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In table 10 the values for 0 to 1,500°K should read:

T°K	$\Delta Hf°$	$\Delta Ff°$	$\log_{10} Kf$
0		-85.746	---
298.16		-81.308	59.5974
300	-86.367	-81.276	59.2086
400		-79.56	43.469
500		-77.83	34.017
600		-76.08	27.710
700		-74.32	23.204
800		-72.57	19.824
900		-70.81	17.196
1,000		-69.06	15.094
1,100		-67.33	13.376
1,200		-65.58	11.943
1,300		-63.83	10.731
1,400		-62.08	9.691
1,500		-60.35	8.793

Effect of Moisture on Compressibility of Natural High Polymers

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Studies are reported of the effect of sorbed moisture on compressibilities of leather, cellulose, wool, and silk fibroin. The general behavior of all materials is similar. For low moisture contents, compressibility is essentially independent of moisture content. For high moisture contents, compressibility increases markedly. It is suggested that these data are consistent with the concept that moisture exists in hydrogen bonded form at low and as liquid water at high moisture contents. Empirical compression equations are: for dry wool, $-\Delta V/V_0 = 1.37 \times 10^{-5} \ (P-2000) - 6.79 \times 10^{-10} \ (P-2000)^2 + 1.55 \times 10^{-14} \ (P-2000)^3$; for dry silk fibroin $-\Delta V/V_0 = 1.24 \times 10^{-5} \ (P-2000) - 7.00 \times 10^{-10} \ (P-2000)^2 + 2.68 \times 10^{-14} \ (P-2000)^3$, where P is expressed in atmospheres.

1. Introduction

In a previous investigation [21] it was observed that the compressibility of leather at high pressures was apparently independent of small amounts of moisture contained in the leather. The present report describes the results of studies of the effect of moisture content on the compressibilities of leather and other similar hygroscopic fibrous materials over a wide range of moisture contents. These data confirm the previous qualitative observation and show that for low-moisture contents the compressibility is essentially independent of moisture content. For high-moisture contents the compressibility rises markedly.

2. Experimental Method

The apparatus and techniques used in conducting these experiments have been described in detail [21]. Briefly, the sample is immersed in a light petroleum distillate contained in the bore of the pressure vessel and a leak-proof piston is forced into the bore. The position of the piston is measured every 1,000 atm., the pressure being generated by compression of the distillate. Pressure is determined by means of a manganin pressure gage mounted inside the vessel and immersed in the distillate. Direct comparison of the piston displacements in this experiment with those obtained in a similar experiment, in which the specimen is replaced by a steel bar having a volume approximately equal to that of the specimen, permits calculation of the compression of the specimen in terms of that of steel [3].

3. Preparation of Specimens

Measurements were made on commercial chrome upper leather, untanned hide, wool, cellulose, and silk fibroin. Leather samples consisted of a cylindrical stack of disks $\frac{1}{2}$ in. in diameter and 4 in. in length. Each sample contained at least 25 individual leather disks held together by means of a fine wire threaded through each disk. Wool, cellulose, and silk fibroin were compressed into disks $\frac{1}{2}$ in. in diameter and strung together in a similar manner to form a cylinder approximately 4 in. in length. These disks were formed in a cylindrical mold, using a maximum pressure of approximately 50,000 psi.

Commercial chrome upper leather was degreased exhaustively with chloroform and washed with water prior to test. Unhaired, untanned calfskin was degreased with acetone, diethyl ether, and ethyl alcohol after a thorough washing in water.

Wool specimens were made from a native wool designated as "Domestic Fine Top, WC-4", which was supplied by the Textile Research Institute. This sample originated at the Sheep Experiment Station of the United States Department of Agriculture at Dubois, Idaho. Dichlorobenzene had been used as a moth repellent in the container in which the sample was shipped and the sample was therefore extracted with diethyl ether and ethyl alcohol prior to use.

Cellulose was of cotton origin and was designated as "Lockette 140" of 93 percent maturity. This sample was supplied by the Southern Regional Research Laboratory of the United States Department of Agriculture.

Silk specimens were obtained from raw silk of uncertain origin. The specimens were degummed by the usual process and washed thoroughly with water prior to test.

Initial measurements were made on specimens dried by exhaustive evacuation at room temperature for not less than 24 hr. After ascertaining the dry weight, the test specimen was impregnated with the distillate in vacuo and the compressibility measured. Impregnation was conducted under a pressure of approximately 100 mm of mercury. The volume of the test specimen was determined following compression measurements by weighing the specimen in the distillate.

Following the initial measurement, the distillate was removed in vacuo at room temperature, the dry specimen was permitted to adsorb the desired quan-

tity of moisture (determined by weight) by exposure to moist vapor and the above procedure was repeated. It is to be noted that all measurements on a given material were conducted on the same specimen. All measurements were carried out in a temperature controlled room in which the temperature was $20.5° \pm 0.5°$ C.

The following observations on the experimental procedure are to be noted:

1. Evacuation for 24 hr does not remove all traces of moisture from such hygroscopic materials. However, the amount of moisture retained is small and for the purposes of these experiments is considered to have negligible effect on any conclusions to be drawn from the data. The specimens are therefore referred to as "dry".

2. Density measurements were made following compression to insure penetration of the voids by a light petroleum distillate. There is no indication from these or other measurements [22] of an irreversible increase in real density caused by the high hydrostatic pressure. The agreement between real densities determined here and those determined by other methods confirms this conclusion. The reproducibility of the compression data and the rapidity of attainment of pressure equilibrium are taken as indicative of purely elastic effects in time scales of the order involved in these experiments.

3. Reevacuation of distillate-impregnated specimens did not remove all of the distillate, an approx-imately constant amount of 200 mg of presumably trapped material being retained. Moisture contents were therefore referred to the weight of the initial dry specimen before exposure to the distillate. For this reason moisture contents are subject to some uncertainty and are reported only to the nearest percent.

4. Exposure to moisture containing air was generally carried out for 24 hr. Complete distribution equilibrium is unlikely in such a period, but these data are not likely to be sensitive to a nonequilibrium distribution [23].

4. Results and Discussion

The results of compression measurements for various moisture contents are given in table 1 and are shown graphically in figure 1 for chrome leather and cellulose. Compression values, $-\Delta V/V_0$, are computed on the basis of the original (1 atm) volume of the sample but are reckoned from the experimental reference pressure of 2,000 atm. Compressions at 1,000 atm, therefore, appear as negative values that are subject to somewhat larger experimental errors than the other values. These errors, as well as the uncertainty introduced by the assumed compression occurring between 1 and 2,000 atm, have been considered previously [21, 22].

TABLE 1. *Compression of natural fibrous polymers containing various amounts of moisture*

Pressure	Chrome leather					Untanned hide				
	Dry $V_0=7.367\,cm^3$ $\rho=1.401g/cm^3$ $-\Delta V/V_0$	6 percent H_2O $V_0=7.988\,cm^3$ $\rho=1.404g/cm^3$ $-\Delta V/V_0$	13 percent H_2O $V_0=8.542\,cm^3$ $\rho=1.389g/cm^3$ $-\Delta V/V_0$	20 percent H_2O $V_0=9.334cm^3$ $\rho=1.364g/cm^3$ $-\Delta V/V_0$	38 percent H_2O $V_0=10.882\,cm^3$ $\rho=1.315g/cm^3$ $-\Delta V/V_0$	Dry $V_0=7.125\,cm^3$ $\rho=1.330g/cm^3$ $-\Delta V/V_0$	5 percent H_2O $V_0=7.648\,cm^3$ $\rho=1.334g/cm^3$ $-\Delta V/V_0$	17 percent H_2O $V_0=8.469\,cm^3$ $\rho=1.317g/cm^3$ $-\Delta V/V_0$	30 percent H_2O $V_0=9.613cm^3$ $\rho=1.287g/cm^3$ $-\Delta V/V_0$	37 percent H_2O $V_0=10.382\,cm^3$ $\rho=1.267g/cm^3$ $-\Delta V/V_0$
atm										
10,000	0.0641	0.0666	0.0664	0.0717	0.0784	0.0672	0.0694	0.0694	0.0785	0.0790
9,000	.0599	.0602	.0614	.0654	.0721	.0615	.0631	.0632	.0719	.0716
8,000	.0535	.0533	.0548	.0579	.0643	.0544	.0557	.0557	.0641	.0638
7,000	.0465	.0460	.0476	.0500	.0555	.0473	.0480	.0481	.0578	.0556
6,000	.0396	.0390	.0396	.0429	.0465	.0406	.0411	.0410	.0477	.0469
5,000	.0317	.0307	.0312	.0337	.0372	.0319	.0321	.0320	.0385	.0369
4,000	.0218	.0210	.0222	.0230	.0260	.0218	.0224	.0217	.0275	.0258
3,000	.0121	.0111	.0114	.0121	.0141	.0114	.0121	.0116	.0157	.0134
2,000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
1,000	−.0209	−.0126	−.0124	−.0139	−.0174	−.0122	−.0140	−.0130	−.0120	−.0151

Pressure	Cellulose			Wool		Raw silk		
	Dry $V_0=7.230\,cm^3$ $\rho=1.538\,g/cm^3$ $-\Delta V/V_0$	5 percent H_2O $V_0=7.639\,cm^3$ $\rho=1.534\,g/cm^3$ $-\Delta V/V_0$	9 percent H_2O $V_0=8.043\,cm^3$ $\rho=1.509\,g/cm^3$ $-\Delta V/V_0$	Dry $V_0=5.281\,cm^3$ $\rho=1.316\,g/cm^3$ $-\Delta V/V_0$	10 percent H_2O $V_0=5.862\,cm^3$ $\rho^a=1.316/cm^3$ $-\Delta V/V_0$	Dry $V_0=9.447\,cm^3$ $\rho=1.351\,g/cm^3$ $-\Delta V/V_0$	6 percent H_2O $V_0=9.838\,cm^3$ $\rho=1.357\,g/cm^3$ $-\Delta V/V_0$	11 percent H_2O $V_0=10.458\,cm^3$ $\rho=1.348\,g/cm^3$ $-\Delta V/V_0$
atm								
10,000	0.0536	0.0536	0.0565	0.0738	0.0733	0.0679	0.0678	0.0686
9,000	.0484	.0491	.0513	.0680	.0680	.0618	.0618	.0627
8,000	.0426	.0429	.0453	.0599	.0604	.0549	.0549	.0556
7,000	.0365	.0370	.0392	.0524	.0529	.0476	.0476	.0484
6,000	.0307	.0309	.0327	.0449	.0442	.0400	.0398	.0407
5,000	.0236	.0239	.0256	.0360	.0350	.0317	.0312	.0319
4,000	.0164	.0169	.0182	.0246	.0245	.0222	.0214	.0225
3,000	.0092	.0094	.0097	.0136	.0136	.0117	.0115	.0118
2,000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
1,000	−.0093	−.0097	−.0099	−.0185	−.0143	−.0138	−.0141	−.0141

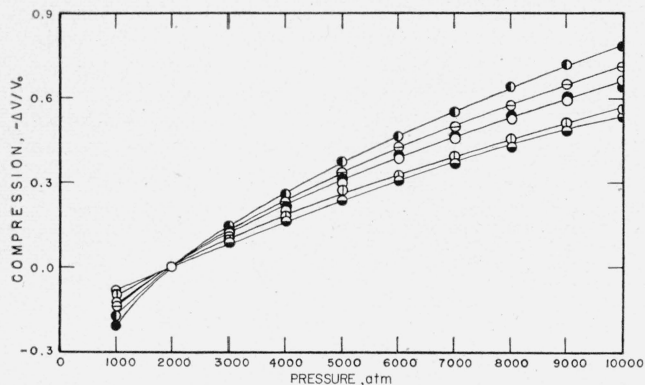[a] ρ calculated as described on page 137.

FIGURE 1. *Effect of moisture on compression of chrome leather and cellulose.*

Chrome leather: ●, dry, ○, 6 percent of moisture, ⊖, 20 percent of moisture, ◑, 38 percent of moisture. Cellulose: ◓, dry and 5 percent of moisture, ⌽, 9 percent of moisture.

FIGURE 2. *Effect of moisture on isobaric compression of chrome leather.*

Moisture contents, measured densities, and initial volumes appear at the head of corresponding columns of compression values in table 1. All densities were obtained from weight and volume measurements except that for wool containing moisture. A single measured density of dry wool was assumed to apply also to wool containing 10 percent moisture. Measurements by King [14] show that the error arising from this assumption in this moisture range is rather small. The necessity for this assumption as well as the lack of data on wool at higher moisture contents arose because wool specimens proved difficult to handle. Compressed disks of wool exhibited great resiliency, and the samples were generally ruptured in extraction from the pressure vessel.

Density values of table 1 agree well with previously published data on these materials [5, 7, 9, 10, 14, 17, 18]. However, the density maximum for chrome leather, as shown by these data, lies below 13 percent moisture as compared to the data of Pomeroy and Mitton [17], in which the maximum is found at approximately 15 percent. The variation of density with moisture content is also somewhat less than that reported by these authors. A corresponding maximum density for untanned hide is shown by the present data to lie below 17 percent of moisture.

Consideration of the effect of moisture content on compression shows that the general behavior of these materials is quite similar. Most thorough studies were performed on leather, but sufficient data were obtained on other materials, except wool, to show the similarities in behavior. It is observed that the compression changes relatively little at low moisture but increases markedly at high moisture contents. Inasmuch as the experimental errors involved in these experiments are known to produce variations of a few digits in the third significant figure, differences noted in compression at low-moisture contents are most probably real. These variations, however, are rather small compared to the change that 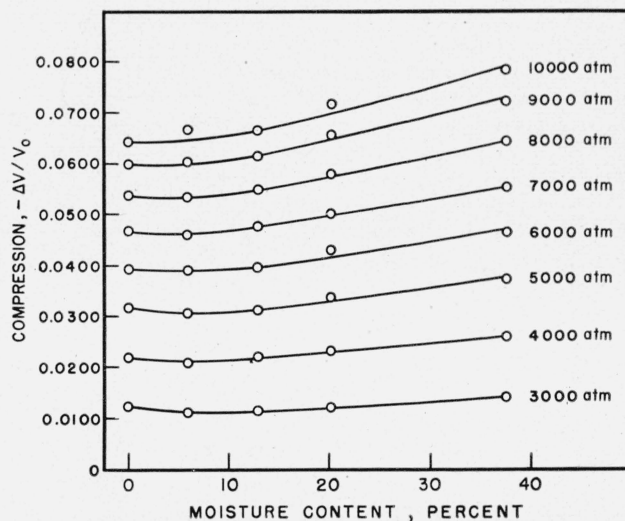occurs at high-moisture contents. Therefore, at a given pressure the compression may be considered to be essentially constant at low-moisture contents. The implications of the relative constancy in compression at low-moisture contents at a given pressure appear to be rather complex. As the moisture content increases the value of V_0 invariably increases as shown in the table. However, the change in volume, ΔV, at a given pressure appears to be just sufficient to keep the ratio constant. This result is true in the data on collagen and cellulose, two materials which are dissimilar chemically and which exhibit considerably different compressibilities. This finding shows that the added moisture on compression behaves in a manner to make it indistinguishable from an equivalent volume of the dry adsorbent. Since compressibility is dependent on the magnitude of the internal molecular forces, this near equality between compression of specimen and adsorbed moisture imples a corresponding similarity in these forces.

The variation of compression with moisture content is shown for chrome leather at several pressures in figure 2.

From these data it may be concluded that adsorbed moisture in low ranges of moisture content does not behave like liquid water. Although it is possible to calculate an effective pressure on liquid water that will produce the observed volume of moisture plus adsorbent at 1 atm, it is difficult to explain the agreement between the compressibilities of this water and the fibers over the whole pressure range, the variation of compressibilities with pressure being different for water and these fibrous polymers [1, 4, 22]. The observation that the compressibilities of moist and dry fibers essentially coincide at all pressures in the low-moisture range seems to offer a strong argument against the hypothesis that the adsorbed moisture be considered as water under high

TABLE 2. *Calculated compressions of moist chrome leather*

Pressure	6 percent of H_2O				13 percent of H_2O				38 percent of H_2O			
	Leather $V_1=0.9221$ $(-\Delta V/V_0)V_1$	Water $V_2=0.0779$ $(-\Delta V/V_0)V_2$	Total calc. $-\Delta V/V_0$	Calc. minus obs.	Leather $V_1=0.862$ $(-\Delta V/V_0)V_1$	Water $V_2=0.138$ $(-\Delta V/V_0)V_2$	Total calc. $-\Delta V/V_0$	Calc. minus obs.	Leather $V_1=0.677$ $(-\Delta V/V_0)V_1$	Water $V_2=0.323$ $(-\Delta V/V_0)V_2$	Total calc. $-\Delta V/V_0$	Calc. minus obs.
atm												
10,000	0.0591	0.0094	0.0685	0.0019	0.0553	0.0166	0.0719	0.0054	0.0434	0.0388	0.0822	0.0038
9,000	.0551	.0091	.0642	.0040	.0515	.0161	.0676	.0062	.0405	.0377	.0782	.0061
8,000	.0494	.0082	.0576	.0043	.0461	.0146	.0607	.0059	.0362	.0341	.0703	.0060
7,000	.0429	.0072	.0501	.0041	.0400	.0128	.0528	.0052	.0315	.0300	.0615	.0060
6,000	.0365	.0062	.0427	.0037	.0341	.0109	.0450	.0054	.0268	.0256	.0524	.0059
5,000	.0292	.0049	.0341	.0037	.0273	.0088	.0361	.0019	.0215	.0205	.0420	.0048
4,000	.0201	.0036	.0237	.0028	.0188	.0061	.0251	.0029	.0148	.0147	.0295	.0035
3,000	.0111	.0019	.0130	.0019	.0104	.0034	.0138	.0024	.0082	.0030	.0162	.0021
2,000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
1,000	−.0190	−.0024	−.0214	−.0094	−.0178	−.0043	−.0221	−.0097	−.0141	−.0099	−.0240	−.0066

pressure [7, 9, 10, 19]. Typical results obtained by considering moist fibers as a binary mixture of water and adsorbent are shown for chrome leather in table 2 for three moisture contents.

The calculated compression contributions of leather and water are based on the respective experimentally measured volume fractions of the two components assuming no compression of the leather. The experimental volume fractions are shown at the heads of the corresponding columns. The differences between calculated and measured compressions (taken from table 1) increase much less in the high moisture range than in the low range. This implies that liquid water is present at high moisture contents as has been suggested [10, 16].

The concept that compressed water is present in these moist fibers would appear to require modification in the light of these data. Three alternatives appear possible, namely, both adsorbed moisture and adsorbent exist under an effectively high pressure; the adsorbed moisture penetrates into molecular-sized holes which are inaccessible to other liquids [9, 10]; and the adsorbed moisture enters into chemical or psuedochemical combination with the adsorbent.

The concept of effectively high pressures compressing the water has been based on the assumption that the adsorbent, being a solid, is affected by this pressure to a negligible degree. For such fibrous materials, and the high polymers which have been studied, the assumption is incorrect, the compressibilities of the two components being of the same general order of magnitude. It is doubtful if such an assumption is valid even in the case of a relatively incompressible solid since the short-range anisotropic nature of the forces might produce large local distortions. However, the consideration of the compressions of both components will not remove the difficulty of equal dependence of the compressibilities on pressure.

The concept of penetration of moisture into holes accounts for the increased density observed on adsorption of a liquid which, in bulk, is less dense than the adsorbent. The problem of pressure dependence of compressibility is not explained and data of

Pomeroy and Mitton [17] obtained on leather do not exhibit the dependence of density on molecular size of the liquid to be expected from such concepts.

It is suggested, therefore, as a result of this and previous work [23] that the adsorbed moisture in the range of low moisture contents is bound by secondary valence forces. In view of the widely accepted ideas of the hydrogen bonded structure of the materials studied here, it is believed that the moisture exists largely in the hydrogen bonded form between the polymer chains and produces small changes in the original structure of the dry material. The small increase, produced by this moisture, in the enormous number of similar bonds existing in the dry material might be expected to cause the negligible effect on compression that is observed. The similarity of the new bonds with those already existing implies a similar pressure dependence of compressibility. The findings of Katz [13] that the X-ray pattern of cellulose is unchanged by moisture may be indicative as suggested [12], that the effects of the moisture are largely confined to a limited number of chains near the surface of the micelles.

It is noted that the major increase in compression occurs in the moisture content range in which the slopes of differential heat of adsorption curves are changing most rapidly [2, 8, 11, 20]. This moisture content also corresponds to that range in which the electrical properties of leather begin to change rapidly [23]. Similar electrical effects have been noted in cellulose and wool [6, 15]. The correlation of these effects substantiates the suggestion that liquid water exists at high moisture contents.

The absolute values of compressions of leather and cellulose reported here agree well with values reported earlier [21, 22]. As far as can be ascertained compressibility data for wool and silk fibroin are being reported for the first time. In view of the similarities of the structures of these materials and leather [16], the compressions are of the order of magnitude expected, but it is surprising to note the close agreement in data obtained for these materials. It would appear that the presence of ring structures such as proline and hydroxyproline in collagen, and of disulfide cross linkages in wool, produces a rather

small variation in the nature of the intrachain forces.

The compression of dry wool and silk may be represented by the following empirical equations, which were fitted to the data by the method of least squares:

wool:

$$-\Delta V/V_0 = 1.37 \times 10^{-5}(P-2000) - 6.79 \times 10^{-10}(P-2000)^2 + 1.55 \times 10^{-14}(P-2000)^3$$

silk fibroin:

$$-\Delta V/V_0 = 1.24 \times 10^{-5}(P-2000) - 7.00 \times 10^{-10}(P-2000)^2 + 2.68 \times 10^{-14}(P-2000)^3.$$

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