

## RESEARCH PAPER RP980

*Part of Journal of Research of the National Bureau of Standards, Volume 18,**March 1937*

## REACTION OF WOOL WITH STRONG SOLUTIONS OF SULFURIC ACID

By Milton Harris, Ralph Mease, and Henry Rutherford<sup>1</sup>

## ABSTRACT

Data on the effect on wool of treatment with solutions of sulfuric acid of different concentrations at 5, 25, and 50° C for 15 minutes and of an 80-percent solution of sulfuric acid at 25° C for different lengths of time are presented. The results suggest that strong sulfuric acid reacts with the basic groups in wool to form sulfamic acid derivatives. The acid-combining capacity of wool decreases and the base-combining capacity increases in proportion to the number of sulfamic acid groups formed.

## CONTENTS

	Page
I. Introduction.....	343
II. Materials and methods.....	343
III. Results and discussion.....	345
1. Effect of temperature and acid concentration.....	345
2. Effect of the duration of treatment.....	346
3. Nature of the reaction of wool with strong sulfuric acid.....	346
4. Acidic and basic properties of the sulfamic acid derivative of wool.....	348
IV. References.....	350

## I. INTRODUCTION

The use of strong solutions of sulfuric acid for the removal of cotton from mixtures with wool has been suggested by several investigators [1, 2, 3].<sup>2</sup> In studies relating to the analysis of wool-cotton textiles, Mease and Jessup [4] found that during treatment with an 80-percent solution of sulfuric acid,<sup>3</sup> wool gained from 5 to 8 percent in weight. Their results indicate that a relatively stable compound is formed, since this combined acid is not removed by prolonged washing with water or with solutions of ammonium hydroxide, sodium carbonate, or triethanolamine.

The present investigation was undertaken to study the nature of the reaction of wool with strong solutions of sulfuric acid and to study some of the properties of its product.

## II. MATERIALS AND METHODS

The material used in this work was worsted cloth, plain weave, weighing 8 ounces per running yard (56 inches wide) or white worsted yarn prepared from raw wool which had been extracted with Stoddard

<sup>1</sup> Dr. Harris and Mr. Rutherford are research associates at the National Bureau of Standards, representing the American Association of Textile Chemists and Colorists. The work reported here was aided by grants from the Textile Foundation, Inc., and the Chemical Foundation, Inc.

<sup>2</sup> The numbers in brackets refer to literature references at the end of this paper.

<sup>3</sup> This concentration was obtained by mixing 80 ml of concentrated sulfuric acid (94 percent, sp gr 1.84) with 25 ml of water. The wool was immersed for 15 minutes in 80 to 100 times its weight of solution at room temperature.

solvent and washed with water. All the samples were further purified by extractions with alcohol and ether, followed by washing with water at about 50° C.

The samples of wool were treated with about 50 times their weight of sulfuric acid solutions. After the treatment with acid, the wool was immediately transferred to a large volume of running cold water and vigorously stirred in order to prevent local heating during the dilution of the excess of acid. The samples were then washed in running distilled water until the wash waters no longer gave tests for sulfate, the time required generally being about 72 hours.<sup>4</sup> The test for sulfate was made by allowing the samples of wool to remain in contact with a small amount of distilled water for about one-half hour and testing the liquor with barium chloride.

The percentage increase in weight of the wool before and after treatment was computed on the basis of the oven-dry weight.

The combined sulfuric acid in the wool was determined by the method of Mease [5]. Ammonia nitrogen was determined by measuring the ammonia liberated when the wool was boiled in a saturated solution of magnesium oxide.

The yellowing of the wool by the acid treatment was determined by measuring the reflectance of the sample with respect to a magnesium-oxide standard, at wave length 435.8 millimicrons, with a Martens photometer, mercury-arc lamp, and suitable filter. The reflectances of the dyed samples were determined with the same instrument at wave length 578 millimicrons, which is located in the region of maximum absorption for the blue dyes used.

The breaking strength of the cloth was determined on a pendulum-type testing machine using the strip method. The samples were 6 inches long and 1 inch wide, cut warpwise of the cloth. The distance between the jaws was 3 inches at the start of the test. All the samples were conditioned and tested in a room maintained at a relative humidity of 65 percent and a temperature of 70° F.

The acid- and base-combining capacities were determined by soaking samples of the wool for 4 hours (equilibrium appears to be reached in this time) in 0.1*N* solutions of hydrochloric acid,<sup>5</sup> sulfuric acid, and sodium hydroxide, the last being at 1 to 2° C to prevent decomposition of the wool fiber. The amount of acid or base combined was then found by titration of an aliquot of the mother liquor.

<sup>4</sup> Samples of wool which had been treated with a 4-percent solution of sulfuric acid for 30 minutes and then washed for 72 hours, regained 98 to 99 percent of their original acid-combining capacities.

<sup>5</sup> The limiting acid-combining capacity appears to be reached at about pH 1.

TABLE 1.—Effect on wool of treatment with different concentrations of sulfuric acid at 5, 25, and 50° C for 15 minutes

Concentration of H <sub>2</sub> SO <sub>4</sub> , by weight	SO <sub>4</sub> from sulfuric acid treated wool	Reflectance <sup>1</sup> R <sub>z</sub> /R <sub>MgO</sub>	Breaking strength of 1-in. strip	Ammonia nitrogen
TEMPERATURE 5° C				
Percent	Percent	R <sub>z</sub> /R <sub>MgO</sub>	lb	mg/g
19	0.42	46.2	29	0.43
34	.66	47.1	29	.42
48	.68	47.0	29	.41
60	.64	47.5	29	.48
69	.69	46.2	29	.43
80	1.02	46.3	27	.43
85	3.42	44.3	28	.50
94	11.00	43.9	26	1.67
TEMPERATURE 25° C				
19	0.88	45.6	28	0.52
34	1.20	47.8	28	.48
48	1.21	46.1	28	.68
60	1.38	46.0	26	.64
69	1.37	45.3	27	.52
80	6.91	43.2	26	.60
85	10.20	40.4	24	1.20
94	11.70	39.1	23	2.28
TEMPERATURE 50° C				
19	0.65	47.6	28	0.43
34	.71	47.1	26	.63
48	.72	47.0	25	.62
60	3.50	41.2	18	.70
69	3.79	37.0	16	.79
80	6.14	35.4	19	.92
85	8.13	34.7	21	.91
94	9.39	35.2	21	1.60

<sup>1</sup> The values represent the ratio of the brightness of the sample to that of a standard white magnesium-oxide surface under the same conditions of illumination and observation, for light of wave length 435.8 millimicrons. The darker (or yellower as in this case) the specimen, the smaller the value for light reflected.

### III. RESULTS AND DISCUSSION

#### 1. EFFECT OF TEMPERATURE AND ACID CONCENTRATION

In view of the procedures [4] recommended for the removal of cotton from mixtures with wool by the sulfuric acid method, it seemed advisable to study first the effect of different concentrations of sulfuric acid on wool. The effects of the different treatments at 5, 25, and 50° C for 15 minutes are summarized in table 1. The results indicate marked changes in the amount of acid combined between 69- and 80-percent sulfuric acid at 5 and 25° C and between 48- and 60-percent acid at 50° C. Since wool, in an 80-percent solution of sulfuric acid at 25° C, reacts with a relatively large amount of acid, as shown by the sulfate analyses, and since the reaction is accompanied by comparatively little deterioration of the fiber, as evidenced by reflectance, breaking strength and ammonia-nitrogen determinations, this concentration and temperature of acid solution were chosen for the further studies.

## 2. EFFECT OF THE DURATION OF TREATMENT

Samples of wool were treated with an 80-percent solution of sulfuric acid at 25° C for different lengths of time, and washed as previously described. The increase in weight and the sulfate obtained from the treated wool are recorded in table 2. The data indicate that a maximum increase in weight is obtained in the treatment for 30 minutes. On treatment for periods longer than 30 minutes, the wool not only decreased in weight, but the amount of sulfate obtained from it also decreased. The appearance of the wool treated for periods of longer than 30 minutes indicated that considerable degradation had occurred.

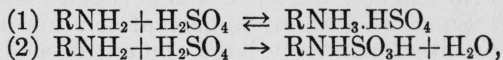
TABLE 2.—Effect on wool of treatment with an 80-percent solution of sulfuric acid at 25° C for different lengths of time

Duration of treatment	Increase in weight	SO <sub>4</sub> from treated wool
<i>Minute</i>	<i>Percent</i>	<i>Percent</i>
3	0.56	0.81
6	2.35	3.53
9	3.82	4.82
12	5.60	6.37
15	6.20	7.23
20	6.77	7.90
30	7.19	8.38
40	7.03	8.34
60	6.71	7.78
105	6.58	7.17
150	4.93	6.74

## 3. NATURE OF THE REACTION OF WOOL WITH STRONG SULFURIC ACID

Of the two principal theories to account for the acid taken up by wool, namely, the chemical and the physical or adsorption theories, the work of Knecht [6], Mayer [7], Porai-Koschitz [8], and Speakman [9] favors the former. These investigators showed that wool has an acid-combining capacity of about 0.80 millimole of acid per gram of wool. In addition, Harris and Kanagy [10] showed that this combined acid may be accounted for by the free amino groups and by the guanidine nucleus of the arginine in wool. Speakman [9], utilizing his own data and also the data of Dietl [11], Fort and Lloyd [12], and Georgievics and Pollack [13] to calculate the amounts of acid combined as a function of pH, demonstrated that sulfuric acid was practically monobasic in reaction with wool.

On the basis of the above work, the following equations which give a schematic representation of two possible mechanisms by which sulfuric acid may be taken up and held by the basic groups in wool, are postulated.



where R represents the portion of the wool molecule to which the basic group is attached.

The acid in the compound formed in equation 1 should be reversibly held; that is, it should be slowly removed by washing with water, rapidly removed by pyridine [14], triethanolamine [15], sodium terephthalate [15] and other alkaline reagents, and readily replaceable by

acid dyestuffs. Equation 1 indicates the reaction which is assumed to take place in dilute solutions of sulfuric acid.

On the other hand, the acid in the compound formed according to equation 2 should be irreversibly held under the conditions mentioned above. It appears that such a compound would be formed only under dehydrating conditions, for example, in the presence of strong sulfuric acid, and that the acid would be removed by hydrolytic processes<sup>6</sup> according to the reverse of equation 2. In other words, the fact that sulfate is obtained when the acid-treated wool is analyzed by the method of Mease [5], is no indication that it existed as such in the wool.

It should be possible, therefore, to determine which type of compound is formed when wool is treated with strong or dilute solutions of sulfuric acid by recalculating the data on the  $\text{SO}_4$  obtained from the

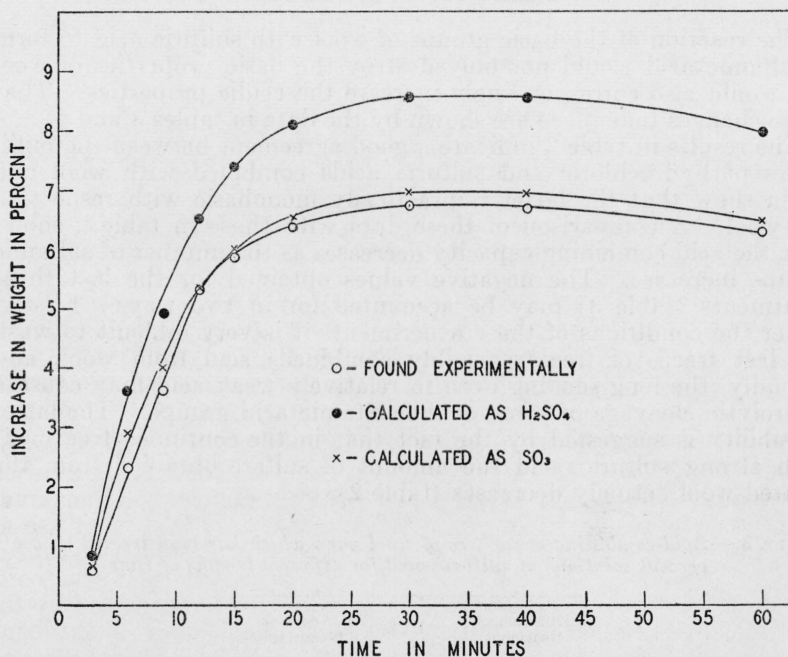


FIGURE 1.—Comparison of the actual increase in weight of wool resulting from treatments with an 80-percent solution of sulfuric acid at 25° C for different lengths of time with the increase obtained by calculating the  $\text{SO}_4$  obtained from the treated wool as  $\text{H}_2\text{SO}_4$  and as  $\text{SO}_3$ .

treated wool in terms of  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$ , and comparing the calculated weights with the actual increase in weight of the wool after treatment with sulfuric acid. The data obtained by recalculating the data given in table 2 are shown graphically in figure 1. The results suggest that the reaction of wool with the strong solutions of sulfuric acid has proceeded according to equation 2, and that a sulfamic acid derivative of wool has been formed.

That the reaction of wool with dilute solutions of sulfuric acid proceeds in a different manner is demonstrated by the following

<sup>6</sup> The hydrolytic conditions necessary for the reverse of equation 2 are so drastic as to cause degradation of the wool fiber. Accordingly, equation 2, which represents the manner in which the acid is assumed to be held by the original wool fiber, is written as an irreversible reaction.

experiment. A 2-g sample of wool was treated with 100 ml of a 4-percent solution of sulfuric acid for 30 minutes, after which the excess of acid was squeezed out by hand. The sample was then soaked for 15 seconds in 100 ml of distilled water, squeezed again, and then partially dried by allowing it to remain in contact with air at room temperature for about 6 hours. It was finally dried to constant weight in the oven at 105° C. The sample showed a 5.5 percent increase in weight. The calculated increases in weight, based on the sulfate analyses, were 5.3 percent calculated as  $\text{H}_2\text{SO}_4$  and 4.3 percent calculated as  $\text{SO}_3$ . These results suggest that this reaction has proceeded as shown in equation 1.

#### 4. ACIDIC AND BASIC PROPERTIES OF THE SULFAMIC ACID DERIVATIVE OF WOOL

The reaction of the basic groups of wool with sulfuric acid to form a sulfamic acid would not only destroy the basic properties of wool but would also correspondingly increase the acidic properties. That these changes take place are shown by the data in tables 3 and 4.

The results in table 3 indicate a good agreement between the millimoles of hydrochloric and sulfuric acids combined with wool and again show that the latter is practically monobasic with respect to the wool. A comparison of these data with those in table 2 shows that the acid-combining capacity decreases as the number of sulfamic groups increases. The negative values obtained for the last three treatments (table 3) may be accounted for in two ways. Firstly, under the conditions of these experiments it is very difficult to wash the last traces of free (reversibly combined) acid from wool, and secondly, the long soaking even in relatively weak acid may cause a hydrolytic cleavage of some of the sulfamic acid groups. The latter possibility is suggested by the fact that in the continued treatment with strong sulfuric acid the amount of sulfate obtained from the treated wool actually decreases (table 2).

TABLE 3.—*Acid-combining capacities of wool yarn which has been treated with 80-percent solutions of sulfuric acid for different lengths of time*

Duration of treatment	HCl	Acid-combined $\text{H}_2\text{SO}_4$
<i>Minutes</i>	<i>Millimole</i>	<i>Millimole</i>
0	0.81	0.84
3	.62	.63
6	.34	.35
9	.28	.33
12	.21	.26
15	.00	.04
20	-.08	-.09
30	-.08	-.06
40	-.11	-.09

TABLE 4.—Alkali-combining capacities of wool yarn which has been treated with 80-percent solutions of sulfuric acid for different lengths of time

Duration of treatment	NaOH combined	Increase in base-combining capacity of the treated wool	
		Found	Calculated on the basis of the combined SO <sub>3</sub>
Minutes	Millimoles	Millimole	Millimole
0	0.64		
3	.80	0.16	0.09
6	1.17	.53	.38
9	1.29	.65	.52
12	1.39	.75	.70
20	1.50	.86	.88
40	1.62	.98	.94

Although the acid-combining capacities of the treated wools decrease, the data in table 4 show a corresponding increase in base-

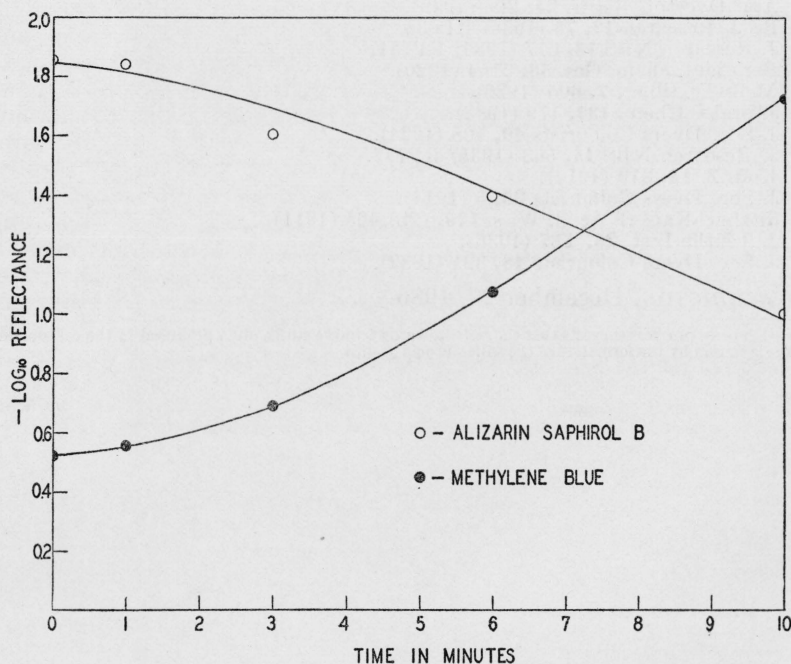


FIGURE 2.—Effect of treatment with an 80-percent solution of sulfuric acid on the dyeing characteristics of wool cloth, as shown by change in reflectance of light at wave length 578 millimicrons.

combining capacity with an increasing number of sulfamic acid groups. The increase in alkali-combining capacity, as found experimentally, is in good agreement with the values which were calculated on the assumption that 1 mole of the combined SO<sub>3</sub> reacts with 1 mole of sodium hydroxide. This also constitutes further evidence that the product of the reaction of wool with strong sulfuric acid is a sulfamic acid derivative since, if the acid were held as shown in equation 1, 2 moles of sod-

ium hydroxide would be required for each mole of combined acid [14], because the wool is regenerated.

The changes in acidic and basic properties of the treated wool are also manifested in the dyeing characteristics of the fiber. Samples of wool cloth which had been treated with 80-percent solutions of sulfuric acid for different lengths of time were dyed in the same bath containing approximately 2 percent of alizarin saphirol *B* (based on the weight of fiber). A second set of the acid-treated samples were similarly dyed using methylene blue.

The curves in figure 2 show that the amount of acid dyestuff (alizarin saphirol *B*) absorbed decreases and the amount of basic dyestuff (methylene blue) absorbed increases with increasing time of treatment with strong sulfuric acid.<sup>7</sup>

#### IV. REFERENCES

- [1] *J. Textile Inst.* **23**, P214 (1932);
- [2] R. G. Griffin. *Technical Methods of Analysis*, p. 506. (McGraw-Hill Book Co., Inc., N. Y., 1927).
- [3] *Am. Dyestuff Repr.* **25**, 296 (1936).
- [4] *BS J. Research* **12**, 75 (1934) RP635.
- [5] *J. Research NBS* **13**, 617 (1934) RP731.
- [6] *Ber. deut. chem. Ges.* **53**, 2164 (1920).
- [7] *Mell. Textilber.* **7**, 605 (1926).
- [8] *J. prakt. Chem.* **137**, 179 (1933).
- [9] *J. Soc. Dyers Colourists* **40**, 408 (1924).
- [10] *J. Research NBS* **14**, 563 (1935) RP787.
- [11] *Koll. Z.* **14**, 319 (1914).
- [12] *J. Soc. Dyers Colourists* **30**, 5 (1914).
- [13] *Sitzber. Kaiserl. Acad. Wiss.* **120**, (2b) 465 (1911);
- [14] *J. Textile Inst.* **26**, T87 (1935).
- [15] *J. Soc. Dyers Colourists* **48**, 321 (1932).

WASHINGTON, December 29, 1936.

<sup>7</sup> Work now in progress suggests that the resist towards acid dyes, often produced in the carbonizing process, is caused by the formation of the sulfamic acid groups.