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Factors Affecting the Water-Vapor Permeability of Leather[1]

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This investigation was undertaken at the request of the Office of the Quartermaster General, which is endeavoring to obtain fundamental information on the transfer of water vapor through leather, which may be applied in the development of improved Army shoes. The method used for measuring the water vapor permeability is based on the present approved procedure of the American Leather Chemists' Association, but considerable improvement was made in the technique of assembling the permeability cell and in the procedure applied in making the determinations.

The water vapor permeability of leather depends upon a number of factors including thickness of sample, grease content, and the relative humidity and temperature of the atmosphere. It is greatly reduced by the presence of the natural glyceride greases. The grain layer of the leather appears to be the first stratum to become saturated with grease and consequently is a highly influential stratum with respect to water vapor permeability. The finish on the grain layer also has an influence on water vapor transmission. There is no dependent correlation between water vapor permeability and air permeability.

Studies on leathers impregnated with different types of materials, including rubber and acrylate resins, show that the water vapor permeability decreases in the following order: sulfonated oils, acrylate resins, rubber, and stuffing greases. The comparatively high water vapor permeability of the leathers treated with the sulfonated oils and acrylate resins is attributed to the influence of the polar groups in these impregnants.

Studies indicated that flexing of the specimen had no influence on the water vapor permeability of degreased leathers; however, for leathers that contained grease, there was an increase in water vapor permeability on flexing.

The results of the experiments indicate that, in addition to gaseous diffusion, water is transmitted through leather by conduction over the surface or by some form of activated diffusion. Evidence for the conduction mechanism is given by the behavior at low relative humidities, existence of an energy of activation, influence of temperature, comparison of air permeability and water vapor permeability, experiments with fabrics and glass disks, variations of diffusion constants, and the results of studies of the effect of gross air pressure with the dynamic equipment.

I. Introduction

The ability to transmit water vapor is one of the important properties of leather that makes it so desirable for use in the construction of shoes. A knowledge of the factors involved in this property is, therefore, important in the proper selection and manufacture of materials that will give improved service and yet maintain a sufficiently high level of water vapor permeability to assure comfort to the wearer.

The water vapor permeability of leather is inherently high. However, the use of fats and greases to improve water resistance of shoe leather may lower water vapor transmission to the point below the critical level, which has not been determined, at which the foot may be comfortable

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under a particular set of temperature and humidity conditions which the wearer of the shoes may encounter. It would be desirable to maintain water vapor transmission at a high level while simultaneously liquid water transmission is maintained at a low level.

The purpose of the present investigation was to study the mechanism of water vapor transmission and to attempt to develop and standardize a more suitable method for measuring it. In this connection the work of Bradley, McKay, and Worswick [1],[2] Edwards [2], Mitton [3], Hobbs [4], and Maeser [5] on leather has given considerable information which has been applied in this study. The work of the Institute of Paper Chemistry [6] and Carson and Worthington [7] on paper, a study of the permeability to moisture of synthetic resins for aircraft by Kline [8], the work of Doty, Aiken, and Mark [9, 10] on organic films, and the work by Harris and Fourt [11] on fabrics have been helpful in this investigation.

II. Test Method

The basic principle in all water vapor permeability tests developed for leather is the use of the specimen as a diaphragm with a region of high relative humidity on one side and one of low relative humidity on the other. The gain in weight per unit area on the low relative humidity side in unit time is expressed as the water vapor permeability. One of the earliest and simplest tests was developed by Wilson and Lines [13]. They put sulfuric acid in a bottle, over which a leather specimen was placed by fastening it in the cap, which was then screwed down on the top. The bottle and contents were weighed from time to time to determine the gain in weight.

Work by Mitton [3] and by the Institute of Paper Chemistry [6] has shown that a static air space between the specimen and the desiccant influences the result since the diffusion of water vapor is retarded by air. Thus, for highly permeable leathers the result may be the permeability of the underlying air space rather than that for the specimen. The atmospheres of high and low relative humidities should, therefore, make immediate contact with the opposite faces of the specimen.

This condition is readily achieved on the outer face by rapid ventilation. On the low relative humidity side, circulation involves complicated apparatus, but has been accomplished by the rapid passing of dry air. The necessary conditions can be more conveniently met in a cell (dish) by placing the desiccant in contact with the leather. The former has been used successfully by Edwards [27] and by Maeser [5], whereas the latter has been used successfully by Carson [7] and by the Institute of Paper Chemistry [6] and is applied in the present ALCA test [12].

1. Description of Method Used

The method used in this work is a modification of the ALCA test. This procedure was adopted because of its speed, convenience, ease of application, and ease of duplication of conditions.

The water vapor permeability cell devised is shown in figure 1, A. It consists of a circular aluminum cup with a flange. The total diameter is about 4 in. The flange is bent in such a way that a raised rim is formed at the edge of the cup upon which the leather fits tightly. In preparing the cells, the cup is filled with the desiccant, and the leather specimen having a larger diameter than the cup is placed over the rim. A circular copper template (fig. 1, D) having one surface

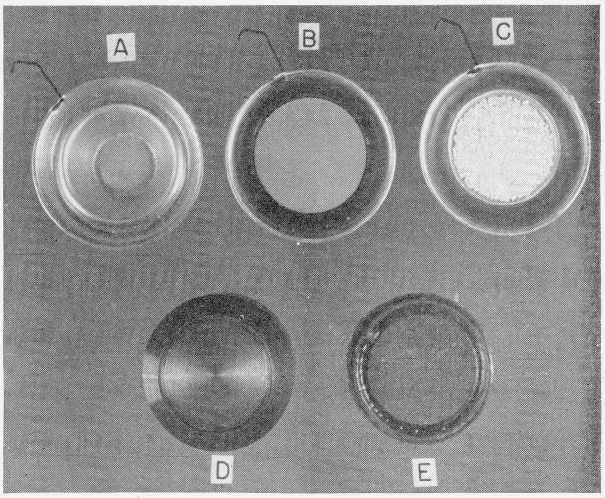

FIGURE 1. *A, Empty aluminum cell used in the water vapor permeability studies; B, assembled cell and leather specimen ready for measurements; C, assembled cell with transparent cellulose film showing desiccant; D, template used in assembling the cell; E, side of leather specimen next to desiccant after determination of water vapor permeability was made.*

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

machined to have the same diameter as the cup is then fitted as nearly as possible directly over the cup. Molten microcrystalline wax is poured around the groove formed by the template and the flange. This seals the edge of the leather and fastens it to the cell. After the wax has hardened, the copper template is removed, leaving an area of 25 cm^2 of the leather exposed. Cooling the template in a refrigerator prior to use assists in preventing adhesion of the wax.

In figure 1, C the position of the desiccant with respect to the specimen is shown, and figure 1, E shows the side next to the desiccant of a leather specimen on which tests have been completed.

The completed cell is hung in a cabinet of the type described by Carson and Worthington [7] at the desired temperature and relative humidity. The cells are weighed at various intervals of time in place without removal from the cabinet to determine the rate at which the leather transmits moisture.

Unless otherwise stated, the temperature at which the measurements are made is 100° F. This temperature is used because it closely approximates body temperature. Less time is also required to reach a steady state at this temperature than at a lower temperature. Conditions of relative humidity in the range 40 to 65 percent were found satisfactory. The time required for a measurement by this method is 4 to 5 hrs compared to 4 or 5 days required in the present ALCA test. The cells may be prepared in about 5 percent of the time required by the ALCA test. The period over which the rate of gain of the cell was most nearly constant was taken as the value for the water vapor permeability. This was usually over the time interval of 2 to 4 hrs. The rates of gain during this period were averaged and expressed as gain per 100 min.

The success of the desiccant method depends upon the capacity for water vapor of the particular salt used. The salt used as the desiccant should maintain a high capacity for water over a great enough time period for completion of a test. This time period must permit the specimen to come to equilibrium and then continue the adsorption of water at a constant rate. The rate of adsorption per unit time may be taken at any point after a constant rate of gain has been reached. In figure 2 the behavior of anhydrous calcium chloride, anhydrous magnesium perchlorate, and Drierite (anhydrous calcium sulfate) when used in the cell is shown. The results were obtained with chrome-tanned calfskin at 44-percent relative humidity on the high vapor pressure side. They show that calcium chloride is highly superior to Drierite and better than magnesium perchlorate with respect to the maintenance of a high capacity for water vapor over an extended period of time. The curve for calcium chloride is a straight line, whereas the other two curves tend to level off.

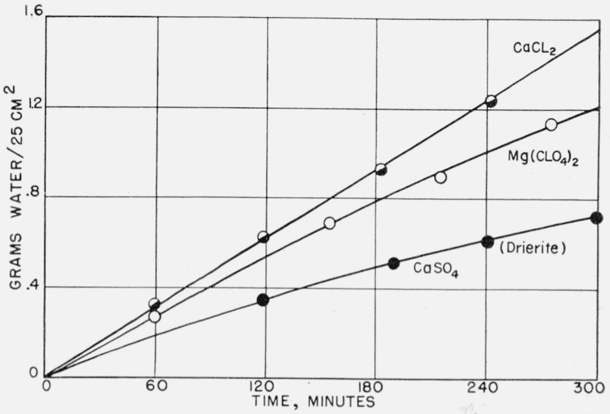

FIGURE 2. *Rate of moisture pickup by various desiccants used in the cells.*

All of the following determinations, unless otherwise stated, were made at 100° F with a relative humidity of 53 percent on the high-pressure side and calcium chloride in contact with the specimen on the low-pressure side.

2. Some Typical Results With the Method

In table 1[3] are shown water vapor permeability

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[3] In this study water vapor permeability is expressed in grams passing through 25 cm^2 of the specimen in 100 min. This unit was chosen for convenience in calculation. The total area exposed was 25 cm^2, and 100 is a convenient figure to handle arithmetically. The results were not expressed in the unit, grams/m^2×24 hours, which is used by the ALCA, since they could not be directly compared because of the difference in conditions under which the tests were made. The ALCA test was designed to be run at 70° F and 65-percent relative humidity, whereas the test applied in this study was performed at 100° F and 53-percent relative humidity. From our present knowledge of water vapor permeability, the results have only relative significance, and comparisons can be made only under uniform sets of conditions. As a result of this work, the need for the clarification of definitions and a standard unit for the expression of water vapor permeability was emphasized with the result that a committee was appointed at this Bureau to consider these matters. Recently this committee has recommended that water vapor permeability be expressed in cgs units; namely, grams/cm^2×sec. This recommendation will be offered for consideration by the Federal Specification Committee, the ASTM, and other scientific associations.

In order to show the relation between these units, the results in table 1 are expressed in three different ways: (1) By the unit used for all the data in this study, grams/25 cm^2×100 min, (2) by the cgs unit which may be standard in the near future for all water vapor permeability measurements, grams/cm^2×sec, and (3) by the unit used in the ALCA test, grams/m^2×24 hr. The data expressed in grams/25 cm^2×100 min may be converted to grams/cm^2×sec by dividing by 15×10^4, and it may be converted to grams/m^{2}24 hr by multiplying by 5760.

TABLE 1. *Water vapor permeabilities of various leathers at 100° F with 53-percent relative humidity on the high vapor pressure side and 0 relative humidity on the low vapor pressure side*

Type of leather	Thickness	Grease	Water vapor permeability		
	Mils	*Percent*	*g/cm²×sec*	*g/25 cm²×100 min*	*g/m²×24 hr*
Vegetable-tanned sealskin	107	1.0	3.00×10^{-6}	0.45	2592
Chrome-tanned calfskin	36	5.1	3.33	.50	2880
Vegetable-tanned calfskin	37	13.8	2.47	.37	2131
Vegetable-tanned sheepskin	43	6.7	5.07	.76	4378
Chrome-retanned upper	78	10.2	2.07	.31	1786
Do	81	10.2	1.73	.26	1498
Do	85	22.8	0.14	.02	115
Vegetable-tanned strap	105	4.7	2.13	.32	1152
Vegetable-tanned sole	200	5.9	1.93	.29	1670
Do	271	3.1	0.47	.07	403
Do	179	6.5	.08	.12	691
Chrome-retanned sole	215	1.2	1.93	.29	1670
Chrome hydraulic packing	165	7.1	1.07	.16	922
Alum-formaldehyde	42	6.9	3.80	.57	3283
Indian-tanned lace	129	25.4	0.07	.01	58
Rawhide lace	128	43.8	.02	.003	17

values obtained with the above-described method for a number of different types of leather. The thickness and grease contents of the leathers are also given. It may be observed that the water vapor transmission is dependent upon both grease content and thickness.

The correlation between the ALCA method [12] and the new method used in making the tests in this invesigation is shown in figure 3. In the ALCA method, a cell is prepared by cementing the leather specimen on the top of a tannin dish. This is a circular dish, about 3 in. in diameter and 1.5 in. deep. Drierite is placed in the dish prior to the sealing of the specimen. The prepared cell is placed on a rack in a room at a constant temperature and relative humidity. The cell is turned specimen side down, so that the desiccant is in contact with the specimen. Weighings are made from time to time to determine the rate at which water vapor passes through the leather. The results obtained with this method shown in figure 3 were obtained at 50-percent relative humidity and 73° F. The correlation is good except that it is curvilinear. The nature of the correlation is undoubtedly caused by the fact that Drierite is used in the ALCA test. Its capacity for holding water is low, and therefore the rate of pickup will decrease rapidly with time. There will then be a tendency for the curve showing increasing water vapor permeabilities to become asymptotic to some maximum value that would approach the saturation point of the Drierite used in the cup.

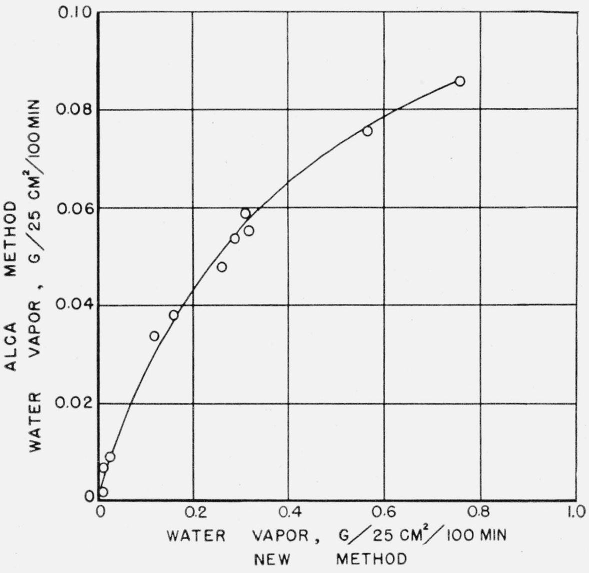

FIGURE 3. *Correlation of ALCA method with the new method for determining water vapor permeability.*

III. Mechanisms of Transmission of Water Vapor

The mechanism of water vapor transmission through a fibrous organic material or through an organic film has generally been accepted as consisting of gaseous diffusion through pores or by conduction. By conduction is meant migration by means of solution, activated diffusion, or capillary action from a region of high concentration to a region of low concentration over a water attracting surface. In transmission by capillary action, it is conceived that water condenses in small pores on the high relative humidity side and the migration proceeds automatically toward the region of low concentration on the low relative humidity side. Mitton [3] states that the diffusion of water vapor occurs mainly in the free spaces within the leather. On the other hand, Wilson [13] and Edwards [2] believed that the water vapor was transmitted by capillary action.

According to the most generally accepted concept of the fibrous structure of leather, long parallel chains of polypeptides form submicroscopic fibrils. These fibrils, in turn, form larger fibrils. The fibrils form fibers that are interwoven to give the physical structure that is visible on close examination of the hide or leather. Such a network produces a large number of pores or capillaries that vary in size. These might be divided into four categories according to Schulze (See Paine) [17]: (1) Macroscopic and microscopic cracks and spaces, (2) submicroscopic capillaries and canals, (3) intermolecular spaces, (4) intramolecular spaces. It would be expected that the macroscopic and microscopic spaces would be associated with gaseous diffusion. Submicroscopic capillaries would be involved in capillary flow and activated diffusion, categories (3) and (4) would be associated only with activated diffusion. According to Doty, Aiken, and Mark [9], two types of activated diffusion are involved in water vapor transmission—one in which the transmission takes place through preformed pores and one where the transmission takes place through the formation of temporary pockets caused by the kinetic action of the molecules. The former type of activated diffusion would occur through both macroscopic and microscopic pores, whereas the latter type would occur only through inter- and intramolecular spaces.

Results from X-ray studies [18] indicate that when water enters the region of the submicroscopic fibrils composed of polypeptide chains, swelling occurs and the distance between chains is increased. It appears, therefore, that a certain energy change must be involved when water becomes associated with these groups, and therefore transmission through this fine structure could occur only by an activated diffusion. The activated diffusion through the macroscopic and microscopic capillaries proceeds by the adsorption of the water molecules on the water attracting group on the surface. When the energy of adsorption has been dissipated, the water molecule will vibrate and acquire the kinetic energy for desorption. The molecule will then proceed further over the surface of the fiber to another active spot. This action will continue until the water molecule passes through the leather. The migration will proceed from the region of high concentration to that of a low concentration. The activated diffusion through intermolecular spaces will proceed by the same mechanism, except that the molecules will have to depend upon temporary openings consisting of pockets and crevices formed at random, and the rate of transmission will be much lower.

It is conceivable that capillary action occurs in the microscopic and submicroscopic pores by condensation on the high relative humidity side and then migration and evaporation on the low relative humidity side. Migration by solution is not considered to be important in leather. However, the behavior of the water in the region of the polypeptide groups might be interpreted as a solution process. The ways in which water vapor transmission depends upon important variables provide clues to mechanisms involved in the process. The succeeding sections of this paper give results of such studies.

IV. Effect of Important Variables on Water Vapor Permeability

1. Fundamental Equation for Diffusion

Many attempts have been made to represent water vapor transmission data by means of the linear diffusion equation, one form of which is given:

$$m = KA\,\frac{(C_2-C_1)}{h}\,t,$$

where m=mass of water in grams passing in t seconds;

A=the area of the diaphragm in square centimeters;

C_2-C_1=difference in concentration at the two surfaces in grams per cubic centimeters;

h=thickness of the diaphragm in centimeters;

K=diffusion constant

This equation has the same form as the equation for the heat conductivity, where K depends upon the nature of the substance.

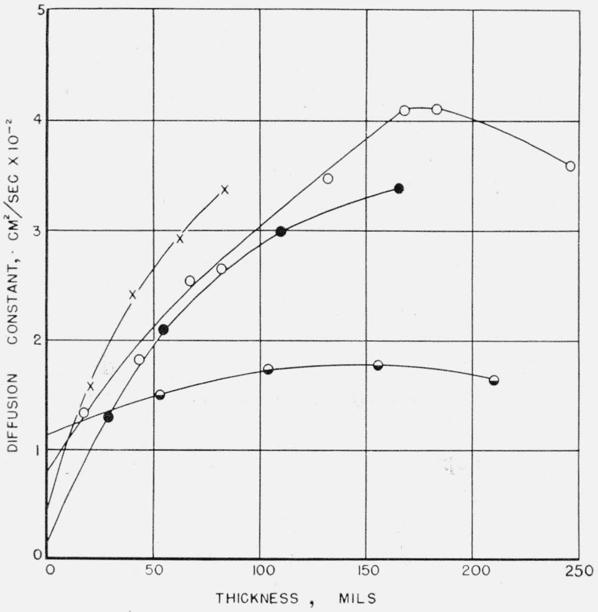

FIGURE 4. *Change of the diffusion constant of glass cloth, leather, cotton duck, and nylon with thickness.*
×, Glass cloth; ○, leather; ●, cotton duck; ◑, nylon.

In figure 4 the change in *K* with the thickness of the material is shown. The data show that *K* is not constant except possibly for nylon; therefore some mechanism other than or in addition to gaseous diffusion must be involved. With leather, cotton duck, and glass cloth, the values for *K* increase as the thickness increases, which indicates that the material has a specific influence on the diffusion. *K* values for nylon do not increase appreciably with thickness, which indicates that linear diffusion fairly well represents the behavior of this material and the material itself has little influence on the transmission of water vapor. The fact that the diffusion constant increases with increasing thicknesses for all except nylon indicates that there is an induction period involved in the process. This is probably in the initial contact of the water vapor with the material, some time apparently being required for the water molecules to attach themselves. After this has occurred, the diffusion proceeds more or less rapidly, depending on the type of material. The highly polar glass, cotton, and leather appear to be more influential on the conduction of the water vapor than the less polar nylon.

The variation of the diffusion constant with the relative humidity is shown in figure 5. The diffusion "constant" increases as the relative humidity increases and appears to decrease to 0 at a relative humidity of about 10. At low relative humidities the constant will necessarily be low, since the permeability is low for the reason given when figure 11 is discussed. However, at the higher relative humidities when the attracting groups in the protein become covered with water molecules, the conductivity of the material will be increased. It appears that water may be conducted most rapidly over other water molecules.

The results obtained for the diffusion coefficient of leather given in figure 4 are of the same order of magnitude as those obtained by Mitton [3]. Mitton's values for the diffusion coefficient also appear to be greater for the thicker samples of leather.

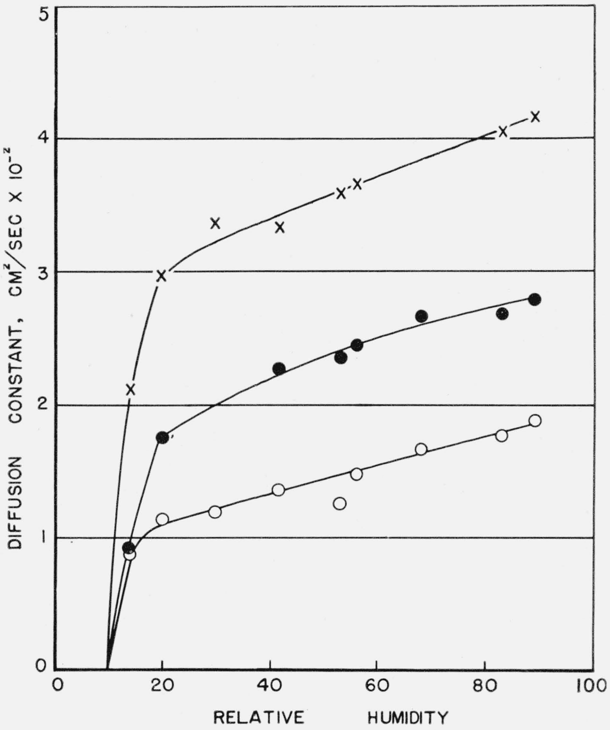

FIGURE 5. *Change in the diffusion constant of vegetable-tanned sealskin* ×, *vegetable-tanned sheepskin* ●, *and chrome-tanned calfskin* ○ *with relative humidity.*

2. Air Permeability Versus Water Vapor Permeability

The relation between air permeability and water vapor permeability for a number of leather splits is shown in table 2. The first four values given are for chrome-retanned sole leather. The others are for vegetable-tanned sole leather. Air permeability was determined by the method described by Carson and Worthington [15]. The thickness and grease contents of the splits are given along with the air and water vapor permeabilities. It may be noted that as the air permeability decreases, the water vapor permeability also decreases; however, the range of the air permeability is about 200 to 1; whereas the range of the water vapor permeability is little more than 2 to 1. For the same types of leathers those having high water vapor permeability usually have high air permeability also; however, the relation between these two properties apparently involves other factors that are independent of each other.

TABLE 2. *Relation between air permeability and water vapor permeability of leather splits*

Thickness	Grease	Air permeability	Water vapor permeability at 53% relative humidity on wet side
Mils	*Percent*	*$cm^3/sec/m^2$*	*$g/25\ cm^2 \times 100$ min.*
24	1.43	9120	0.98
17	2.00	7540	1.13
33	0.74	6795	1.00
51	.54	5785	0.80
15	11.87	489	.81
25	11.25	285	.59
36	6.18	185	.66
35	5.71	162	.66
40	8.96	103	.54
33	8.24	93	.55
44	9.12	51	.48

Often new ideas and important information may be obtained by studying the properties of materials somewhat different in character from those with which the tests are directly concerned. For this reason some tests were made with various types of cloth fabrics and Pyrex-glass disks.

Figure 6 and table 3 compare the air permeability and water-vapor permeability of nylon and glass fabrics. Water-vapor permeability was determined on disks of the material about 2¾ in. in diameter by the same method as was used for the leather specimens. Air permeability was determined by the method described by Schiefer and Boyland [16]. Thickness of the fabrics was varied by increasing the number of plies. It may be observed that the ratio of the water-vapor permeability to air permeability for glass fabric is higher than that for nylon fabric.

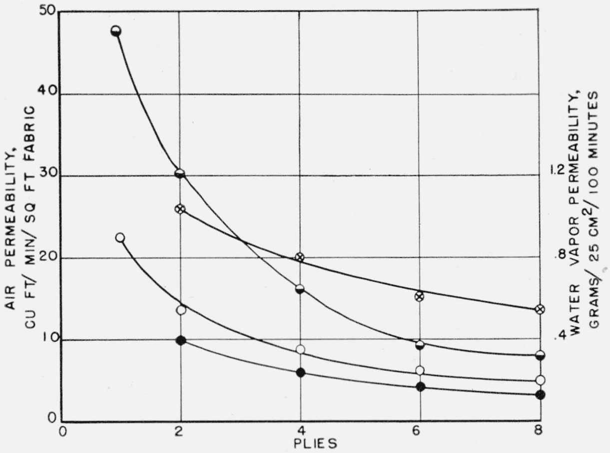

FIGURE 6. *Comparison of the air permeability and the water vapor permeability of glass and nylon fabrics, as a function of number of plies.*

Air permeability: ○, nylon; ◑, glass. Water vapor permeability: ●, nylon; ⊗, glass.

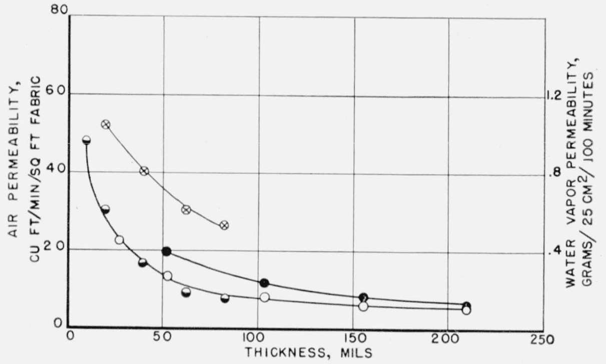

FIGURE 7. *Comparison of the air permeability and the water vapor permeability of glass and nylon fabrics as a function of thickness.*

Air permeability: ○, nylon; ◑, glass. Water vapor permeability: ●, nylon; ⊗, glass.

TABLE 3. *Comparison of air and water vapor permeabilities of glass and nylon fabrics*

(Air permeability determined at pressure of 0.5 in water)

	Plies	Thickness	Air permeability	Water-vapor permeability
		Mils	*$ft^3 min \times ft^2$ fabric*	*$g/25\ cm^2 \times 100$ min*
Nylon	1	27	22.3	----
	2	53	13.4	0.41
	4	104	8.4	.35
	6	156	6.2	.18
	8	210	6.0	.13
Glass	1	10	48.2	----
	2	20	30.4	1.05
	4	40	16.8	.81
	6	62	9.4	.64
	8	83	8.0	.55

In figure 7 the data obtained with the cloth fabrics are plotted against thickness. The air permeabilities of both types of cloth happen to be the same for given thickness, whereas the water-vapor permeabilities are different. This indicates that although the air permeabilities of the two types of cloth correlate with each other, the water-vapor permeabilities do not correlate and are obviously dependent upon the properties of the materials. The glass fabric shows much higher water-vapor permeability per unit thickness than the nylon.

Experiments were made with fritted Pyrex-glass disks about 2¾ in. in diameter and of the type used in filtering equipment. These disks were obtained from the Corning Glass Co. The approximate pore size for each disk and values for the air permeability and water penetration were furnished by the manufacturer. These values are given in table 4, along with the water-vapor permeabilities that were determined by the same method as was used for the leathers. It may be noted that both water penetration and air permeability increase rapidly with increase in pore size, whereas water-vapor permeability decreases for the two greatest pore sizes. Surface area would also decrease as the pore size increases, and it appears from these results that the water-vapor permeability is a function of the surface area.

Table 4. *Comparison of the water vapor permeability, liquid water permeability, and air permeability of Pyrex glass fritted disks*

Designated porosity	Average pore diameter	Liquid water penetration pressure difference 100 mm Hg	Air flow pressure difference 50 mm Hg	Water vapor permeability at 53% relative humidity on wet side	
				Trial No.	
				1	2
	Microns	*cm³/min*	*cm³/min*	*g/25 cm²×100 min*	*g/25 cm²×100 min*
Fine	5	9	190	0. 251	0. 249
Medium	14	70	1, 200	. 276	. 283
Coarse	40	500	6, 000	. 261	. 275
Extra coarse	160	3, 500	20, 000+	. 172	. 173

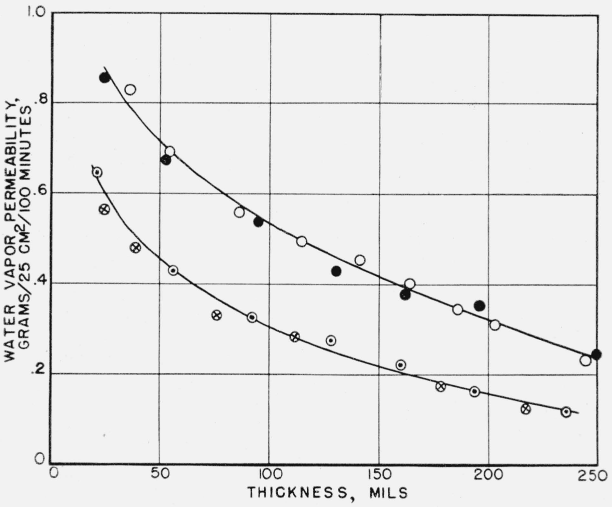

Figure 8. *Effect of thickness on the water vapor permeability of leather.*

Leather: ○, Vegetable tanned crust; ●, degreased crust; ⊗, vegetable tanned sole; ⊙, vegetable tanned sole degreased.

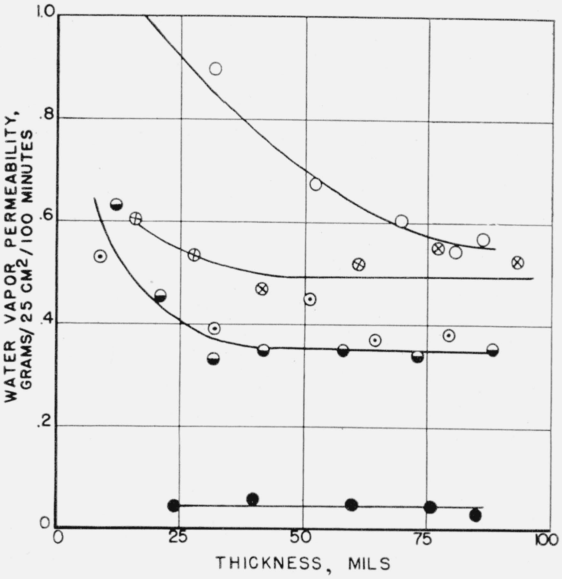

Figure 9. *Effect of grease content and thickness on the water vapor permeability of upper leather.*

Increments of flesh side split off. Upper leather, 22.8% grease: ●, as received; ○, degreased. Upper leather 10.2% grease: ◑⊙, as received; ⊗, degreased.

3. Effect of Grease Content and Thickness on Water Vapor Permeability

The results of table 1 indicate that thickness and grease content influence water vapor permeability. A more detailed study of these factors was made. Figure 8 and table 5 show the effect of thickness on the water vapor permeability of vegetable-tanned crust and vegetable-tanned sole leathers. The curves for the two leathers are nearly parallel. Degreasing had little effect, since the grease content in these leathers was less than 5 percent. The water vapor permeability increases with decrease in thickness and is greater for crust leather than for sole leather. The differences in the water vapor permeabilities of these two types of leather can probably be explained by the differences in their densities.

In figure 9 and table 6 is shown the influence of grease and of thickness on the water vapor permeability of upper leather. The sample containing 22.8 percent of grease shows very low water vapor permeability, which does not increase with decrease in thickness. The thickness was varied by splitting successive layers off of the flesh side. Thus the results show definitely that the grain layer of this leather governs its transmission properties. After degreasing, this leather shows the same variation of water vapor permeability with thickness as was shown in figure 8. The leather containing 10.2 percent of grease was a fat-liquored type.[4] Degreasing had little effect on its permeability. The grain layer in this leather appears to influence the water vapor permeability

TABLE 5. *Effect of thickness on water vapor permeability*

(Thickness varied by removal of increments of flesh layer)

Chrome-retanned sole (as received)		Chrome-retanned sole (degreased)	
Thickness	Water vapor permeability	Thickness	Water vapor permeability
Mils	*g/25 cm² ×100 min*	*Mils*	*g/25 cm²×100 min.*
246	0.21	256	0.22
183	.32	203	.31
168	.35	161	.37
132	.38	95	.46
82	.46	77	.53
67	.55	34	.75
43	.61	23	.83
Vegetable-tanned sole (as received)		**Vegetable-tanned sole (degreased)**	
223	0.12	236	0.12
178	.18	194	.17
143	.22	160	.23
111	.29	128	.28
76	.33	92	.33
39	.48	56	.43
25	.57	22	.65
Vegetable-tanned crust (as received)		**Vegetable-tanned crust (degreased)**	
244	0.23	249	0.24
186	.34	196	.36
164	.40	162	.38
141	.46	130	.43
114	.50	95	.54
86	.56	53	.68
54	.70	24	.85
36	.83		

TABLE 6. *Effect of thickness and grease content on water vapor permeability of upper leather*

(Thickness varied by removal of increments of flesh layer)

Upper leather (1) (22.8% grease)		Upper leather (1) (degreased)	
Thickness	Water vapor permeability	Thickness	Water vapor permeability
Mils	*g/25 cm²×100 min*	*Mils*	*g/25 cm²×100 min*
85	0.03	86	0.57
76	.05	81	.55
60	.05	69	.61
40	.05	52	.68
24	.05	32	.90
		16	1.01

Upper leather (2) (10.2% grease)				Upper leather (2) (degreased)	
Sample No.		Sample No.			
1	2	1	2		
79	88	0.38	0.35	93	0.53
64	73	.38	.35	77	.55
51	58	.45	.35	61	.52
32	42	.39	.35	42	.47
9	33	.53	.35	28	.54
	21		.45	16	.61
	12		.64		

Increments of grain layer removed Upper leather (1) (22.8% grease)	
86	0.09
74	.34
64	.47
50	.54
32	.65
26	.72
[a] 17	[a] .07

[a] Top grain layer.

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[4] The addition of grease by tumbling the leather in an oil-in-water emulsion is known as fat-liquoring.

of both degreased and greased samples. This is apparently caused by the fact that the finish was sufficiently stable to resist the action of the chloroform, which was used in removing the grease. Mitton [3] and Wilson and Lines [13] have shown that the finish on the grain influences the water vapor permeability.

The variation of the water vapor permeability with thickness when increments of the grain side are removed is shown in figure 10 and table 6. The curve shows a very rapid increase in water vapor permeability with decrease in thickness. This is further proof that the grain layer of heavily greased upper leather exerts the predominating influence on the water vapor transmission.

4. Effect of Relative Humidity on Water Vapor Permeability

The dependence of water vapor permeability on relative humidity at constant temperature is shown in figure 11 and table 7. Approximately straight-line relationships are shown for each type of leather. These lines, with the exception of that for the heavily greased lace leathers, on extrapolation show zero transmission at about 10-percent relative humidity. This behavior is surprising, and no definite explanation can be offered at this time. It has been shown that the heat of adsorption of water by leather is highest in atmospheres of less than 10-percent relative humidity, or where low concentrations of water are adsorbed. It is probable then that under these conditions the water is held within the leather so strongly that a steady state of transmission is not established under the conditions of the experiment. When the active sites within the leather are satisfied, which happens when higher concentrations of water are adsorbed, then the water vapor will be transmitted rapidly. These results again indicate that the leather surface has some influence on the water vapor that passes through, and therefore the mechanism must involve other factors than that of gaseous diffusion.

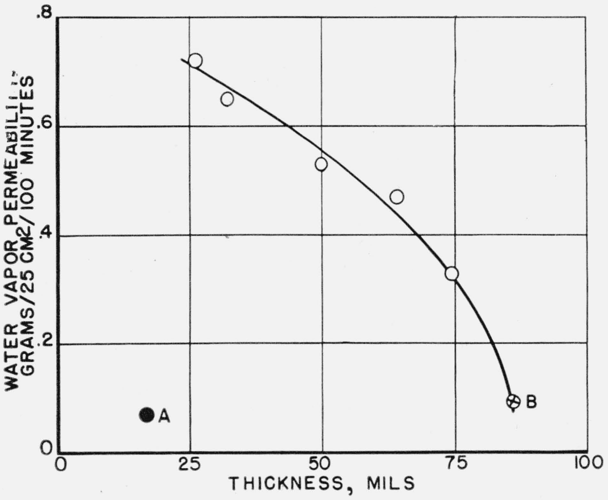

FIGURE 10. *Effect of thickness on water vapor permeability when increments of the grain side are split off.*

A, Grain split; B, full thickness; rest, flesh splits; ○, grain split off; ●, flesh split off; grain removed first.

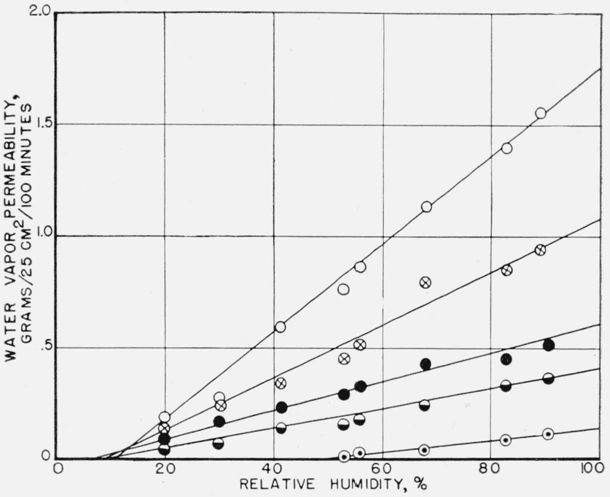

FIGURE 11. *Influence of relative humidity on water vapor permeability.*

Leather: ○, sheepskin; ⊗, sealskin; ●, sole; ◑, chrome; ⊙, Indian tanned lace.

TABLE 7.—*Effect of relative humidity on water vapor permeability*

Water vapor permeability in g/25 cm²×100 min

Leather	Relative humidity (percent)							
	20	30	42	53	56	68	83	89
Vegetable-tanned sheepskin	0.19	0.31	0.60	0.79	0.87	1.14	1.40	1.56
Vegetable-tanned sealskin	.15	.26	.35	.45	.52	.80	.85	.94
Vegetable-tanned sole	.10	.18	.24	.29	.33	.44	.44	.51
hrome	.05	.07	.14	.16	.19	.25	.34	.36
Indian-tanned lace	0	0	0	.01	.03	.04	.10	.11

5. Effect of Apparent Density on Water Vapor Permeability

Since the apparent density of leather varies inversely as the pore volume, it is expected that there might be a correlation between this factor and the water vapor permeability. In the study of the effect of apparent density, the same group of samples as shown in table 1 was used. All the leathers were degreased prior to the tests. However, they did not have uniform thicknesses, and the results are therefore modified somewhat by this factor, which was shown previously to be significant. In a study of the results, it was found that the best correlation was obtained if the water vapor permeability was plotted against the product of the thickness in centimeters and the apparent density. This is shown in figure 12, and the data are tabulated in table 8. These results suggest that the water vapor permeability is inversely proportional to the mass or density of fibers between the atmosphere of high and low relative humidity. However, a low apparent density not only is indicative of high pore volume, but also of high surface area. When the fibers are packed closely together, the leather loses not only pore volume but also surface area.

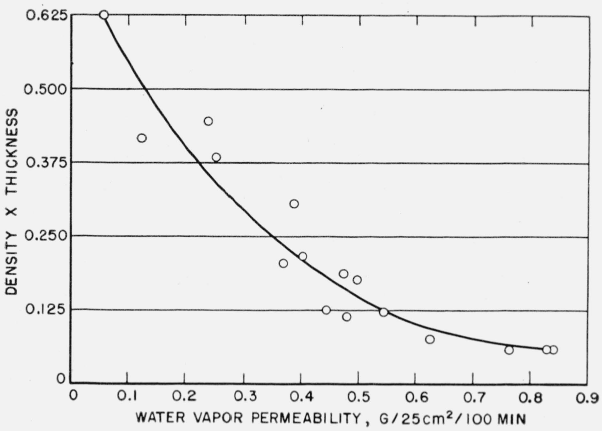

FIGURE 12. *Correlation of the water vapor permeability of leather with the product of the density and the thickness in centimeters.*

TABLE 8. *Effect of apparent density on the water vapor permeability*

Leather	Thickness	Apparent density	Density×thickness in cm	Water vapor permeability
	Mils			*g/25 cm²×100 min*
Vegetable-tanned sealskin	108	0.660	0.180	0.50
Chrome-tanned calfskin	42	.560	.061	.84
Chrome-retanned	80	.614	.124	.54
Chrome hydraulic packing	175	.704	.312	.39
Vegetable-tanned sole	199	.772	.391	.26
Indian-tanned lace	131	.666	.221	.40
Chrome-retanned	79	.639	.127	.45
Rawhide lace	122	.616	.191	.47
Vegetable-tanned strap	104	.789	.208	.37
Alum-formaldehyde	45	.696	.079	.63
Chrome-retanned	79	.574	.114	.48
Vegetable-tanned sole	184	.906	.424	.12
Vegetable-tanned calfskin	37	.649	.061	.83
Van Tassel chrome-retanned sole	242	.738	.452	.24
Vegetable-tanned sole	246	1.022	.638	.06
Vegetable-tanned sheepskin	47	.502	.061	.78

6. Effect of Temperature on Water-Vapor Permeability

Since the kinetic energy of the water molecules increases with increase in temperature, it might be expected that the water-vapor permeability should also increase. In these tests duplicate specimens of different types of leather were used as received. Tests were made at 30° and 45° C at three different relative humidities for each temperature. These results are given in table 9 and figure 13. In figure 13 the logarithm of the permeability is plotted against the logarithm of the vapor pressure. These parameters were chosen because their relation can be shown fairly well by a straight line. The numbers at the ends of the curves signify the leather specimens. The curves show the variation of the log of the permeability with the log of the vapor pressure for each temperature. The unfilled dots are for 30° C, whereas the filled dots are for 45° C. All points except that for one specimen at the lowest

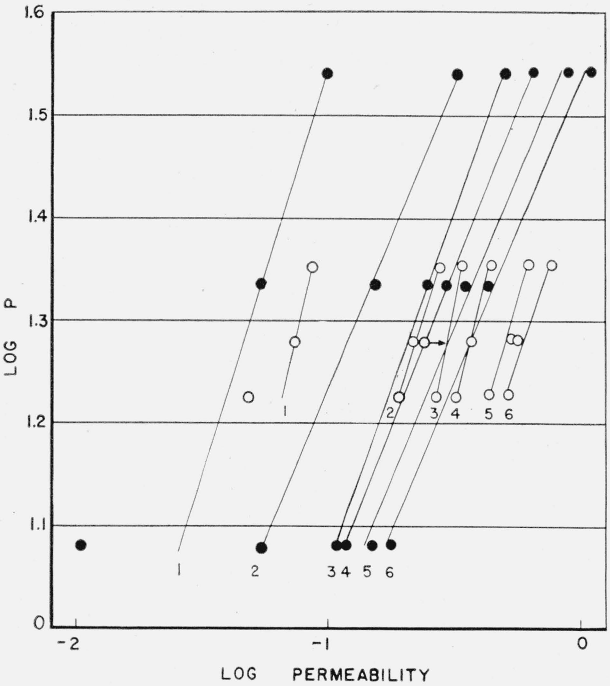

FIGURE 13. *Influence of temperature on water vapor permeability.*

Relation between the logarithm of the vapor pressure and the logarithm of the permeability. Determinations made at 30° C, ○; at 45° C, ● ⊙.

TABLE 9. *Effect of temperature on water-vapor permeability*

(Water-vapor permeability expressed in g/25 cm^2×100 min)

Temperature	30° C			45° C		
Relative humidity, percent	54	61	72	17	31	49
Chrome-hydraulic packing	0.05	0.07	0.09	0.01	0.05	0.10
Chrome-retanned sole	.19	.22	.28	.05	.16	.32
Vegetable-tanned strap	.27	.24	.34	.11	.25	.50
Retanned upper (degreased)	.32	.37	.45	.12	.30	.64
Alum-formaldehyde	.44	.54	.62	.15	.34	.91
Vegetable-tanned sheepskin	.52	.55	.77	18	.43	1.11

relative humidity at both 30° and 45° C show fairly good straight-line relationships.

The results indicate that at the same vapor pressure the permeability is less at 45° than at 30° C. The relation of temperature and relative humidity to permeability is often confused. This is because for equal relative humidities the vapor pressure is much greater at the higher temperature, and the absolute humidity or total moisture content must be considered. Therefore the statement is often made that the permeability increases with temperature. Bradley, McKay, and Worswick [1] have stated that the water vapor permeability increases 6.5 percent for each degree rise in temperature. This occurs probably under conditions of constant relative humidity.

Work on the adsorption of water vapor by leather and collagen has shown that at the same vapor pressure the adsorption decreases with increase in temperature [14]. This indicates, therefore, that the permeability may be influenced by the amount adsorbed or by the ease with which the water makes contact with the leather surface. Work on plastic films [9, 10] has shown that permeability increases with temperature. This work was also done at constant relative humidity rather than constant vapor pressure. The plastic films however, do not adsorb appreciable amounts of water, and it is probable that the mechanism of penetration of these two types of materials is different.

According to the activated diffusion mechanism postulated for water vapor transmission, a certain amount of energy is required to free adsorbed or bound water from an active site before it can go on to the next one. This energy is analogous to heat of vaporization and is often called "energy of activation for permeation." A value for this energy of activation for leather can be evaluated from the data in figure 13. For equal permeability values at the two temperatures, the logarithm of the vapor pressure difference is read off corresponding to each temperature, and the values substituted in the Clausius-Clapeyron equation:

$$\Delta H = 2.303R\,\frac{\log P_2 - \log P_1}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}.$$

Log P_1 was taken at 1.3 on each of the 30° C lines. The corresponding value of P_2 in each case was found by going vertically upward to the intersection with the 45° C line for the same sample of leather.

The average value obtained from the six curves in figure 11 was 3,575 calories/mole. That there is an energy of activation for permeation is further evidence that the water vapor permeability of leather is not solely gaseous diffusion, but involves also some form of "activated diffusion" or surface conduction.

7. Effect of Type of Impregnant on Water Vapor Permeability

In an application of the hypothesis that water is transmitted more rapidly over a polar than a nonpolar medium, experiments were made in

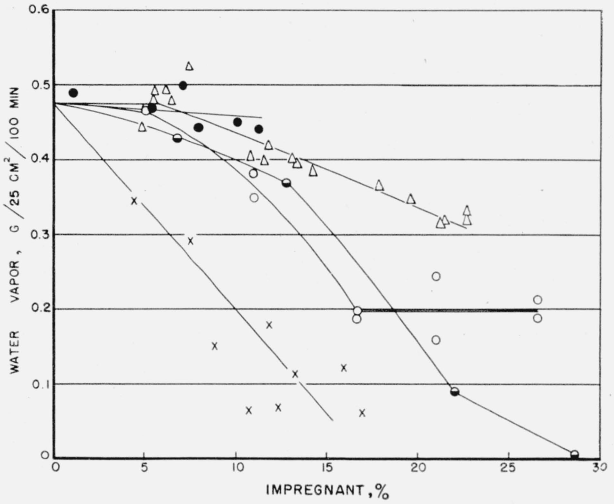

FIGURE 14. *Effect of various leather impregnants on the water vapor permeability.*

●, Sulfonated oil; △, acrylate resins; ◑, solvent stuffing; ○, rubber; ×, wet stuffing.

which degreased chrome-retanned upper leather was treated with various types of impregnants. These impregnants included sulfonated oils, stuffing greases, rubber, and acrylate resins. The stuffing greases were added in two ways: (1) by the customary procedure, which is by wetting the leather and then applying the molten greases to the surface, and (2) by using a solvent. The solvent method was used principally so that a legitimate comparison could be made between the grease and the rubber and the resins, the last two of which were added in a solvent. The addition of a small amount of the stuffing grease by the usual procedure cannot be done uniformly, and considerable variation was obtained, as is indicated by the results that are given in table 10 and plotted in figure 14. The stuffing mixture used was obtained from a manufacturer of upper leather and consisted of petroleum wax, moellen, and fatty oils and greases.

TABLE 10. *Water vapor permeability of leathers treated with various types of impregnants*

(Water vapor permeability in g/25 cm^2×100 min)

Stuffing grease				Sulfonated oil	
Customary procedure		Solvent method			
Grease in leather	Water vapor permeability	Grease in leather	Water vapor permeability	Grease in leather	Water vapor permeability
Percent	*g/25 cm^2×100 min*	*Percent*	*g/25 cm^2×100 min*	*Percent*	*g/25 cm^2×100 min*
Blank	0.48	Blank	0.48	Blank	0.48
4.4	.35	6.8	.44	1.1	.49
7.5	.29	12.8	.37	5.3	.47
8.8	.15	22.0	.09	7.1	.50
10.7	.07	28.6	.01	7.9	.44
11.8	.18			10.1	.45
12.3	.07			11.3	.44
13.2	.11	Acrylate resins			
15.9	.12				
16.9	.06			Rubber	
		Blank	0.48		
		4.9	.44		
		5.5	.48	Blank	0.48
		5.6	.49	5.2	.46
		6.2	.49	5.2	.47
		6.5	.48	11.0	.38
		7.5	.53	11.0	.35
		10.8	.41	16.6	.19
		11.6	.40	16.6	.20
		11.8	.42	20.9	.24
		13.1	.40	20.9	.16
		13.4	.40	26.5	.22
		14.2	.38	26.5	.19
		17.9	.37		
		19.6	.35		
		21.3	.31		
		21.5	.32		
		22.7	.32		
		22.7	.33		

As shown in this figure, the stuffing procedure forms a film over the surface of the leather, and a nearly impermeable membrane is formed for low concentrations of grease. This is also shown in figure 9. The stuffing grease added by means of a solvent shows a less rapid decrease in water vapor permeability with increasing grease content, probably because a more uniform distribution of the grease is obtained. The leathers treated with rubber show less decrease in water vapor permeability than the stuffing greases. Sulfonated oil shows very little effect on the water vapor permeability, and the acrylate resins appear to maintain fairly high rates of transmission. These results are in agreement with the hypothesis that polar groups influence the water vapor permeability, since both sulfonated oils and the acrylates contain these types of groups. Rubber also maintains fairly high permeability in leather. This might be explained by assuming that it enters and fills only the larger pores, the smaller pores remaining intact for the transmission of water vapor. The latter hypothesis might be applied to all types of resinous materials. Thus it might be assumed that these particles can enter only those pores that are above a definite range in size. This hypothesis can be further studied by making experiments with polymers with varying molecular weight ranges.

8. Effect of Gross Air Pressure and Flexing on Water Vapor Permeability

In order to perform some tests that would approach more nearly the conditions to which shoes are subjected in actual service, a method of measuring the water vapor permeability of leather during flexing was developed. A sketch of the equipment is shown in figure 15. The principle of dynamic gas streams used by Edwards [2] and by Maeser [5] was applied. The apparatus consists of two chambers separated by a diaphragm of the leather under test. The conditions of relative humidity and pressure in each chamber may be varied as desired. The amount of moisture that penetrates the leather is determined by the pickup in the dry gas stream, the moisture being removed from this stream after it leaves the chamber by passing it through a tube containing a drying agent. The leather specimen may be flexed as a diaphragm, to simulate the flexing of a shoe vamp in walking. The flexing is done by a rod fastened to the center of the specimen and connected by an adjustable cam to a variable speed transmission. Any speed up to 220 rpm with any stroke up to 1.5 in. may be attained. Tests may also be made with the leather diaphragm under static conditions (no flexing).

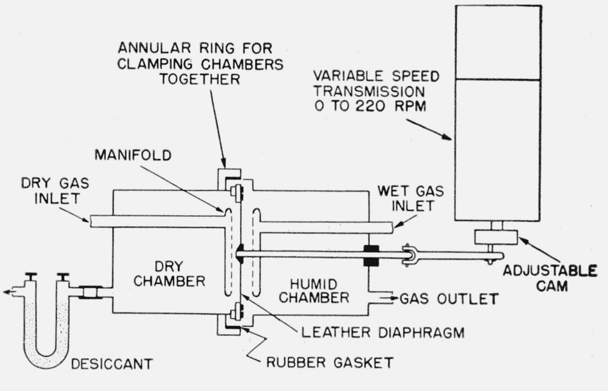

FIGURE 15. *Sketch of the equipment used to determine water vapor permeability under dynamic conditions.*

The results obtained with the dynamic equipment on degreased upper leather are shown in figure 16, where the water vapor permeability is plotted against the difference in pressure of air between the two chambers in centimeters of diamyl phthalate (approximately g/cm.^{2}). The dry air was passed through one chamber at the rate of 2.0 ft^3/hr, whereas air saturated with water vapor at 73° F was passed through the other chamber at different rates to give the differences in pressures of air shown in the figure. Since it was difficult to obtain exactly equal pressures on both sides to give a zero difference, tests were made varying the pressure from a high on one side to a high on the other. The point where the curve crosses the zero pressure line is equivalent to the water vapor permeability at zero air

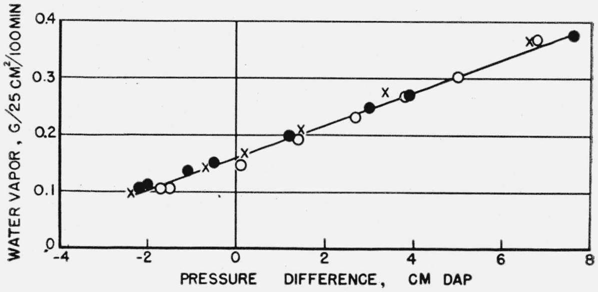

FIGURE 16. *Influence of flexing on the water vapor permeability of degreased upper leather.*

●, Static, before flex; ○, static, after flex; ×, flexing.

pressure difference. The negative pressure given on the graph is indicative of highest pressure on the side through which dry air was passed. The flexing in these experiments was done at a rate of 60/min, and the stroke was ⅜ in.

According to the graph, the water vapor permeability of the degreased leather is the same whether or not the specimen is flexed. The slope of the curve indicating the rate of water vapor transmission with difference in air pressure is the same whether the pressure is high on the dry or moist chambers. This appears to indicate that some of the moisture passes through independently of the air stream and even counter to it. If the moisture moved entirely within the air stream, zero water vapor permeability would be expected at zero pressure. It might be expected that the value for the water vapor permeability at the point where the curve crosses zero pressure is that normally obtained by the difference in concentration of water vapor. The slope of the curve would then be caused by the moisture that passes through the pores of the leather in the air stream. However, the slope of the curve above zero pressure is slightly greater than that which can be accounted for by the moisture content of the air. It is therefore probable that the moisture is adsorbed by the leather and is conducted over its surface more rapidly than if it were carried along with the air stream. The increase in transmission with increase in pressure must be partially caused by increased adsorption of moisture by the leather.

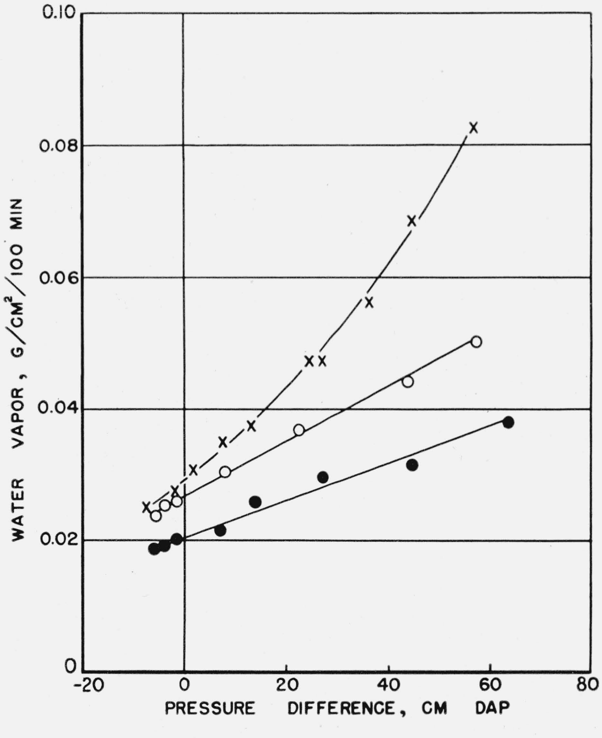

FIGURE 17. *Influence of flexing on the water vapor permeability of upper leather containing a high percentage of grease.*

●, Static, before flex; ○, static, after flex; ×, flexing.

The influence of flexing on the water vapor permeability of upper leather containing grease is shown in figure 17. These experiments were performed by the same procedure as that for the degreased leather. The results show that the water vapor permeability under static conditions after flexing is increased, and the permeability during flexing is substantially increased. In the discussion of figure 5, it was shown that the barrier offering the main resistance to the passing of water vapor for the highly greased upper leather was the thin top grain split. Flexing would undoubtedly break this impermeable film, and after flexing, its permeability to water vapor should be increased as is shown. The further increase in water vapor permeability shown during flexing is probably caused by a wider opening of this film, allowing the moisture to pass on through in the air stream. The difference between the rate of the water vapor permeability at zero air pressure for the flexed leather and that obtained on increasing the air pressure is equal to the amount present in the air stream that passes through the leather. The explanation for the difference in behavior in this respect between the degreased and the greased leather is the lower adsorbing power of the latter.

The fact that the water vapor permeability of heavily greased leather increases on flexing has an important practical significance. The percentage of the total area of the upper of a shoe that is flexed to any extent is probably about 50 percent, so that the increase in total water vapor permeability might be significant. The water vapor permeability increases further on flexing with increase in pressure. There is undoubtedly some increase in pressure in a shoe on walking; however, the amount is not known.

V. Conclusion

The results of the experiments indicate that in addition to gaseous diffusion, water is transmitted through leather by conduction over the surface or by some form of activiated diffusion. The evidence for the conduction mechanism has been pointed out briefly within the paper. This evidence consists of the behavior at low relative humidities, existence of energy of activation, influence of temperature, comparison of air permeability and water vapor permeability, experiments with fabrics and glass disks, variations of diffusion constants, and studies of the effect of gaseous air pressure with the dynamic equipment.

The behavior at low relative humidity shows the influence of strong adsorption forces that appear to hold the water within the leather so that a definite pressure head seems to be required to force it through. The effect of temperature on water vapor permeability also shows the influence of the surface. At a higher temperature the water molecules have a greater kinetic energy so that the diffusion forces are greater; however, for the same vapor pressure, the permeability is actually lower, which is in line with the fact that the adsorption of moisture is decreased as the temperature is increased. Here again is shown the influence of the surface properties.

The fact that water vapor passes through glass disks having small pores at a greater rate than through those having larger pores can be explained only by the fact that the smaller pores are associated with greater surface areas. Likewise the variation of the diffusion constants with the thickness of the materials and with relative humidity gradient shows the influence of the material itself on the permeability. These results indicate the greater activity of the highly polar glass, leather, and cotton surfaces as compared to the less polar nylon surface. The influence of polarity is also shown in the studies of the effects of different impregnants.

Studies of the effect of gross air pressure in the dynamic equipment indicate that the water vapor permeability is not dependent on the air permeability and may proceed counter to it. The variation of water vapor permeability with apparent density is believed to magnify the importance of diffusion; since the surface area will also increase with decrease in apparent density, and this may be the reason for the increased permeability under these conditions. As a result of these studies, it appears that activated diffusion is an important mechanism in the transference of water vapor through leather.

As stated in the introduction, the purpose of this work was to study the mechanism of water vapor permeability and to develop a test method. It would be well to follow this with a study of the comfort and health of the foot as influenced by water vapor permeability. A study of this property as influenced by special treatments and by the use of a variety of materials might lead to the development of a more comfortable and more serviceable shoe and would be extremely valuable to the Armed Services.

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