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THE CARBONIZATION PROCESS: A STUDY OF THE SYSTEM WOOL—SULPHURIC-ACID—WATER[1]

By Milton Harris[2]

ABSTRACT

The purpose of this study was to provide quantitative data on the system wool—sulphuric-acid—water under conditions similar to those in the soaking, drying, and baking of wool in the carbonization process as a basis for the effective study of mill problems relating to the process.

The amounts of sulphuric acid absorbed by wool from 0.1, 1, and 5 percent solutions at 22 C and from a 5 percent solution at 35 C and the rates of absorption are reported. It was found that wool treated with acid retains less moisture than similar wool treated only with water when dried in air of relative humidities 6, 30, 65, and 90 percent, the difference in the amount of water absorbed being greatest for the 30 and 65 percent relative humidities. When the dried wool is baked there is a critical moisture content for each concentration of acid in the wool above which the breaking strength of the wool decreases and the ammonia nitrogen content increases. The physical and chemical break-down increases with an increase in concentration of acid and with an increase in the temperature of baking. The deterioration takes place in the first few minutes of baking.

When acid-treated wool is stored in air of 65 percent relative humidity or less, there is no decrease in breaking strength, but there is chemical deterioration as evidenced by the ammonia nitrogen content which increases with time of storage. The higher the relative humidity of the atmosphere in which the wool is stored and the greater the concentration of acid in the wool the more rapid is the increase in ammonia nitrogen content.

That the deterioration of wool in baking is promoted by the presence of oxygen, moisture, and sulphuric acid is demonstrated in experiments in sealed tubes.

The nature of the system wool—sulphuric-acid—water is discussed. Mechanisms by which moisture and acid may be taken up and held by wool are suggested.

CONTENTS

I. INTRODUCTION

The object of the carbonization process is the removal of vegetable matter from wool. The wool is impregnated with a solution of sulphuric acid,[3] squeezed or centrifuged to remove the adhering acid

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[1] The work reported here was made possible by a grant from the Textile Foundation, Incorporated, to the American Association of Textile Chemists and Colorists.

[2] Research Associate at the Bureau of Standards for the American Association of Textile Chemists and Colorists.

[3] Aluminum chloride and hydrochloric acid are sometimes used instead of sulphuric acid. These reagents are not considered in this paper.

liquor, dried at about 160 F, baked at about 250 F, and finally washed or neutralized. The control of the process to avoid damage to the wool must be considered one of its important phases. It is probable that many, if not all, of the troubles in the subsequent processing of wool that are attributable to faulty carbonization arise from incipient damage to the wool.

A considerable amount of acid is absorbed by wool in the carbonization process. A knowledge of the nature of the wool-acid combination and the effect of the variables concerned is obviously basic to the control of carbonization. It is of importance from the standpoint of subsequent processing of the wool fiber; for example, dyeing from acid solutions. The purpose of this research is to supply quantitative data on the system wool—sulphuric-acid—water as a basis for the effective study of mill problems relating to the carbonization process.

The variations in the carbonization process as practiced in industry make it difficult to attempt to set up any one laboratory procedure to cover all of the conditions. Moreover, it was evidently desirable to carry out the experiments under conditions that could be strictly controlled in order to obtain reproducible quantitative values. A large excess of acid over wool was used in the soaking bath and soaking was continued until equilibrium was reached, to insure uniform distribution of the acid in the fiber. Similarly, in drying and baking, the wool was well exposed to the surrounding atmosphere. The conditions of these experiments may be considered to be "ideal" rather than practical, but it is believed that the results have considerable practical significance.

II. MATERIAL AND METHODS

The material used for the experiments was worsted cloth, plain weave, weighing 8 ounces per square yard, mill-processed ready for dyeing. It was purified in the laboratory by successive extractions of 24 hours each with alcohol and ether and, finally, was soaked in water at 60 C for 30 minutes to remove adsorbed solvents.[4] After air drying, the cloth was cut warpwise into specimens measuring 3½ by 6 inches.

The breaking strength of the cloth was taken as a measure of its physical breakdown in the experiments. A pendulum type testing machine and the strip method were used. Specimens 6 inches long and 1 inch wide, cut warpwise of the cloth, were tested. All specimens were thoroughly conditioned and tested in a room maintained at a relative humidity of 65 percent and a temperature of 70 F. The average strength of from 3 to 5 specimens is reported.

The amount of wool protein in a specimen at any stage of processing was obtained by determining the total nitrogen by the Kjehldahl method. This value, multiplied by the factor 6.33 (obtained by dividing a known weight of the purified wool by its nitrogen content), gave the figure taken for the amount of wool protein.

The chemical breakdown of the fiber in the experiments was followed by analyzing specimens for ammonia nitrogen; that is, that portion of the nitrogen which is liberated when the wool is boiled in a saturated solution of magnesium oxide.

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[4] R. T. Mease, Adsorption of alcohol by fibrous materials, Ind. & Eng. Chem. Analytical Edition, vol. 5, p. 317, 1933.

Experiments in which specimens were exposed to air of different relative humidities were carried out by suspending the specimens in desiccators containing suitable saturated salt solutions. The salts used and the relative humidities are indicated in table 1.

TABLE 1.—*Relative humidities over saturated solutions at 70 F.*

	Relative humidity
Sodium hydroxide (NaOH)	[a] 6
Phosphoric acid ($H_3PO_4 \cdot \frac{1}{2} H_2O$)	[a] 9
Sodium chloride, potassium nitrate, and sodium nitrate (NaCl, KNO_3 and $NaNO_3$)	[b] 30
Zinc sulphate ($ZnSO_4 \cdot 7H_2O$)	[c] 90

[a] Obermiller, Die Einstellung von Luft, Zeit. Phys. Chem., vol. 109, p. 145, 1924.
[b] Bronsted, Kgl. Danske Videnskab. Selskab, Math., fys. Medd. vol. 1, p. 5, 1918.
[c] Sedgewick and Eubank, Jour. Chem. Soc. vol. 125, p. 2268, 1924.

The moisture content of the wool specimens was determined with the apparatus shown in figure 1. The specimen is placed in chamber *A*. The **U**-tube *B* is immersed in liquid air. The apparatus is then evacuated. The moisture from the specimen passes over into the **U**-tube where it freezes. It is then weighed directly. *D* is a cotton plug to prevent particles of ice from passing out of the tube. The rate of removal of moisture from wool by this method is slower than oven drying, equilibrium being reached in 24 to 30 hours. However, oven drying at temperatures above 100 C was found to be unsatisfactory, especially when much acid and water were present. Not only was it difficult to obtain a constant weight, but when the moisture and acid concentrations were high, the wool was degraded.

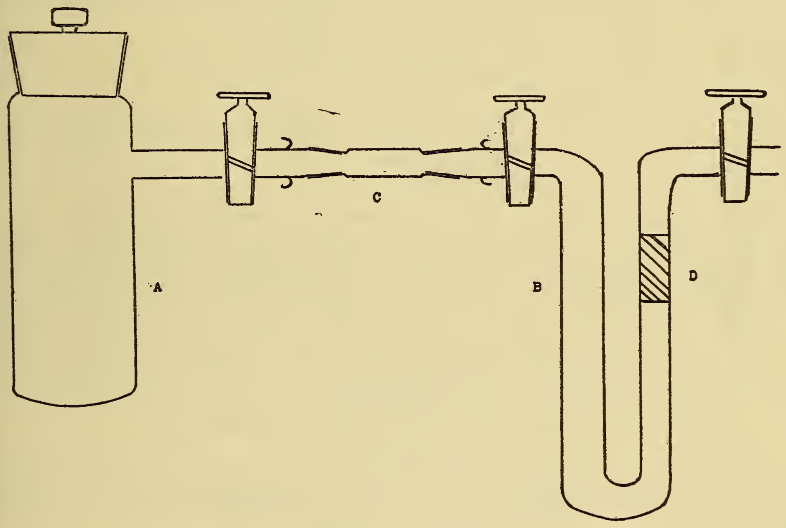

FIGURE 1.—*Apparatus for moisture determination.*

The amount of sulphuric acid in an acid-treated wool specimen was determined as barium sulphate by the following procedure. A 2-gram specimen of the wool was dissolved in 50 ml of an aqueous 5 percent solution of potassium hydroxide by warming on a steam bath.

The solution was made slightly acid with hydrochloric acid. Twenty ml of a 10 percent solution of barium chloride were added. The solution was filtered and the precipitate was washed with water until free from chloride and then ashed in an electric muffle furnace at 700 to 800 C.[5]

III. EXPERIMENTAL

1. DISTRIBUTION OF SULPHURIC ACID BETWEEN WOOL AND WATER IN THE SOAKING BATH

Two-gram specimens of wool were soaked in 50 ml portions of 0.1, 1, and 5 percent solutions of sulphuric acid. At intervals of time, the pH value of each solution was determined with the hydrogen electrode. For concentrations of acid greater than 1 percent, there was little if any variation in pH value because the quantity of acid taken up by the wool was very small compared with the amount present.

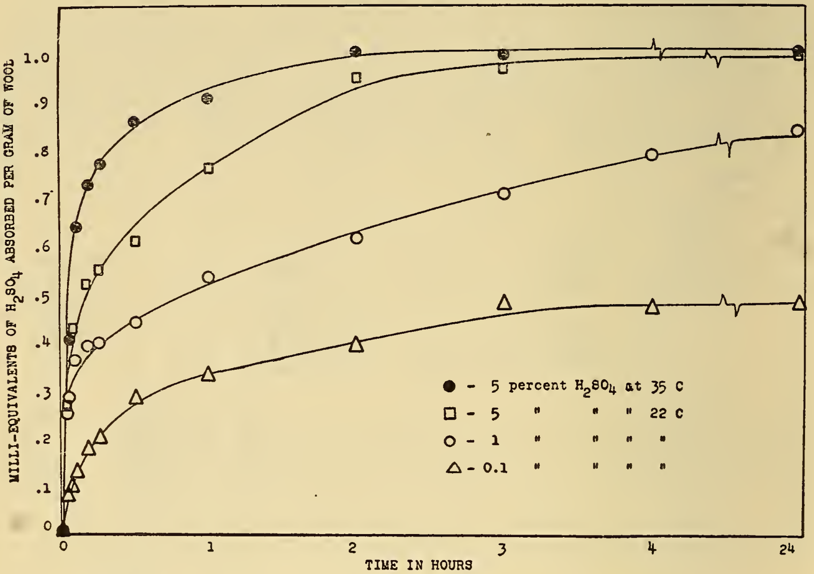

FIGURE 2.—*Rate of absorption of sulphuric acid by wool.*

The amount of sulphuric acid absorbed by the wool as a function of time was determined. Specimens of the conditioned wool cloth containing 2 grams of wool protein were placed in flasks with 50 ml portions of sulphuric acid solution and the flasks were kept at a temperature of 22 C. The flasks were shaken frequently. At stated intervals, aliquots were taken from the flasks and titrated with standard sodium hydroxide solution. Only one aliquot was taken from each flask. The decrease in acid present in solution, or absorbed acid, obtained for each time interval is the average of three titrations. The results are shown in figure 2 in which the milliequivalents of absorbed acid are plotted as a function of time. The amount of acid

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[5] Analyses of purified wool and of purified wool plus known amounts of sodium sulphate indicated that this method gives results satisfactory for present purposes. R. T. Mease, of the Bureau of Standards, is making a study of methods for analysis of wool for total and sulphate sulphur.

absorbed increases with increasing acid concentrations up to about 5 percent.

The curve through the solid circles in figure 2 shows the rate of absorption of acid by the wool cloth when soaked in a 5 percent solution of sulphuric acid at 35 C. The rate of absorption evidently increases with increase of temperature. However, the amount of acid absorbed at equilibrium is nearly the same as the amount absorbed in a 5 percent acid solution at 22 C.

2. WOOL-ACID-WATER SYSTEM WHEN THE WOOL IS DRIED

Specimens of wool were soaked in a 5 percent solution of sulphuric acid at 22 C for 3 hours and centrifuged for 3 minutes. They were then exposed to atmospheres of 9, 30, 65, and 90 percent relative humidities at 70 F. The samples were analyzed for sulphate, moisture and wool protein. The values in table 2 are given in grams per gram of wool protein at equilibrium and each is the average of three determinations.

TABLE 2.—*Moisture and sulphate contents of wool specimens treated with 5 percent sulphuric acid and exposed to atmospheres of different relative humidities at 70 F.*

[Quantities are per gram of wool protein]

Relative humidity	Moisture	Sulphate
Percent	*Gram*	*Gram*
9	0.0380	0.0813
30	.1118	.0810
65	.1372	.0806
90	.2484	.0810

The moisture contents of wool soaked in 2.5 and 5 percent solutions of sulphuric acid, centrifuged and dried to equilibrium with atmospheres of different relative humidities, and the moisture contents of similarly dried untreated wool are recorded in table 3.

TABLE 3.—*Moisture contents of acid-treated and untreated wool specimens after exposure to atmospheres of different relative humidities at 70 F.*

Relative humidity	H_2O per gram wool protein		Difference (3−2)
	Treated with 2.5% H_2SO_4	Untreated	
Percent	*Millimols*	*Millimols*	
6	1.98	2.47	0.49
30	5.19	6.19	1.00
65	7.37	7.98	.61
90	9.73	9.99	.26
	Treated with 5% H_2SO_4	Untreated	Difference
6	1.81	2.53	0.71
30	5.09	6.29	1.20
65	7.41	7.96	.55
90	10.04	10.22	.18

The wool treated with sulphuric acid absorbs less moisture than untreated wool. The difference in the amount absorbed varies with the relative humidity, a maximum difference being reached between 6 and 65 percent relative humidity. This observation will be discussed later.

WOOL-ACID-WATER SYSTEM WHEN THE DRIED WOOL IS BAKED

Specimens of the wool cloth were soaked for 3 hours at 22 C in 2.5, 5.0, 7.5, and 10 percent solutions of sulphuric acid and centrifuged. They were exposed to atmospheres of different relative humidities and then baked for different lengths of time. Samples containing 40 percent or more moisture were obtained by squeezing the excess liquor from the wool. Samples prepared this way contained only a very slightly larger amount of acid. The moisture contents of duplicate specimens which were not baked were determined. The baking was done in a laboratory electric drying oven (inside dimensions 1 ft by 1 ft by 1 ft). A beaker of water was kept in the oven in order to maintain high relative humidity.

The breaking strengths and ammonia nitrogen contents of the specimens after baking were determined as already described. The results are given in table 4.

These data indicate that for each acid concentration there is a critical moisture content above which the breaking strength of the cloth decreases and the ammonia nitrogen content increases when the wool is baked. Thus the critical moisture content of wool soaked in 2.5 percent sulphuric acid is about 50 percent, for 5 percent acid about 40 percent, and for 7.5 percent about 30 percent. The increase in ammonia nitrogen serves as a more sensitive measure of the deterioration taking place during the baking process than decrease in breaking strength. This is evident from table 4 in which samples treated with 2.5, 5.0, and 7.5 percent sulphuric acid solutions and containing 3 percent moisture showed no decrease in tensile strength after baking, but showed appreciable increases in ammonia nitrogen content. Both the physical and chemical breakdowns increase with increasing acid concentration in the specimen and increasing temperature in the baking oven. The decrease in breaking strength resulting from baking is independent of the time of baking. This can be explained by the assumption that the moisture content drops below the critical value in the first few minutes of baking after which no further breakdown occurs.

TABLE 4.—*Effects of acid and moisture contents and time and temperature of baking on the breaking strength and ammonia nitrogen contents of wool specimens*

H_2O in specimen before baking	Time of baking	Temperature of baking	Breaking strength 1-in. strip	Ammonia nitrogen per gram of specimen after baking[1]
Percent	*Minutes*	° *F*	*Pounds*	*Milligrams*
Original	------------	------------	27	0.20
12	60	250	27	0.54
Wool soaked in 2.5% sulphuric acid (0.058 g H_2SO_4 per gram wool protein)				
3	60	250	27	.58
9	60	250	27	.54
12	60	250	27	.64
21	60	250	27	.59
30	60	250	27	.71
50	60	250	26	1.01
65	60	250	23	1.25
Wool soaked in 5% sulphuric acid (0.081 g H_2SO_4 per gram wool protein)				
3	60	250	27	1.06
9	60	250	26	.96
12	60	250	26	.98
21	60	250	27	.96
30	60	250	27	1.09
40	60	250	25	1.15
50	15	250	23	1.53
50	30	250	22	1.59
50	45	250	23	1.50
50	60	250	23	1.52
64	15	250	20	1.66
64	30	250	19	1.72
64	45	250	19	1.65
64	60	250	20	1.60
50	60	225	27	1.50
50	60	200	25	1.38
50	60	175	25	1.30
50	60	150	25	1.41
Wool soaked in 7.5% sulphuric acid (0.098 g H_2SO_4 per gram wool protein)				
3	60	250	27	1.38
9	60	250	26	1.49
12	60	250	27	1.33
21	60	250	24	1.47
30	15	250	14	2.33
30	30	250	16	2.30
30	45	250	15	2.51
30	60	250	14	2.42
50	60	250	9	3.19
Wool soaked in 10% sulphuric acid (0.117 g H_2SO_4 per gram wool protein)				
3	60	250	21	2.15
9	60	250	20	2.13
12	60	250	21	2.19
21	60	250	20	2.30
30	60	250	8	3.90
40	60	250	3	4.75
50	60	250	1–2	5.92

[1] Specimens conditioned at a relative humidity of 65% and a temperature of 70 F.

4. AGENTS WHICH INFLUENCE THE DETERIORATION OF WOOL IN BAKING

Specimens of the wool cloth were soaked in a 5 percent solution of sulphuric acid for 3 hours at 22 C, centrifuged, and air dried. The cloth was cut into strips (6 in. by 1 in.), and 4 strips were placed in each of 4 glass tubes (10 in. by 1.5 in.) which had been drawn out at the ends. The 4 tubes were treated as follows:

1. Evacuated with a high-vacuum pump for 4 hours and sealed.
2. Moist carbon dioxide (CO_2 bubbled through water) was passed through the tube for 2 hours. This tube was then sealed.
3. Same as (2) substituting oxygen for carbon dioxide.
4. Same as (2) substituting air for carbon dioxide.

The tubes were placed in an oven at 250 F for 1 hour.

Similar experiments were made using untreated wool. The results given in table 5 indicate that both oxygen and moisture promote the deterioration of wool during baking. Sulphuric acid increases the deterioration considerably.

TABLE 5.—*Effect of baking on untreated specimens of wool and wool treated with 5 percent H_2SO_4 for 3 hours at 22 C, in vacuo and in moisture saturated atmospheres*

Atmosphere in tube	Appearance of specimen		Breaking strength 1-inch strip		Ammonia nitrogen per gram of specimen	
	Treated	Untreated	Treated	Untreated	Treated	Untreated
			Pounds	*Pounds*	*Milligrams*	*Milligrams*
Vacuum	Slightly yellow	No change	21	27	6.4	0.20
Carbon dioxide	do	Very slightly yellow	15	26	10.5	1.29
Oxygen	Dark brown	Yellow	0	18	23.2	3.88
Air	Yellow	Very slightly yellow	6	23	12.5	2.32

5. EFFECT OF STORAGE ON THE DRIED WOOL

Specimens of the wool cloth were soaked in 2.5, 5.0, 7.5, and 10 percent solutions of sulphuric acid for 3 hours at 22 C, centrifuged, and stored in atmospheres of relative humidities of 6, 30, 65, and 90 percent. They were exposed to a low intensity, incandescent light. At intervals of time, the ammonia nitrogen contents and breaking strengths were determined. The physical and chemical breakdowns of the specimens on storage are shown in figures 3 and 4, respectively.

There is no evidence of any marked increasing physical breakdown of any of the acid-treated specimens on storage in atmospheres of 6 and 30 percent relative humidities. The data suggest the possibility of some break-down increasing with time of exposure with 90 percent relative humidity using 5, 7.5, and 10 percent solutions of sulphuric acid. The samples were weaker within 24 hours after treatment with acid than before treatment, this initial loss in strength being greater at the higher acid concentrations.

With the exception of the specimens treated with 2.5 and 5 percent solutions of sulphuric acid, and exposed to a relative humidity of 6 percent, all of the specimens showed increasing ammonia nitrogen contents during storage. The ammonia nitrogen content increased with increasing relative humidities, acid concentrations, and time of storage.

Here again it is shown that the ammonia nitrogen content gives a more sensitive measure of the deterioration taking place in the wool

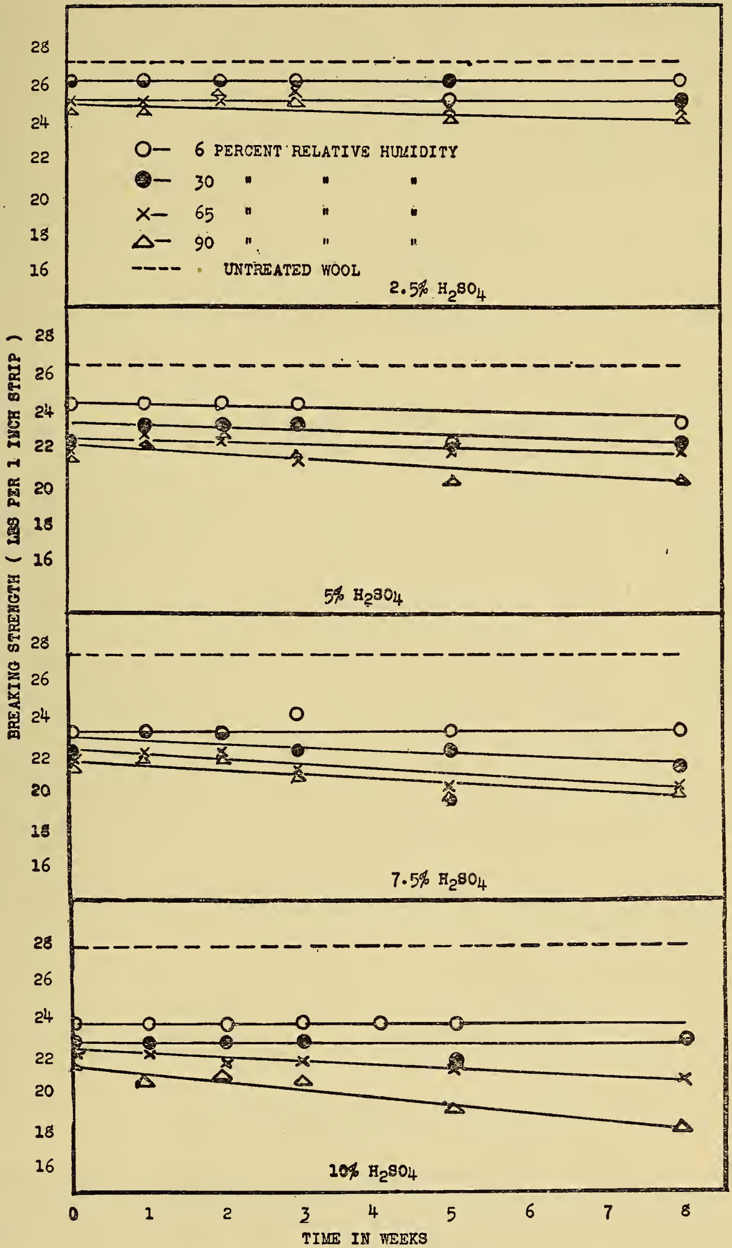

Figure 3.—*The effect of storage at different relative humidities on the breaking strength of acid-treated wool.*

cloth than the breaking strength. That ammonia is found during protein deterioration is well known. Lloyd [6] states that ammonia is

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[6] D. J. Lloyd, Chemistry of the Proteins, p. 13, J. & A. Churchill, 1926.

always released during protein hydrolysis, apparently from the acid amide groups. Leiben and Urban [7] studied the splitting of ammonia from amino acids and other substances and found the ammonia cleavage proceeds much more rapidly in acid than in an alkaline or neutral medium. In studying the photochemical decomposition of silk [8] the writer found that the deterioration was accompanied by the formation of ammonia and that the greatest amounts were formed in a given time in acid-treated samples.

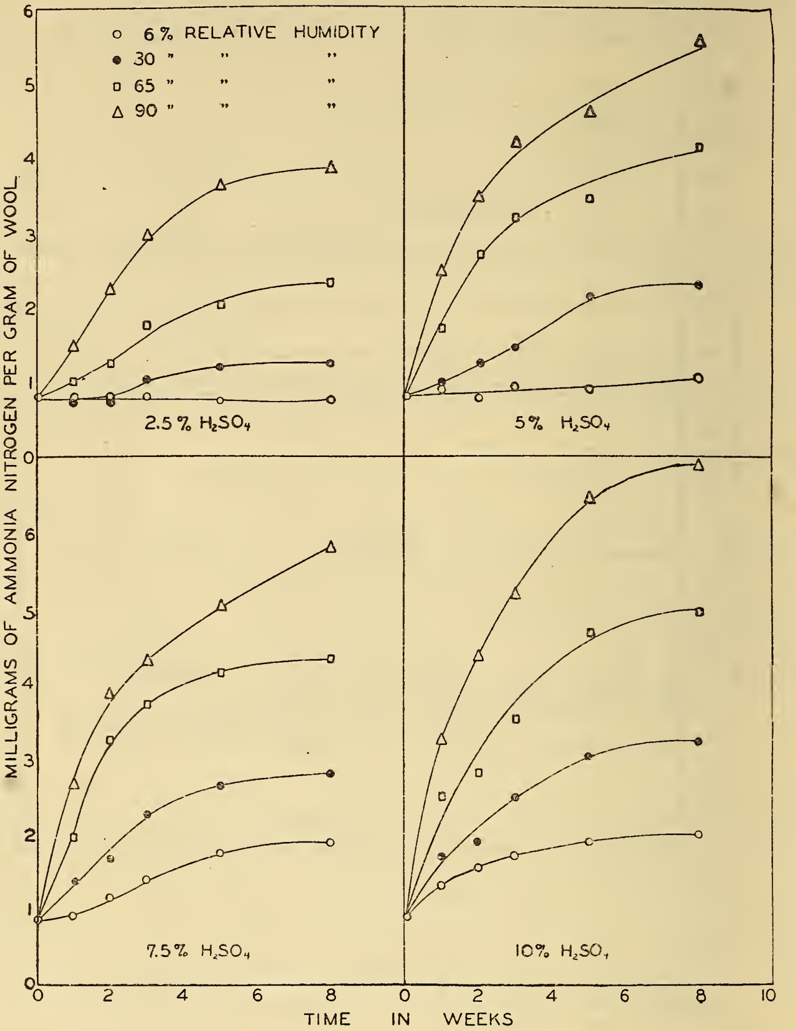

Figure 4.—*The effect of storage at different relative humidities on the ammonia nitrogen content of acid-treated wool.*

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[7] F. Leiben and F. Urban, The Splitting of Ammonia From Amino Acids and Other Substances in the Light of a Quartz Lamp, Biochem. Zeit., vol. 239, pp. 250–6, 1931.

[8] Unpublished results.

IV. NATURE OF THE SYSTEM WOOL—SULPHURIC-ACID—WATER

The reaction of sulphuric acid with wool depends on the chemical constitution and molecular organization of the wool protein. Sulphuric acid may be taken up and held by wool in three ways. First, it may be chemically combined, the combined acid being bound by primary valence forces at the free amino and imino groups and at the peptide linkages. Second, it may be absorbed at micellar interfaces and held by secondary valence forces. Third, it may be absorbed in capillary spaces in the wool fiber.

Considerable evidence has been presented for both the chemical type and adsorption type of combination of acids with proteins.[9] Additional evidence that at least some of the acid is chemically combined with the wool protein was obtained in a study on the absorption of iodine by wool.[10] The iodine number of wool is 14.1. After the wool is soaked in normal sulphuric acid the iodine number is only 2.6. On rinsing the acid-treated wool in running water, the iodine number rises after 1 hour to 9.6 and remains at that value on continued rinsing. If an acid-treated specimen is first treated with a 1 percent sodium carbonate solution to neutralize the acid and is then rinsed, the iodine number is the same as that of untreated wool. Since the iodine reacts with the free amino groups of the wool, these observations indicate that the sulphuric acid combines with the free amino groups and occupies a place that would ordinarily be available to iodine. The combined acid is only removed by neutralization with alkali.

However, not all of the acid absorbed by the wool can be accounted for by assuming combination with the free amino groups. In figure 2 it is shown that wool treated with 5 percent sulphuric acid absorbs about 1 milliequivalent of acid per gram of wool. Meunier and Rey [11] employing a modification of the Van Slyke apparatus found wool to contain 0.57 percent of amino nitrogen. This would account for only 0.41 milliequivalent of acid. Speakman and Hirst [12] using similar technique concluded that the amount of free amino nitrogen obtained from wool approached a limiting value of 0.92 percent. This amount accounts for only 0.66 milliequivalent of the acid.

That the amount of acid bound by the free amino groups of proteins does not account for the total acid taken up has long been known. Hitchcock [13] found that gelatin combined with 0.89 milliequivalent of hydrochloric acid whereas deaminated gelatin combined with 0.44 milliequivalent. Osborne [14] found that the amount of hydrochloric acid taken up by edestin was roughly 5 times the amount calculated on the basis of the amino groups. Sturin [15] neutralizes about 8 times as much acid as can be accounted for by the free amino groups.

It is evident that a large proportion of the acid absorbed by wool is not accounted for by its free amino nitrogen content. Several

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[9] W. Hoffman and R. Gortner, Physico-Chemical Studies on Proteins, Colloid Symposium Monograph, vol. 2, pp. 209–368, 1925. The Chemical Catalog Co.

[10] Unpublished work by H. A. Neville, W. Fritz, and Milton Harris.

[11] L. Meunier and G. Rey, Sur les Proprietés de la Laine, Jour. Soc. Leather Trade Chem., vol. 11, pp. 508–519, 1927.

[12] J. B. Speakman and M. C. Hirst, The Constitution of the Keratin-Molecule. Trans. of the Faraday, Soc., vol. 29, pp. 148–164, 1933.

[13] Hitchcock, The Combination of Deaminized Gelatin with Hydrochloric Acid. Jour. Gen. Physiol. vol. 6, pp. 95–104, and 457, 1923.

[14] T. B. Osborne, The Basic Character of the Protein Molecule, Jour. Am. Chem. Soc., vol. 24, pp. 39–78, 1902.

[15] A. Kossel and F. Weiss, Zeit. Physiol. Chem., vol. 78, pp. 402–413, 1912. Uber das Sturin.

workers have shown that the residual combining capacity of proteins may be attributed to the peptide linkages[16] [17] and to the imino groups. It is probable that these groups also account for a portion of the acid in wool in excess of that necessary to react with the amino groups.

The absorption of moisture from the atmosphere by wool is, in general, very similar to the absorption of acids from solution. The amount of moisture absorbed depends upon the relative humidity; that is, the effective moisture concentration, whereas the amount of acid absorbed depends on the pH; that is, the effective hydrogen-ion concentration. Both also depend on the physical and chemical nature of the specimen under consideration. Analogously to the way in which wool takes up acids, it is assumed that moisture may be taken up in 3 ways; namely, by chemical combination, by adsorption, and by capillary condensation.

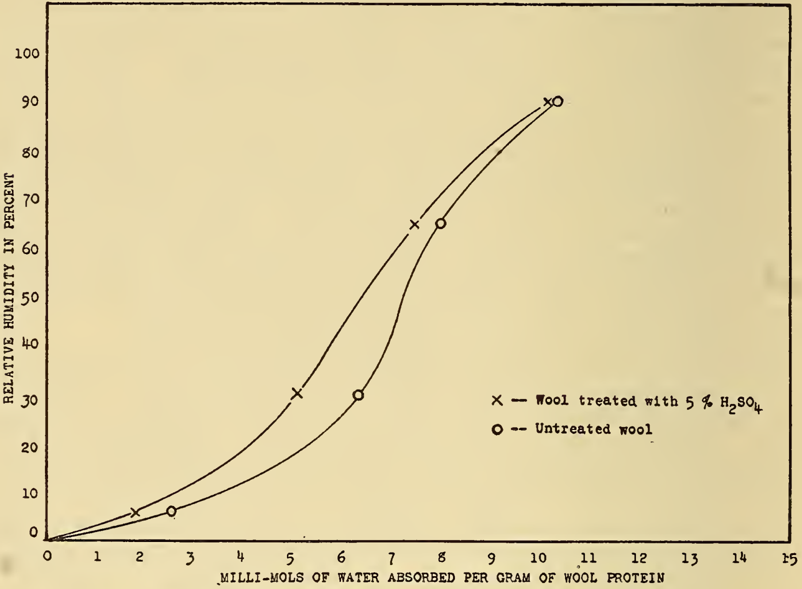

FIGURE 5.—*The absorption of water by untreated and acid-treated wool.*

It is shown in table 3 that wool treated with sulphuric acid absorbs less moisture than untreated wool. Evidence is presented above that sulphuric acid combines with the amino groups of wool. It seems logical to conclude that the difference observed in column 4 of this table may be attributed either to combined sulphuric acid occupying places that would ordinarily be available to water, or that the combined and/or adsorbed acid has altered the forces capable of attracting the water.

Not all of the moisture taken up by the wool is combined or adsorbed, for if this were the case the two curves shown in figure 5 should lie parallel to each other. At the lower relative humidities the

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[16] T. B. Osborne and C. S. Leavenworth, Protein Copper Compounds, Jour. Biol. Chem., vol. 28, p. 109, 1916.

[17] M. Siefried, Die Carbamino und Hydroxykohlensaurereaktion. Ergebnisse Physiol., vol. 9, p. 334, 1910.

moisture may be taken up largely by adsorption and chemical combination and these processes occur simultaneously. At higher relative humidities the third process also occurs, namely, the capillary condensation of moisture. At very high relative humidities, for example 90 percent, a large proportion of the moisture taken up is held by the capillary forces. Assuming that the acid in the wool has not changed the nature of these forces, both the acid-treated and untreated specimens would take up like quantities of moisture by this process. This would account for the converging of the two curves. The curves for wool treated with higher concentrations of sulphuric acid may cross at the higher relative humidities because of the hygroscopic nature of the excess of sulphuric acid present.

WASHINGTON, D.C., February 23, 1934.