	73	3.1	---

III. Methods of Test and Procedure

The conditioning equipment was developed by Carson and Worthington for use in studying water-vapor permeabilities of sheet materials. This equipment is shown in figures 1 and 2, and a detailed description is given in reference [8]. It consists essentially of a sealed temperature-controlled chamber in which a constant relative humidity is maintained by means of the proper saturated salt solution. Air is circulated over the salt solution and throughout the chamber continually. It is equipped with a mechanism for weighing the samples in the chamber. This is done by means of the rotating disk (36), figure 2, from which the samples (1) are suspended. Each sample is weighed by rotating it to the position of the weighing arm (40), and transferring it from the disk to the extended arm of the balance by means of a device on top of the chamber.

The water-adsorption measurements were made with leather samples ground to pass a 4-mm sieve. Weighed portions of the samples were placed in small cylindrical baskets (approximately 2 in. in diameter by 2½ in. high, shown in fig. 3) made

from 40-mesh copper screen. The samples and containers were hung from the disk in the chamber.

The same sample of each particular material was used to obtain all the data in the adsorption and desorption procedure. The samples were allowed to come to equilibrium at a constant relative humidity at 100° F. The salt solution was then changed, and the same samples were brought to equilibrium at a slightly higher relative humidity. This procedure was repeated at 10 different points from 0 to 96 percent. The desorption determinations were made by reversing this procedure by starting at 96-percent relative humidity and ending at about 0 percent. The salts used for maintaining the constant relative humidities and their values as determined by the wet-dry bulb, and by direct vapor-pressure determination [9] are shown in table 2.

To correct for the moisture adsorbed by the container, an empty basket was used as a blank and weighed each time weighings were made with
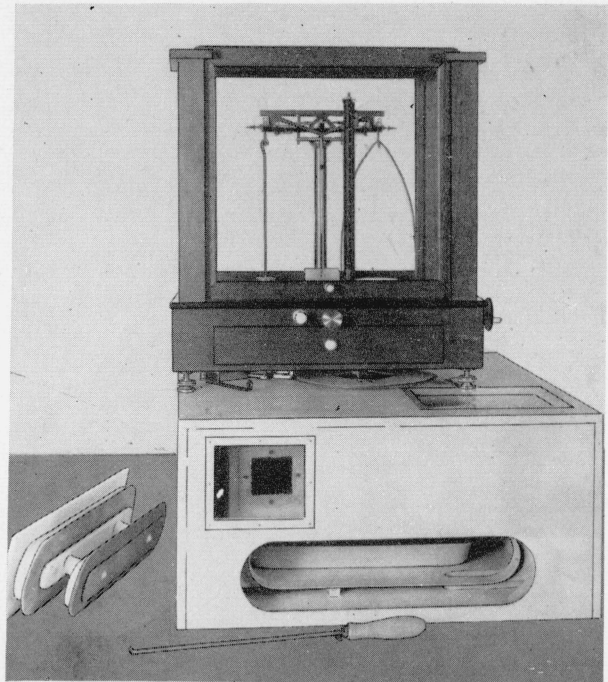

FIGURE 1.—*Equipment used in obtaining data on adsorption of water vapor by untanned hide and various leathers at 100° F.*
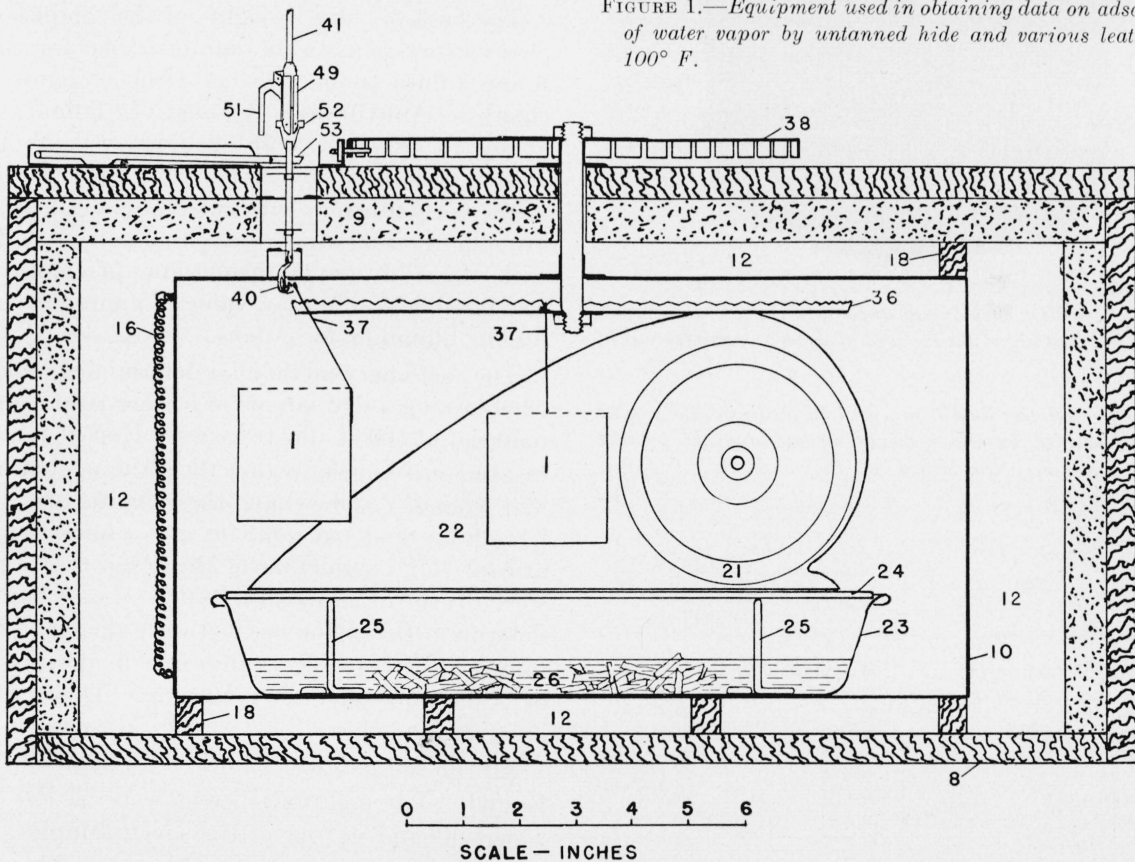

FIGURE 2.—*Details of the conditioning chamber used in obtaining data on the adsorption of water vapor by untanned hide and various leathers at 100° F.*
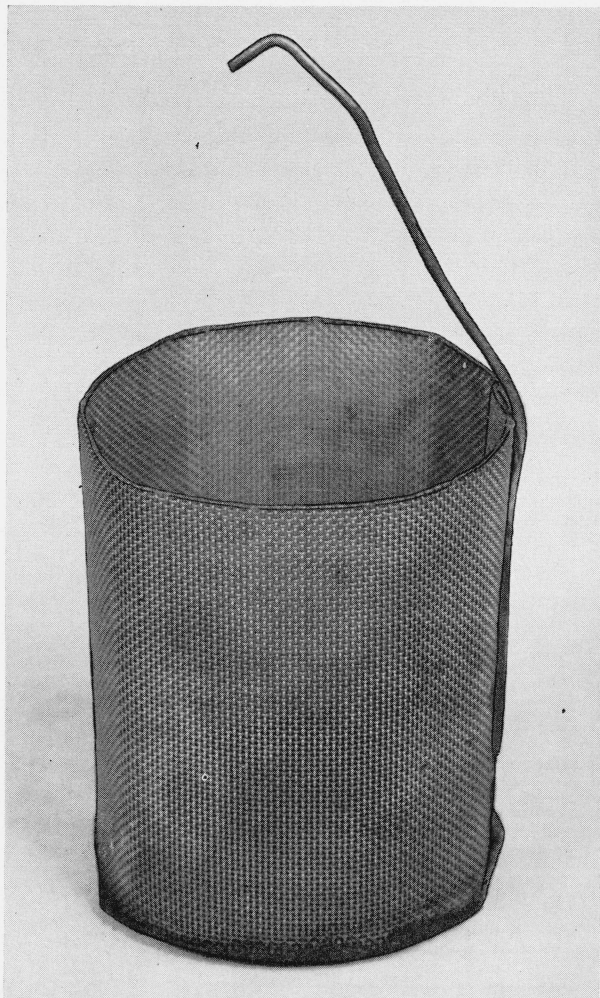
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FIGURE 3.—*Wire basket used to contain the leather samples used in the study of the amount of water vapor adsorbed at 100° F.*

TABLE 2.—*Relative humidities used in obtaining the results as determined by the wet-bulb method and the relative vapor pressure determined at the Institute of Paper Chemistry* [9]

Salt	Method	
	Wet-bulb	Relative vapor-pressure
MgClO₄ (Anhydrone)	0 (approx.)	----------
LiCl	12. 4	11. 1
KC₂H₃O₂	20. 2	20. 4
MgCl₂.6H₂O	31. 8	31. 9
K₂CO₃	43. 0	43. 4
NaBr	53. 5	53. 7
NaNO₂	61. 3	61. 8
NaCl	74. 4	75. 1
K₂CrO₄	84. 3	85. 6
K₂SO₄	96. 2	----------

the samples. The increase in the weight of the blank was subtracted from the increase in the weight of the basket and the sample. The amount of moisture adsorbed by the basket was quite low and amounted to a total of only about 0.35 percent for a 5-g sample of leather for all relative humidities up to 96 percent. At 96-percent relative humidity, an additional correction of about 0.45 percent was necessary for the same weight of leather.

No difficulty was experienced in weighing the samples at any condition of relative humidity except at 96 percent. At this humidity, moisture condensed on the rod leading from the balance arm to the sample. It was, however, possible to make a correction for this so that the error in the determinations was minimized.

IV. Results of Measurements

1. "Dry" Weight of the Samples

The base or "dry" weights of the samples used in the experiments were obtained from the equilibrium values in the presence of magenesium perchlorate Anhydrone. A relative humidity of about 10 (dry-wet bulb reading) was obtained with this material by first permitting the attainment of equilibrium with calcium chloride. This brought the humidity to about 2 percent. Then with the addition of magnesium perchlorate, it was possible to obtain a value of approximately 0 for the humidity for 3 days.

The customary method for determining moisture or obtaining a dry sample of leather is to heat the material at 100° C for 18 hours. However, as this treatment is known to alter the structure of leather and collagen somewhat, these materials might have been rendered unfit for use at lower temperatures. On completion of the tests, the samples were placed in an oven at 100° C for 18 hours to determine the difference between the values obtained after reaching equilibrium in the presence of Anhydrone and after heating. These results are given in table 3.

All the samples lost additional weight on being heated. The additional losses were all less than 1 percent and in four of the seven samples, they were under 0.5 percent.

TABLE 3.—*Difference in weights of samples in equilibrium in presence of Anhydrone and after heating 18 hours at 100° C in dry-air stream*

Sample	Weights of samples		Differ-ence	Per-cent
	After equilibrium in presence of Anhy-drone	After heating at 100° C in dry air stream		
	g	*g*	*g*	
Untanned hide_____	6. 0326	5. 9928	0. 0398	0. 66
Sole leather_____	4. 3611	4. 3199	. 0412	. 94
Chrome leather_____	3. 3005	3. 2756	. 0249	. 76
Chrome-retanned leather, degreased_____	4. 7728	4. 7497	. 0231	. 49
Sole leather, degreased, washed_____	5. 0998	5. 0937	. 0061	. 12
Vegetable-tanned calfskin__	6. 2107	6. 2011	. 0096	. 15
Belting leather_____	5. 5106	5. 4971	. 0135	. 25

2. Adsorption Isotherms

The time required to reach equilibrium at a definite relative humidity is shown in figure 4, where the rate at which equilibrium was reached at 11- and 54-percent relative humidity is given. Equilibrium is reached in 1 day at a relative humidity of 11 percent, whereas at 54 percent a 5- to 7-day period was required.

Adsorption isotherms at 100° F for six different leathers and for untanned hide are given in figure 5. The curves are all of the sigmoid type, with a
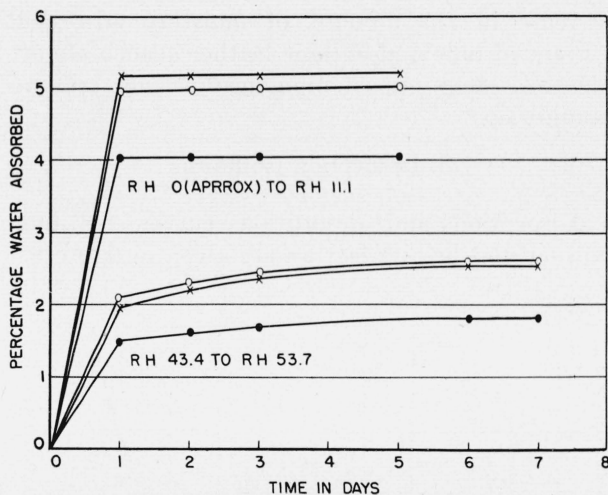

FIGURE 4.—*Rate at which equilibrium is reached at two different relative humidities by hide substance, chrome leather and belting leather when exposed in an atmosphere of water vapor at 100° F.*

○=hide substance; ✕=chrome leather; ●=belting leather.

fairly rapid initial rise, then a leveling off, and finally at a relative humidity of 75 percent, again a rapid rise. The very rapid rise shown by sole leather above 75-percent relative humidity is apparently caused by the magnesium sulfate and glucose it contains. The sample of sole leather which was degreased and washed shows no such
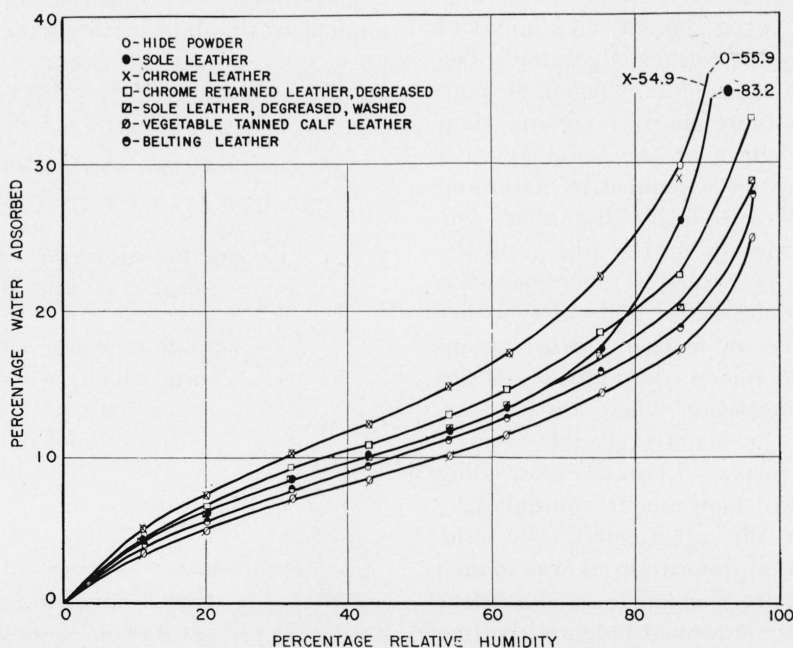

FIGURE 5.—*Increase in the amount of water vapor adsorbed with increase in relative humidity for various leathers and untanned hide at 100° F.*

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increase in the amount of moisture adsorbed. Untanned hide and chrome leather adsorb almost identical amounts of moisture at all relative humidities.

3. Desorption Isotherms

Adsorption and desorption curves for hide powder and belting leather are given in figure 6.
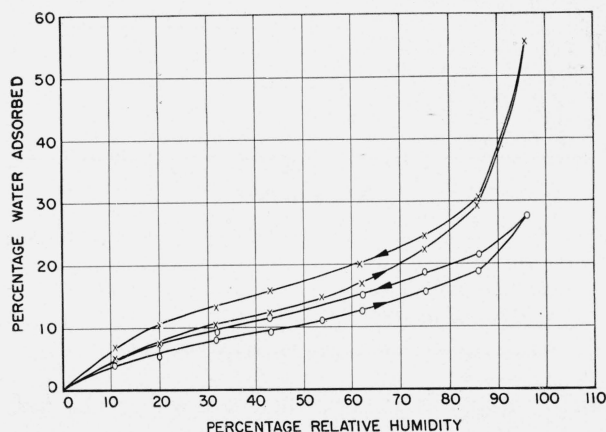

FIGURE 6.—*Adsorption and desorption of water vapor by hide powder and belting leather at various relative humidities at 100° F.*

×=hide powder; ○=belting leather.

The hysteresis for untanned hide is no greater than that for leather, even though the amount of moisture adsorbed by the former is greater. The steep portion of the curve for collagen at high relative humidities is more nearly reversible than the flat part of the curve at the lower relative humidities. This may be explained by assuming that at high values of relative humidity, the adsorption consists mainly in the filling of the larger pores, which is reversible, because condensation of water on water molecules rather than water molecules on leather surface is involved. At the lower relative humidities adsorption consists in condensation where leather surface is involved, and this is not reversible because the surface area has increased because of swelling under the conditions of high relative humidity.

All samples give off practically the same amounts of moisture on desorption as was gained on adsorption; the curves coincide at 0 relative humidity as shown for untanned hide and belting leather in figure 6. Sole leather (table 4) shows a loss of nearly 3 percent more weight on desorp-

tion than was gained on adsorption which might be due to loss of salts or glucose. The weight gained on adsorption and lost on desorption for all the samples is given in table 4.

TABLE 4.—*Amounts of moisture adsorbed by samples on adsorption and lost on desorption*

Sample	Adsorption moisture gained	Desorption moisture lost
	Percent	*Percent*
Collagen (hide powder)	55.9	56.2
Sole leather	83.2	86.2
Chrome leather	55.0	55.2
Chrome-retanned leather, degreased	33.1	32.5
Sole leather, degreased, washed	28.7	28.7
Vegetable-tanned calf skin	25.0	24.8
Belting leather	27.9	27.9

V. Calculation of Derived Quantities

1. Application of Brunauer, Emmett, and Teller Equations

Brunauer, Emmett, and Teller [10] have developed a theory to account for the adsorption of gases in multimolecular layers. This theory was developed by a generalization of Langmuir's treatment of the unimolecular layer and has recently been used to calculate surface areas by a number of authors [7, 11].

Two equations are developed [10] that may be applied to the data of this paper.

$$\frac{p}{V(p_0-p)}=\frac{c-1}{V_m c}\frac{p}{p_0} \qquad (1)$$

$$V=\frac{V_m cx}{1-x}\frac{1-(n+1)x^n+nx^{n+1}}{1+(c-1)x-cx^{n+1}}, \qquad (2)$$

$V=$ volume of water vapor adsorbed per gram at 0° and 760 mm

$V_m=$ volume of water vapor at 0° and 760 mm, which, when adsorbed, covers the surface of 1 g of the adsorbent with a unimolecular layer

$p=$ pressure

$x=$ relative pressure of the water vapor that is equal to p/p_0, where p_0 is the saturation pressure of the water vapor at the temperature of the adsorption

$n =$ maximum number of adsorbed layers

$c =$ a measure of the increase of the heat of adsorption E_1 of the first layer on the adsorbent over the heat of liquefaction (E_L), according to the equation $E_1 - E_L = 2.303 RT \log c$.

From equation 1, which holds only at values of p/p_0 less than 0.5, a straight line may be obtained by plotting experimental values of $p/V(p_0-p)$ as ordinate against p/p_0 as abscissa. The intercept will be $1/V_m c$ and the slope $(c-1)/V_m c$. From the experimental values of intercept and slope thus obtained, c and V_m may be calculated. Typical plots of this type are shown in figure 7, and the values of c and V_m for hide substance and all the leathers are given in table 5.

TABLE 5.—*Values of surface properties for hide powder and various leathers calculated from the Brunauer, Emmett, and Teller equations*

Sample	V_m[1]	c	Surface area	$E_1 - E_L$
	ml/g		*m²/g*	*cal/mole*
Collagen (hide powder)	110.0	8.3	298	1,307
Sole leather	86.7	10.2	235	1,434
Chrome leather	110.1	8.0	298	1,284
Chrome-retanned leather (degreased)	97.2	8.7	263	1,336
Sole leather (degreased and washed)	89.0	9.0	241	1,357
Vegetable-tanned calfskin	76.3	8.2	206	1,299
Vegetable-tanned belting leather	83.3	8.8	225	1,343

[1] V_m is the volume of water vapor at 0°C and 760 mm that is required to form a unimolecular layer on the surface of the sample.
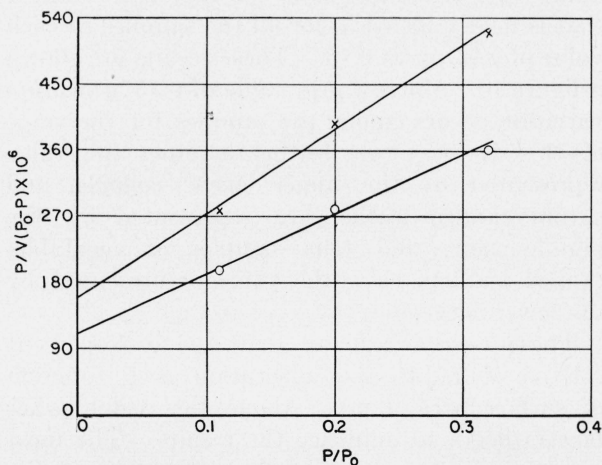
FIGURE 7.—*Linear plot of $p/v\,(p_0-p)$ against p/p_0 for the adsorption of water vapor on vegetable-tanned calfskin and hide powder at 100° F.*
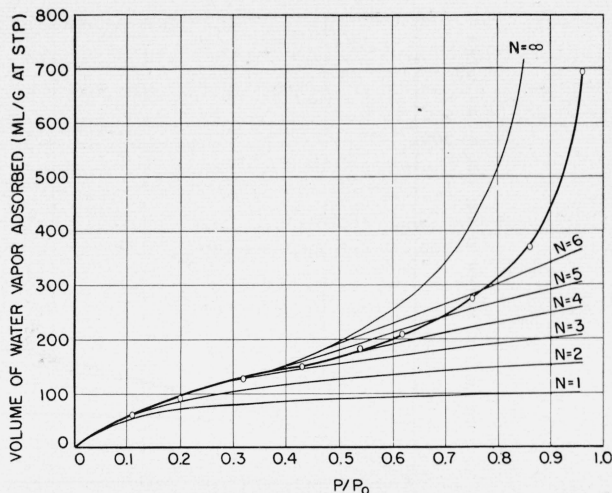
X = vegetable calfskin; O = hide powder.

FIGURE 8.—*Observed and calculated isotherms for the adsorption of water vapor on untanned hide at 100° F.*

The values for c and V_m may be substituted into equation 2, and V calculated for different values of n, where n equals the number of adsorbed layers. These values may then be compared with the determined results for the volume of water vapor adsorbed to ascertain the number of adsorbed layers which are equivalent to them. Such results are given in figure 8 for untanned hide, and in figure 9 for leather. The amounts of moisture adsorbed by leather at high relative humidities appear to be equivalent to five or six layers, whereas with untanned hide a large number of layers appears to be formed at these pressures, which probably indicates that the capillaries in the latter are much larger than in the former.

2. Calculation of Surface Areas

With the values for V_m (milliliters of water vapor adsorbed per gram of sample) it is possible to calculate the surface areas of the materials if the volume occupied by each molecule of water is known. Taking the value determined by Smith and Green [12], namely, 10 square angstrom units as the area occupied by the water molecule and 2.705×10^{19}, the number of molecules per milliliter at 0° and 760 mm, the surface area per gram of material is calculated as follows:

$$(V_m \times 2.705 \times 10^{19} \times 10 \times 10^{-20})m^2 = 2.705 V_m.$$

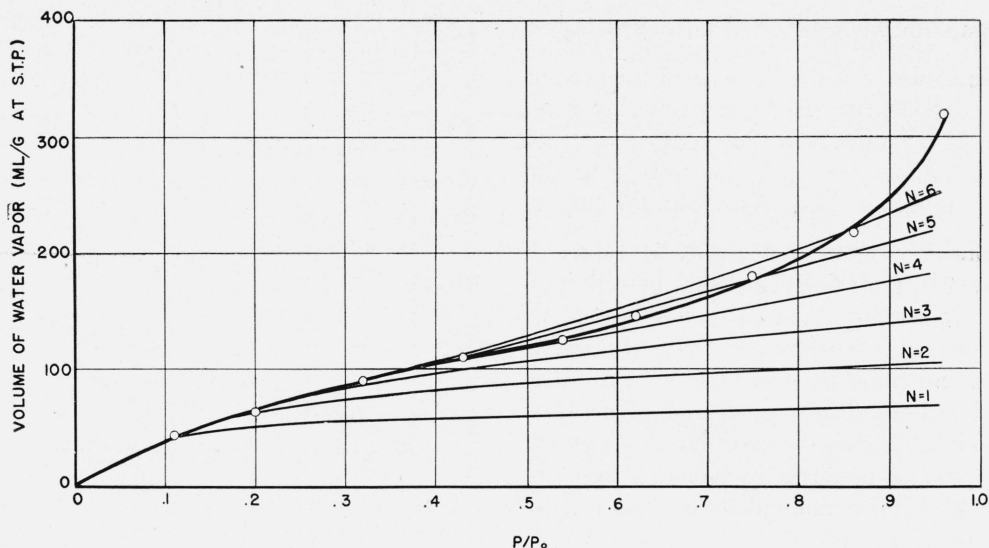The values for the surface area of all of the samples in square meters per gram are given in table 5.

FIGURE 9.—*Observed and calculated isotherms for the adsorption of water vapor on vegetable-tanned calfskin at 100° F.*

Collagen and chrome-tanned leathers have the largest surface areas. The leathers tanned with the vegetable tanning materials have smaller surface areas, as would be expected, since they are composed of less hide substance and the capillaries are reduced to smaller diameters, in some cases probably completely filled by tanning materials. The surface areas of hide and the leathers are lower than that found in general for charcoals. This might be due to the granular nature of ground charcoal. The value of 298 m^2/g of collagen is considered to be in fairly good agreement with the value of 337 m^2/g obtained by Bull [7].

3. Heats of Adsorption

By substituting the values for c given in table 4 in the equation $E_1 - E_L = 2.303R\ T \log\ c$, it is possible to calculate the difference between the heat of adsorption and the heat of liquefaction of water on collagen and leather. The values for $E_1 - E_L$ are given in table 5. The positive value for $E_1 - E_L$ in contrast to the negative value obtained when water is adsorbed on charcoal [13] gives evidence of the effect of polar groups on the attraction of water. The fact that the magnitude of the value obtained for collagen, 1,307 cal/mole, is comparable with that obtained for the leathers, 1,284 to 1,434 cal/mole, may indicate that there is little alteration of groups that attract water when tanning occurs. The small difference between the heats of adsorption and heats of

liquefaction, calculated by applying the B. E. T. theory, suggests strong Van der Waals adsorption. Chemisorption is generally accompanied by higher heats of adsorption (20,000 to 50,000 cal/mole) [13]. Further work is planned in which calculations of the differential heats of adsorption will be made.

VI. Discussion

1. Reduction to Unit Surface

If the volumes of water vapor adsorbed at each relative humidity are divided by the calculated values of V_m given in table 5, a factor is obtained that is nearly identical for all the samples at each value of p/p_0 up to 0.75. These results are shown in figure 10. Above a p/p_0 value of 0.75, a definite variation occurs among the samples for the value of this factor. Sole leather assumes the value represented by the upper curve, collagen and chrome-tanned leather are represented by the middle curve, and four samples of vegetable-tanned leathers have the values represented by the lower curve.

These results indicate that up to 75-percent relative humidity the adsorption is a function of surface area alone. Above this value other factors begin to influence the results. The most important of these is probably differences in the sizes of the pores. The rapid increase for sole leather is undoubtedly due to the deliquescent nature of the glucose and magnesium sulfate
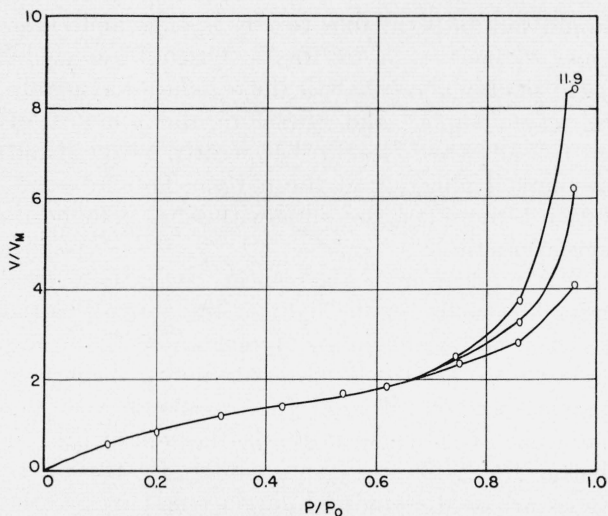
FIGURE 10.—*Adsorption isotherms of water vapor on various leathers and untanned hide at 100° F reduced to unit surface in a plot of V/V_m against p/p_0.*

used in the finishing process. The difference in the behavior of collagen and chrome-tanned leather, on the one hand, and the four vegetable tannages, on the other, can be explained by assuming that the former have larger pores on the average and consequently adsorb more moisture at high relative humidities.

2. Diameter of the Collagen Fiber

As the surface area and the density of collagen are known, it is possible to calculate the diameter of the fiber if it is assumed that it is a uniform cylinder and that the calculated adsorption area is identical with the total surface of collagen fibers. The areas of the ends of cylinder are negligible.

As a cylinder of radius r and length L has a surface $S=2\pi r L$ and a volume $V=\pi r^2 L$, the diameter $2r=4V/S$. If the density of collagen is taken as 1.4 g/cm³ (specific volume 0.7 cm³/g), V in the above equation is 0.7 cm³/g and S (table 5) is 298×10^4 cm²/g. Therefore,

$$2r=\frac{4\times0.7}{298\times10^4}=94\times10^{-8}\text{ cm.}$$

Bear [14] found from X-ray data a distance of about 11 A between the polypeptide chains in collagen, which is equivalent to about one-eighth the dimension calculated here. Bear also found a separation of polypeptide chains when he observed the X-ray pattern of wet collagen. Apparently water goes between the chains and spreads them apart. These results indicate that moisture does not go between all of the chains at the low relative humidities at which the B. E. T. calculations were made. It is probable that this occurs at the higher relative humidities.

3. Unimolecular Layer of Oil in Leather

From the surface area of leather it is interesting to make a calculation as to the amount of oil that would be required to cover all the surface with a unimolecular film. Leather oils are composed of a mixture of triolein and tristearin and a number of other constituents that are decomposition products of these two compounds.

From Langmuir's data [15] on the molecular sizes of these compounds, it is possible to make a calculation as to the amount that would be required for a unimolecular layer by using the data for washed and degreased sole leather. If the orientation of the chains is assumed to be perpendicular to surface, with tristearin, 53.7 percent would be required for a single layer; with triolein, 27.7 percent would be required. If it is assumed that the molecules lie flat on the leather surface, with tristearin, 17.7 percent would be necessary; with triolein 24.4 percent would be required. These results are obviously not in harmony with practical experience. The reason is that surface available to water is not available to oils, as the oil molecules are 6 to 10 times larger in diameter.

4. Relation of Adsorption to Capillarity

It has been shown that the adsorption of water vapor by leather and hide shows correlation with the multimolecular adsorption theory of Brunauer, Emmett, and Teller for relative humidities below 50 percent. The adsorption may also be considered especially at the higher relative humidities to be the result of capillary condensation. The surface of leather may be considered as consisting of numerous capillaries of different sizes. This concept arises from its fibrous structure. Between each fibril water may be adsorbed. The openings of various sizes between fibers give, in effect, the same characteristics as capillaries of various sizes. In the first stages of adsorption, the small capillaries will be filled, whereas the last stages will consist in filling the larger pores.

Calculations may be made in accordance with the Kelvin equation, which applies to the condensation of liquids in cylindrical capillaries.

$$\ln (p/p_0) = -2yv/rRT,$$

in which

Y=surface tension

v=molar volume of the liquid

r=radius of the capillary.

A plot showing the amounts of liquid water adsorbed per gram of sample at values of p/p_0 of 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9, in relation to the values for the radius calculated by substituting these values for p/p_0 in the Kelvin equation is shown in figure 11.
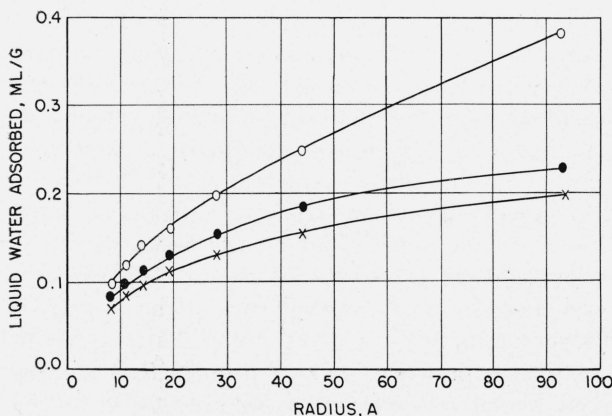

FIGURE 11.—*Adsorption of water vapor at 100° C on un-tanned hide and two samples of leather in a plot of the volume of liquid water, V_1, per gram of adsorbent against the corresponding radius of a cylindrical capillary as determined from the Kelvin equation.*

(The points for each sample correspond to p/p_0=0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 consecutively, reading from left to right.) O=hide powder; ●=sole leather degreased and washed; X=vegetable-tanned calfskin.

This figure gives a curve that represents a distribution of capillary sizes in collagen and leather. According to this interpretation, nearly half the water adsorbed by leather below a p/p_0 value of 0.9 could take place in capillaries less than 10 A in radius, whereas about one-third of the water adsorbed by collagen could be taken up in capillaries of this size. It can be seen from these results that much of the surface available to water would not be available to oils having molecular cross sections of 6 to 10 A. Orientation could occur in only about half of the capillaries available to water vapor, and therefore the amount of grease adsorbed would be greatly reduced on account of plugging of the pores. This interpretation is more nearly in line with what is found in actual practice.

An application with respect to particle size might be made, in the light of the above theory, to the practice of tanning, dyeing and fatliquoring of leather. The use of materials having the proper particle-size distribution to correspond with the pore-size distribution in the leather might lead to better results in these processes. If small particles are used along with larger ones, the greater proportion of the smaller particles eventually will be distributed into the small capillaries and the large particles will be in the large pores. Therefore, if an oil having the correct size distribution is used in fat-liquoring, a larger proportion of the surface should become lubricated. Likewise, in tanning, a more uniform distribution of the tanning material would take place.

References

[1] J. Am. Leather Chem. Assn. **17,** 492 (1922).
[2] J. Am. Leather Chem. Assn. **21,** 250 (1926).
[3] J. Am. Leather Chem. Assn. **21,** 351 (1926).
[4] BS Research **11,** 147 (1933) RP583.
[5] J. Am. Leather Chem. Assn. **40,** 378 (1945).
[6] J. Am. Leather Chem. Assn. **41,** 253 (1946).
[7] J. Am. Chem. Soc. **66,** 1499 (1944).
[8] Paper Ind. and Paper World **27,** 1799 (1946).
[9] Inst. Paper Chem., Instrumentation Report No. 40, (February 15, 1945).
[10] J. Am. Chem. Soc. **60,** 309 (1938).
[11] J. Research NBS **29,** 191 (1942) RP1496.
[12] Ind. Eng. Chem., Anal. Ed. **14,** 382 (1942).
[13] Stephen Brunauer, the adsorption of gases and vapors; Physical adsorption (Princeton University Press, Princeton, N. J., 1943).
[14] J. Am. Chem. Soc. **66,** 1297 (1944).
[15] J. Am. Chem. Soc. **39,** 1848 (1917).

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