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## EFFECT OF ALKALIES ON WOOL

By Milton Harris <sup>1</sup>

## ABSTRACT

Data on the effect of various alkaline reagents on the physical and chemical properties of wool yarn are presented. When wool is treated with dilute sodium-hydroxide solutions, a rapid splitting off of a portion of the sulphur occurs. On continued treatment, the sulphur content of the residual wool approaches a constant value of about 1.8 percent. The results indicate that the alkaline treatment has changed a portion of the sulphur to a form which tends to resist further splitting from the molecule. Oxidizing and reducing agents attack the disulphide groups and make wool more susceptible to alkaline treatments. The susceptibility of untreated wool to alkaline reagents appears to be closely associated with the lability of its sulphur in alkaline solutions.

## CONTENTS

	Page
I. Introduction.....	63
II. Materials and methods.....	64
III. Results and discussion.....	65
1. Effect of alkaline reagents on wool yarn.....	65
2. Nature of the action of alkalies on the sulphur of wool.....	66
3. Effect of alkalies on wool treated with oxidizing and reducing agents.....	69
IV. Conclusions.....	71
V. References.....	71

## I. INTRODUCTION

The effect of alkalies on wool has been studied by many workers, generally from the standpoint of the effect of these reagents on the physical properties of the fiber. Wool fibers deteriorate rapidly in dilute solutions of sodium hydroxide. Buntrock (1),<sup>2</sup> Washburn (2), Matthews (3), and Speakman (4) showed, however, that when the concentration is increased above 15 percent, the strength of wool yarn begins to increase and reaches a maximum with a 38-percent sodium-hydroxide solution, at which point the strength of the yarn is 30 percent greater than the original strength. Speakman further demonstrated that the elastic property of a single fiber is unaffected after immersion in a 38-percent caustic-soda solution, and that the increase in strength of the wool yarn is due to surface gelatinization, which causes fibers to bind together in the dried yarn. Chapin (5) studied

<sup>1</sup> Research Associate at the National Bureau of Standards for the American Association of Textile Chemists and Colorists. The work reported here was made possible by a grant from the Textile Foundation, Incorporated.

<sup>2</sup> The figures in parentheses here and elsewhere in the text refer to the numbered references at the end of this paper.

the relative effects of sodium and potassium carbonates and soaps on wool and, for equal molecular concentrations, found them to be about the same.

Recent investigations by Goddard and Michaelis (6), Speakman (7), Pulewka (8), and Marriott (9) have shown that when wool and other keratins are treated with alkaline reducing agents, the disulphide linkages in the molecule are split and the physical structure of the fiber is destroyed. Goddard and Michaelis stated that the reducing agents acted on wool without bringing about any appreciable chemical alteration, other than that concerned with sulphur. Kuster and Koppel (10), however, found that as wool dissolved in sodium-sulphide solutions, a part of it undergoes disintegration with the formation of ammonia and diffusible, nitrogenous, cleavage products.

The present investigation was undertaken to obtain quantitative data on the effect of alkalis on both the physical and chemical properties of wool. Such data are of importance in interpreting the susceptibility of wool to alkaline reagents.

## II. MATERIALS AND METHODS

White worsted yarn prepared from raw wool which had been extracted with Stoddard solvent and washed with water, but which had received no previous chemical treatment, was used in this work. The yarn was further purified by extractions with alcohol and ether for 6 hours each and then washed with water at 125° F. 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 conditioned wool contained 14.3 percent of nitrogen, 0.02 percent of ammonia nitrogen, 3.16 percent of sulphur, and 14.4 percent of moisture.

The breaking-strength tests of the yarn were made by the single-strand method on a pendulum-type machine having smooth grips of the drum type, 1 inch in diameter. The distance between the centers of the drums was 10 inches. The values reported are the averages of 25 determinations.

The resiliency tests were made, employing a compressometer (11). The compressional resilience of the specimen is the amount of work recovered from the specimen when the pressure is decreased from 2.0 to 0.1 pound per square inch, expressed as a percentage of the work done on the specimen when the pressure is increased from 0.1 to 2.0 pounds per square inch. The measurements were made on four layers of yarn, wound on metal frames made from thin brass plates, 2 $\frac{3}{8}$  by 2 $\frac{3}{8}$  by  $\frac{1}{16}$  inch, from the center of which a 2-inch square had been cut. Two layers were put on the frames in each direction, each layer containing nine ends per inch.

The total nitrogen was determined by the Kjeldahl method, the ammonia nitrogen by distillation from magnesium oxide suspension, the total sulphur by the oxygen-bomb method (12) and the cystine sulphur by the Sullivan method (13). An ammoniacal sodium-nitroprusside solution was used for the qualitative detection of the sulphhydryl group.

The yellowing of the wool by the alkaline treatment was determined by measuring the reflectance of the specimen with respect to a magnesium-oxide standard at wave length 435.8 millimicrons with a Martens photometer, mercury-arc lamp, and suitable filter.

## III. RESULTS AND DISCUSSION

## 1. EFFECT OF ALKALINE REAGENTS ON WOOL YARN

Four-gram samples of wool yarn were treated with 200-ml portions of sodium-carbonate and sodium-hydroxide solutions of various concentrations at a temperature of 125° F for 30 minutes. The supernatant liquor was poured off, the wool washed for 4 hours in running distilled water, and then conditioned in an atmosphere of 65 percent relative humidity and 70° F. The effects of the treatments on the physical and chemical properties of the wool are shown in tables 1 and 2. The results indicate that under the conditions of these experiments, there is no appreciable damage done to wool in sodium-carbonate solutions of concentrations lower than about 4 grams per liter (pH 11.1), and in sodium-hydroxide solutions lower than about 0.038 g per liter (pH 11.8). Above these concentrations, the loss in weight of wool, nitrogen, and sulphur increases and the compressional resilience and the reflectance decrease with increasing alkali concentration. The breaking strength showed no significant changes.

TABLE 1.—Effect on wool of aqueous sodium-carbonate solutions at 125° F for 30 minutes

Concentration of Na <sub>2</sub> CO <sub>3</sub>	pH	Nitrogen in mother liquor	Sulphur content	Reflectance <sup>1</sup> R <sub>X</sub> /R <sub>MgO</sub>	Breaking strength	Compressional resilience
g/liter		mg/wool	Percent		kg	Percent
0.....	6.80	0.14	3.16	0.481	1.19	52
0.1.....	10.33	.20	3.17	.480	1.18	51
0.5.....	10.70	.17	3.16	.480	1.19	53
1.0.....	10.89	.15	3.15	.481	1.28	52
2.0.....	11.02	.18	3.17	.482	1.26	50
4.0.....	11.00	.40	3.12	.482	1.25	50
7.0.....	11.24	.61	3.11	.469	1.26	48
10.0.....	11.30	.65	3.03	.469	1.21	43

<sup>1</sup> The values represent the fraction of incident light reflected. The darker (or yellower as in this case) the specimen, the smaller the value for light reflected.

TABLE 2.—Effect on wool of aqueous sodium-hydroxide solutions at 125° F for 30 minutes

Concentration NaOH	Original pH	pH of mother liquor	Loss in weight of wool	Nitrogen in mother liquor	Sulphur content of wool after treatment	Reflectance R <sub>X</sub> /R <sub>MgO</sub>	Breaking strength	Compressional resilience
mg/liter			Percent	mg/g wool	Percent		kg	Percent
0.0.....	6.80	6.68	0.61	0.09	3.15	0.475	1.20	51
0.38.....	9.11	6.90	.60	.10	3.16	.471	1.19	52
3.8.....	10.83	8.77	.65	.08	3.17	.474	1.12	50
19.2.....	11.49	10.14	.69	.08	3.15	.476	1.20	52
38.3.....	11.82	11.33	.67	.11	3.03	.467	1.16	53
153.2.....	12.41	12.26	1.36	.84	2.93	.460	1.14	49
268.1.....	12.61	12.49	2.14	1.79	2.74	.463	1.19	48
383.0.....	12.73	12.66	2.55	2.59	2.55	.455	1.16	35

The effect of various other alkaline reagents was determined by treating 4-gram samples of the wool yarn with 200-ml portions of 0.25-percent solutions of soap, borax, trisodium phosphate, sodium carbonate, and sodium metasilicate, all of which had been brought to pH 12.2 by the addition of sodium hydroxide. The temperature was 150° F and the time of treatment 30 minutes. The skeins were

washed for 4 hours in running distilled water and conditioned. The results are recorded in table 3. The data indicate that at pH 12.2, the solutions of sodium carbonate and trisodium phosphate cause the greatest chemical degradation of the wool. Duplicate experiments with these materials without the addition of sodium hydroxide were not made. The specimens treated with the soap solution were the whitest and most resilient, but showed the greatest decrease in breaking strength. The decrease in strength is attributed to the fact that the soap solution kept the wool yarn soft and fluffy, whereas in the yarn treated with other alkaline solutions, the fibers were matted and stuck together.

TABLE 3.—*Effect on wool of 0.25-percent solutions of various reagents brought to pH 12.2 with NaOH*

[Time of treatment was 30 minutes and the temperature 150° F]

Reagent	Loss in weight			Reflectance $R_x/R_{M_0}$	Breaking strength	Compress- sional resilience
	Wool	Sulphur	Nitrogen			
	mg/g	mg/g	mg/g		kg	Percent
Sodium hydroxide.....	23.0	6.6	3.37	0.424	1.22	44
Soap.....	19.1	5.9	2.85	.477	.94	51
Borax.....	20.8	7.6	2.96	.429	1.14	44
Trisodium phosphate.....	24.8	8.4	3.83	.425	1.12	42
Sodium carbonate.....	26.0	8.2	3.66	.432	1.10	43
Sodium metasilicate.....	20.6	6.9	3.06	.442	1.13	44

## 2. NATURE OF THE ACTION OF ALKALIES ON THE SULPHUR OF WOOL

Although wool contains about five times as much nitrogen as sulphur by weight, the data in table 3 show that about twice as much sulphur as nitrogen was removed from the wool under the conditions of the experiments. This indicated that the susceptibility of wool to alkalis is closely related to the lability of its sulphur in alkaline solutions. It seemed pertinent, therefore, to study the effect of the continued action of alkali on wool, and to determine the rate of removal of sulphur and nitrogen from the wool molecule.

Six-gram samples of wool were treated with 300-ml portions of 0.065 *N* sodium-hydroxide solutions at 150° F for various lengths of time, washed for 4 hours in running distilled water and conditioned. The loss in weight, and the moisture and sulphur contents of the yarns were determined. Aliquots of the mother liquors were analyzed for total and ammonia nitrogen, and sulphur. The results are given in table 4, and are shown graphically in figure 1. The losses in total and ammonia nitrogen are approximately proportional to the loss in weight of wool. The loss of sulphur, however, took place at a more rapid rate until the sulphur content of the wool had dropped to about 1.8 percent, after which the loss was also approximately proportional to the loss in weight of the wool. It is of interest to note that after 4 hours' treatment only 9 percent of the wool had been lost, 41 percent of the sulphur had been lost, and the sulphur content of the treated wool had dropped to 1.86 percent. Similarly after 48 hours' treatment, 66 percent of the wool was lost, but the sulphur content of the residual wool was still 1.87 percent. The broken curve in figure 1 represents the theoretical amount of sulphur that would be lost if the sulphur had split off as an integral part of the wool molecule.

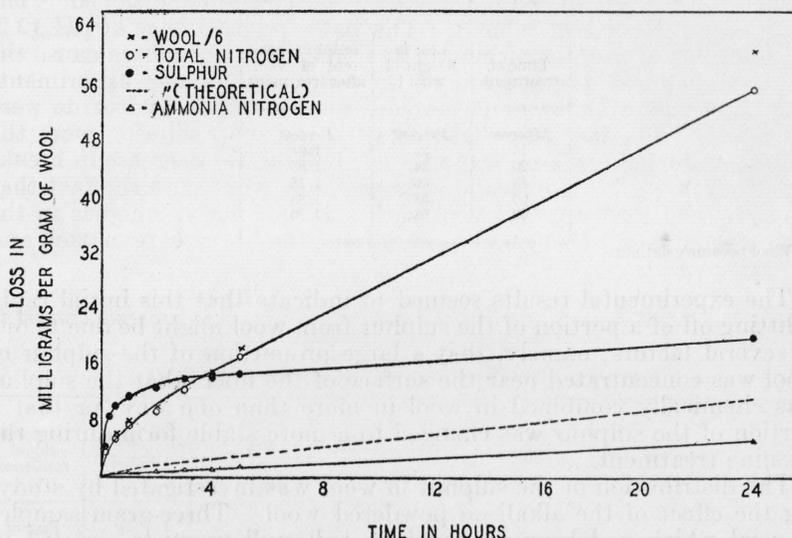


FIGURE 1.—Effect on wool of the continued action of 0.065 N NaOH at 150° F:

TABLE 4.—Effect on wool of the continued action of 0.065 N sodium-hydroxide solution at 150° F

Time of treatment	Loss in weight of wool	Total nitrogen in mother liquor	Ammonia nitrogen in mother liquor	Loss in sulphur content of wool		Sulphur content of wool after treatment	Moisture content of conditioned wool after treatment
				mg/g	mg/g		
<i>Minutes</i>	<i>Percent</i>	<i>mg/g</i>	<i>mg/g</i>	<i>mg/g</i>	<i>mg/g</i>	<i>Percent</i>	<i>Percent</i>
10	2.74	3.7		4.4	4.0	2.76	14.4
20	3.42	4.7		5.8	7.4	2.42	14.3
30	3.87	5.5	0.55	10.1	9.7	2.34	14.4
40	4.27	6.0		10.4	9.8	2.21	14.2
50	4.55	6.5		10.9	10.2	2.20	14.4
<i>Hours</i>							
1	4.83	7.5	.79	11.6	11.3	2.18	14.2
2	5.97	9.3	.98	12.8	12.1	1.97	14.4
3	8.38	12.6	1.28	14.0	13.6	1.90	14.5
4	9.11	14.6	1.37	14.5	14.0	1.86	14.3
5	11.20	17.7	1.79	14.9	14.8	1.85	14.4
24	• 36.00	55.1	5.07	20.0	-----	1.82	15.1
48	• 66.00	92.8	8.02	25.5	-----	1.87	16.6

\* The residual wool after 24- and 48-hour treatment was gelatinous and a portion of the fiber was lost during washing. The accuracy of these values is questionable.

† Calculated from the sulphur content of the residual wool. The sulphur in the wool was determined by the oxygen-bomb method.

‡ Sulphur found in the mother liquor. It was determined by treating an aliquot with *N* hydrochloric acid solution saturated with bromine. The solution was allowed to stand on a steam bath for ½ hour and the sulphur determined as barium sulphate. It has been shown that the sulphur in wool or cystine is not oxidized to sulphate under these conditions. This indicates that the sulphur found by this method is split off from the wool.

When specimens of the wool yarn were treated with 0.25 *N* sodium-hydroxide solutions under the conditions described, the sulphur content of the residual wool became constant after about 20 minutes at about 1.8 percent. The results are given in table 5.

TABLE 5.—*Effect on wool yarn of 0.25 N sodium-hydroxide solution at 150° F*

Time of treatment	Loss in weight of wool <sup>1</sup>	Sulphur content of wool after treatment
<i>Minutes</i>	<i>Percent</i>	<i>Percent</i>
10	22	1.91
20	34	1.85
40	46	1.78
60	58	1.83
90	68	1.79

<sup>1</sup>Wool became gelatinous.

The experimental results seemed to indicate that this initial rapid splitting off of a portion of the sulphur from wool might be due to one of several factors; namely, that a large proportion of the sulphur of wool was concentrated near the surface of the fiber; that the sulphur was chemically combined in wool in more than one way; or that a portion of the sulphur was changed to a more stable form during the alkaline treatment.

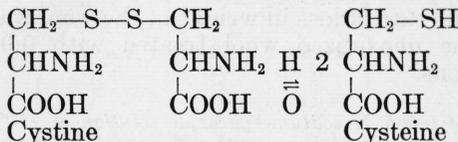
The distribution of the sulphur in wool was investigated by studying the effect of the alkali on powdered wool. Three-gram samples of wool which had been ground in a ball mill (particle size 0.3 to 2 $\mu$ ) were put in 150-ml portions of 0.065 *N* sodium-hydroxide solutions at 150° F for various lengths of time, after which the alkaline solutions were quickly cooled in ice water, centrifuged for 5 minutes at 2,200 rpm and the supernatant liquid decanted. Distilled water was mixed with the residue and the resulting suspension again centrifuged. This rinsing was repeated six times. The powder was dried for 24 hours at 105 to 110° C and the total sulphur determined. The results in table 6 show that the sulphur content decreased at a slightly faster rate than that of the wool yarn, but became constant after 3 hours at about 1.8 percent (calculated on basis of 14.4 percent of moisture). The close agreement of the results obtained on the wool yarn and wool powder indicates that the sulphur is uniformly distributed throughout the wool fiber.

TABLE 6.—*Effect on powdered wool of 0.065 N sodium-hydroxide solution at 150° F*

Time of treatment	Sulphur content of wool after treatment	Time of treatment	Sulphur content of wool after treatment
<i>Hours</i>	<i>Percent</i>	<i>Hours</i>	<i>Percent</i>
1	2.00	4	1.80
2	1.95	5	1.78
3	1.85	24	1.81

That the bulk of the sulphur in wool is not combined in more than one way and is practically entirely present as cystine sulphur, has been shown by Rimington (14) and by Sullivan and Hess (13). Employing the Sullivan method for the determination of cystine, it was found that at least 96 percent of the sulphur of the wool used in these experiments was cystine sulphur. The presence of practically all of the sulphur in one form was further demonstrated qualitatively by the following procedure. When cystine was treated with an ammoniacal solution of sodium nitroprusside no reaction occurred.

On addition of potassium-cyanide solution, the cystine was reduced to cysteine according to the following reaction and a violet-red color was produced. The nitroprusside reaction is a test for the sulphhydryl ( $-SH$ ) group.



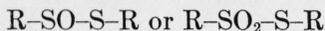
Similarly, wool was treated with an ammoniacal solution of sodium nitroprusside and gave a negative reaction, but after addition of the reducing agent, a violet-red color developed on standing. In view of these results, it appears that the alkaline treatment has changed a portion of the sulphur of wool to a form which tends to resist further splitting off from the molecule on continuation of the treatment.

### 3. EFFECT OF ALKALIES ON WOOL TREATED WITH OXIDIZING AND REDUCING AGENTS

It is well known that when wool and other keratins are treated with alkaline reducing agents, the disulphide linkage (cystine sulphur) is split. Oxidizing agents also react with the disulphide groups in keratins, but their action is not specific for these groups, since they are known to attack other parts of the protein molecule. The oxidation of the disulphide group proceeds very slowly and it is only with difficulty that these linkages are split by oxidation methods.

It is obvious that a number of oxidation products of cysteine and cystine are possible. The intermediate oxidation products have never been definitely isolated although Lavine and Toennies (15), in studies of the oxidation of cystine in nonaqueous media, obtained a precipitate with a composition approximating that of a sulphoxide. There is, as will be shown later, some evidence which indicates the formation of these intermediate products during the oxidation of wool.

The effect of alkali on oxidized wool was studied. Wool yarn was treated with 3-percent hydrogen-peroxide solution for 24 hours at room temperature, after which the yarn was thoroughly rinsed and conditioned. The sulphur content of the treated wool was slightly lower (3.12 percent), but the physical properties were the same as those of the untreated wool. When the oxidized wool was treated with an alkaline nitroprusside solution, a negative test was obtained, but on addition of sodium-cyanide solution, a violet-red color was produced. The color obtained with the nitroprusside test developed much more rapidly with the oxidized wool than with the unoxidized wool. However, when equal amounts of the treated and untreated wool were dissolved in normal sodium-hydroxide solutions and equal amounts of sodium nitroprusside were added to each, the solution of the unoxidized wool was the more deeply colored. The results show that oxidation has made the disulphide group more labile to alkaline reagents, but has also reduced the number of potential sulphhydryl groups in the oxidized wool. This suggests the possibility that under the conditions of the oxidation in these experiments, intermediate products such as the following are formed:



Samples of the oxidized wool were treated with 0.065 *N* sodium-hydroxide solution as previously described. The loss in weight of the wool and the sulphur content of the wool after treatment are given in table 7. The sulphur content became constant after 2 hours at about 1.96 percent. The rate of loss in weight of the wool was much greater than that of the unoxidized wool treated with 0.065 *N* sodium-hydroxide solutions.

TABLE 7.—*Effect of 0.065 N sodium-hydroxide solution at 150° F on wool yarn which had been treated for 24 hours with a 3-percent hydrogen-peroxide solution*

Time	Loss in weight of wool	Sulphur content of wool after treatment
<i>Hours</i>	<i>Percent</i>	<i>Percent</i>
½	7.8	2.41
1	9.9	2.30
2	12.1	2.02
3	14.3	1.97
5	18.9	1.95
24	48.8	1.96

When samples of the wool yarn were treated with 0.065 *N* sodium hydroxide solutions containing 1 percent of sodium sulphide, and with 1 percent sodium-sulphide solutions alone, the wool fibers deteriorated rapidly. All of the samples became gelatinous within a few minutes, which prevented an accurate determination of the loss in weight of the wool. It was estimated that for the shortest period of time (½ hour), the wool lost more than 50 percent in weight. The sulphur contents of the residual wool are given in table 8. Addition of the reducing agent splits the disulphide linkage and the wool rapidly loses its fibrous structure.

TABLE 8.—*Sulphur contents of wool treated with 0.065 N sodium-hydroxide solution containing 1 percent of sodium sulphide and with a 1-percent sodium-sulphide solution alone at 150° F*

Time	Sulphur content of wool treated with 0.065 <i>N</i> NaOH+1% of Na <sub>2</sub> S	Sulphur content of wool treated with 1% of Na <sub>2</sub> S
<i>Hours</i>	<i>Percent</i>	<i>Percent</i>
½	3.03	3.04
1	2.94	-----
2	2.86	2.77

It is of interest to note that while the wool deteriorates very rapidly in the presence of alkaline-reducing agents, the sulphur content of the residual wool was much higher than when sodium hydroxide alone was used. This suggests that the disulphide sulphur is more labile to alkaline treatment than the sulphydryl sulphur. This is in agreement with the results of Gortner and Thor (16), who found that cysteine is more stable toward alkalis than cystine.

## IV. CONCLUSIONS

When wool is treated with dilute sodium-hydroxide solutions, a rapid splitting off of a portion of the sulphur occurs. On continued treatment, the sulphur content of the residual wool approaches a constant value. The results indicate that the alkaline treatment has changed a portion of the sulphur of wool to a form which tends to resist further splitting from the molecule. Oxidizing and reducing agents attack the disulphide group and make wool more susceptible to alkaline treatment. The susceptibility of wool to alkaline reagents appears to be closely associated with the lability of its sulphur in alkaline solution.

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