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CHEMICALLY MODIFIED WOOLS OF ENHANCED STABILITY

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ABSTRACT

Recent work at this Bureau has shown that the disulfide cross-linkages of wool can be transformed to more stable *bis*-thioether linkages by a two-step process. The disulfide groups are first reduced to sulfhydryl groups by means of a mercaptan, and then, by treating the wool with an aliphatic dihalide, pairs of sulfur atoms are linked together through short hydrocarbon chains. Wools modified by such a process have now been studied more extensively. It was found that they are decidedly more stable than untreated wool toward many chemical agents, including alkalies, acids, oxidizing agents, and reducing agents; are stained less easily by metals; and are attacked much less readily by certain biological agents, including moths, carpet beetles, and enzymes.

CONTENTS

I. INTRODUCTION

One of the greatest practical disadvantages of wool has been that it is only moderately stable to a number of chemical agents, especially those that primarily attack the disulfide group of the cystine of the wool. For example, the degradation of wool by alkalies [1],[2] by oxidizing agents such as peroxide [2] or chlorine [3], or by reducing agents such as the bisulfites or dithionites[3] [4], has been shown to result in part at least from the breakdown of these groups. Damage to wool

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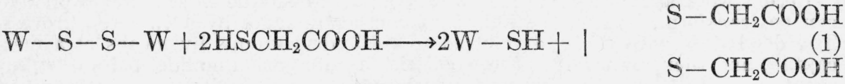
[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.

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

[3] Also termed "hydrosulfites" or "hyposulfites."

by light also involves the breakdown of disulfide groups [5]. In addition, rupture of these groups seems to be involved when moths attack wool [6], and also is necessary before enzymes can digest it [7]. Yet disulfide groups are of primary importance in maintaining the unusual mechanical properties of wool, particularly its elasticity [8], since they serve as cross-links between the peptide chains of the wool protein [9]. For these reasons there would seem to be an obvious advantage in transforming the disulfide groups to more stable ones through a process not deleterious to the mechanical properties of the wool.

Recent work at this Bureau [9] has led to the development of a series of chemical reactions by which this can be done. By treating the wool with a solution of thioglycolic acid or other mercaptan at a pH below 7.0, a portion of its disulfide groups can be reduced to sulfhydryl groups without destroying its fibrous structure, and without detectable changes in other chemical linkages. This reaction may be represented as follows:



$$W-S-S-W+2HSCH_2COOH \longrightarrow 2W-SH+\begin{array}{l}S-CH_2COOH\\ |\\ S-CH_2COOH\end{array} \qquad (1)$$

where W represents the portions of the wool connected by the disulfide groups. By treating the reduced wool with an alkyl dihalide, the sulfur atoms can be linked through short hydrocarbon chains, and new cross-links that are much more stable than the disulfide groups are produced, as the following equation indicates:

$$2W-SH+(CH_2)_nX_2 \longrightarrow W-S-(CH_2)_n-S-W+2HX, \qquad (2)$$

where X represents a halogen atom.

Work already published [9] has demonstrated that wools containing cross-links of this sort possess enhanced stability to alkali. Since then a greater variety of products has been prepared, and their stability to moths, molds, and enzymes, has been studied. In addition, a number of improvements in the process for preparing such modified wools have been made and are described below.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

The yarn used in the present study was part of the lot used in earlier investigations [7, 9]. This yarn was a four-ply worsted prepared from raw wool that had been previously extracted with Stoddard solvent and washed with water. The yarn was further purified by extraction with alcohol and with ether for 6 hours each in a modified Soxhlet apparatus, so constructed that neither hot solvent nor vapor should come in contact with the wool, and finally by washing with distilled water. The cloth used was a plain-woven worsted of the type described in Commercial Standard CS65–36 [10].

2. METHODS

(a) REDUCTION

Wool can be reduced, not only with sodium thioglycolate, as in the earlier work [9], but also with other salts of this acid, with the free acid, or with other mercaptans. Comparison of the results obtained with a number of the salts of thioglycolic acid showed that the calcium salt offered unusual advantages, since the products had the best tactile properties, and possessed the greatest stability toward alkali of any studied.

The reduction was carried out by immersing the wool in a solution of calcium thioglycolate at 50° C and at pH 5. Under these conditions, reduction was complete in 2 hours, while 20 hours was required for reduction by the older procedure. To reduce about one-sixth of the cystine, 50 ml of a 0.02 *N* solution of calcium thioglycolate was used for each gram of wool. To reduce about one-half of the cystine, 20 ml of a 0.3 *N* solution was used for each gram of wool. To obtain products in which two-thirds of the cystine had been reduced, two applications of this latter reduction process were required. Products in which five-sixths of the cystine had been reduced were prepared by applying this reduction process four times. When successive reductions were used, each reduction was followed by alkylation.

(b) ALKYLATION

Immediately after reduction, the wool was washed with water, then with 0.01 *N* phosphate buffer at pH 8.0, and again with water. The wool was then immersed in a 0.1 *M* solution of phosphate buffer at pH 8.0 and 50° C, in which the alkylating agent had been suspended with the aid of a cationic wetting agent. About 0.0005 mole of the alkylating agent and 20 ml of the buffer were used for each gram of wool. The nitroprusside test given by the sulfhydryl groups of the reduced wool ordinarily became negative within 1 hour, but as a precaution the alkylations were continued for a total of 2 hours.

An investigation of the usefulness of a large group of organic dihalides as alkylating agents showed that they may be grouped roughly into three classes. The first class may be termed satisfactory reagents (those which react with reasonable rapidity and yield very stable products) including methylene bromide, trimethylene bromide, tetramethylene bromide, and 1,4-dichlorobutene-2. The second class consists of fair reagents (which react more slowly but yield satisfactory products) such as trimethylene chloride, triglycol dichloride, or *bis*-2-chloroethoxymethane. The third class includes unsatisfactory reagents, such as certain dihalides that are easily hydrolyzed, as benzal chloride and dichloroacetic acid, others with only one sufficiently reactive halogen atom, such as ethylene bromide, 1,3-dichloropropanol-2, and 2,2′-dichlorodiethyl ether, and others that produce side reactions, such as styrene dibromide or 1,3-dibromopropanol-2, which may act as oxidizing agents, since the sulfhydryl groups are rapidly converted to the disulfide stage. The results described in this paper are mainly those obtained with one of the best reagents, trimethylene bromide.

(c) ANALYSIS

The amount of unchanged cystine in the modified wools was determined by the method of Sullivan [11]. The concentration of the solutions of thioglycolic acid was measured by titrating a sample with a 0.05 *N* solution of iodine, using starch as an indicator. The sulfur analyses were made by the oxygen-bomb method [12]. The alkali-solubility was determined by the method of Smith and Harris [2] and represents the percentage of the wool dissolved in 1 hour by 100 times its weight of a 0.1 *N* solution of sodium hydroxide at 65° C.

The breaking strengths of the samples of cloth were determined in the warp direction with a pendulum-type machine by the raveled-strip method [10], and each value represents the average of at least 10 measurements. The reflectances of the samples of cloth were measured by the method of Reimann and Mease [13].

III. RESULTS AND DISCUSSION

1. RESISTANCE TO ALKALI

Wool frequently comes in contact with alkali in processes like laundering and scouring. The action of alkali may diminish the strength and durability of the wool, cause it to turn yellow, and impair its tactile properties, rendering it harsh. Since the linkages of wool protein most susceptible to disruption by alkali are the disulfide groups, transforming them to the more stable *bis*-thioether groups should increase the stability of the wool to alkali. The effect of boiling with dilute alkali on untreated wool and on a modified wool is illustrated by the photomicrographs of fibers in figure 1. It is apparent that the fibers of the untreated wool show far more swelling and disruption than do the fibers of the modified wool.

TABLE 1.—*Action of alkalies on the untreated wool and on the modified wools prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

[Alkali-solubility of the wools, and their reflectance and breaking strength after boiling them for 1 hour with 0.02 *N* sodium carbonate]

Cystine	Alkali-solubility	Reflectance [a]	Breaking strength [b]—	
			Before treatment with Na_2CO_3	After treatment with Na_2CO_3
UNTREATED				
Percent	*Percent*	*Percent*	*kg*	*kg*
12.2	10.0	37.8	14.0	10.0
MODIFIED				
10.0	6.2	37.6	13.5	11.5
6.5	2.9	41.0	13.5	12.0
4.0	2.5	46.5	12.5	12.0
2.0	2.0	47.5	12.5	11.5

[a] With respect to MgO.
[b] Strips 2.54 cm wide, 49 ends.

Three other tests for resistance to alkali were also used: (1) alkali solubility, (2) the extent of yellowing of the products by alkali, and (3) the effect of alkali on the breaking strength of strips of cloth. The alkali-solubilities given in table 1 show that the modified wools have a decidedly greater resistance than does untreated wool. Closer examination of these data also shows that, although the resistance to alkali increased as the cystine content decreased, little advantage was gained by diminishing the cystine content below 6 percent. Treatment with boiling solutions of sodium carbonate, which rapidly turns untreated wool yellow, has considerably less effect upon the modified wools, as the reflectance data of table 1 indicate. The loss in reflectance upon treatment with alkali became less as the content of un-

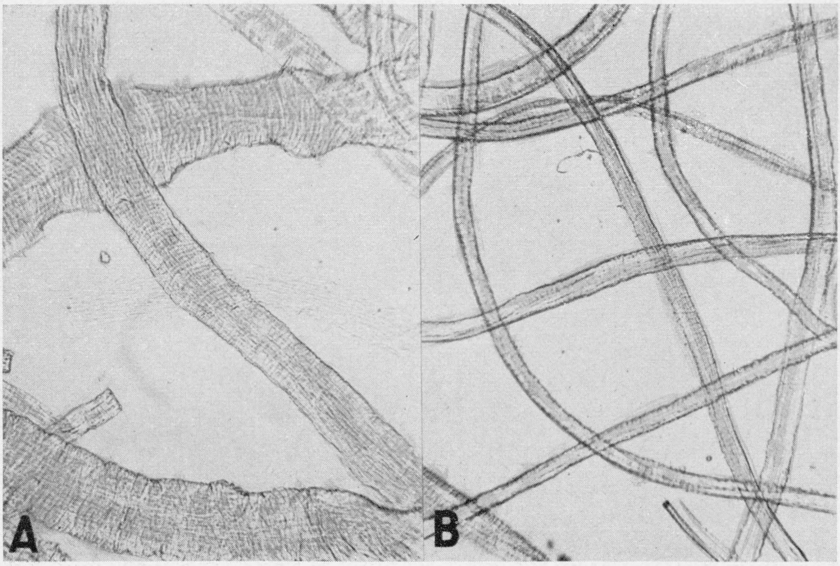


FIGURE 1.—*Wool fibers after treatment for 30 minutes at 100° C with 0.01 N* NaOH.

A, untreated wool; *B*, modified wool (cystine content, 6.5 percent) prepared by reduction with calcium thioglycolate and alkylation with $(CH_2)_3Br_2$. Magnification ×150.

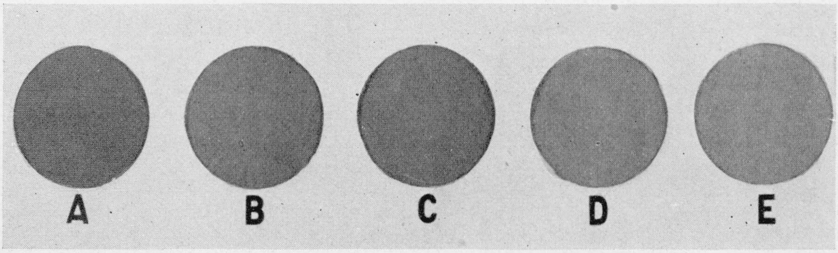


FIGURE 2.—*Wool samples after treatment for 30 minutes at 100° C with 0.02 N lead acetate,* pH 5.0.

Untreated wool, *A;* modified wools prepared by reduction with calcium thioglycolate and alkylation with $(CH_2)_3Br_2$; *B*, 10.0% cystine; *C*, 6.5% cystine; *D*, 4.0% cystine; *E*, 2.0% cystine.

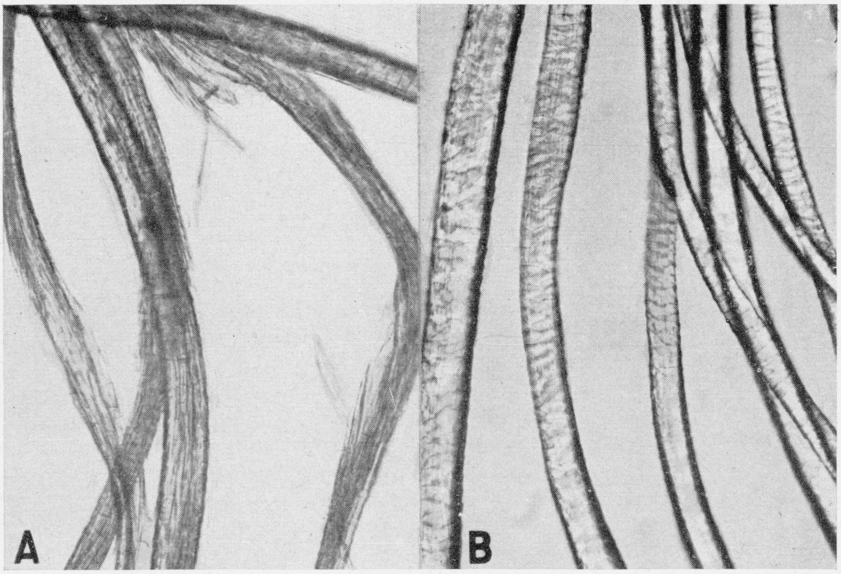


Figure 3.—*Wool fibers after treatment with pepsin for 2 weeks* [7].

A, Untreated wool; *B*, modified wool (cystine content, 6.5%) prepared by reduction with calcium thioglycolate and followed by alkylation with $(CH_2)_3Br_2$. Magnification ×150.

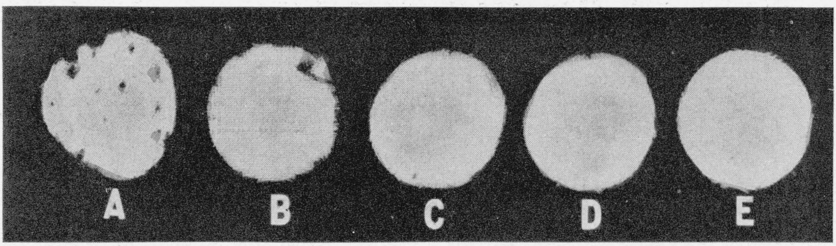


Figure 4.—*Wool samples after subjection to moth larvae.*

Untreated wool, *A*; modified wools prepared by reduction with calcium thioglycolate and followed by alkylation with $(CH_2)_3Br_2$; *B*, 10.0% cystine; *C*, 6.5% cystine; *D*, 4.0% cystine; *E*, 2.0% cystine.

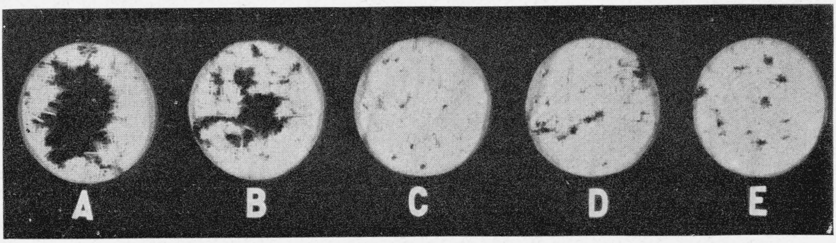


Figure 5.—*Wool samples after subjection to the larvae of black carpet beetles* (*Attagenus piceus*).

Untreated wool, *A*; modified wools prepared by reduction with calcium thioglycolate followed by alkylation with $(CH_2)_3Br_2$; *B*, 10.0% cystine; *C*, 6.5% cystine; *D*, 4.0% cystine; *E*, 2.0% cystine.

changed cystine was diminished. The effect of treatment with boiling solutions of sodium carbonate upon the breaking strengths of strips of wool cloth is also reported in table 1. The loss in breaking strength of the chemically modified wools upon treatment with sodium carbonate was somewhat less than that of the untreated wool.

2. RESISTANCE TO ACIDS

Not only do the modified wools show improved stability to alkali alone, but they also show greater stability to alkali after being treated with acids. Improved stability to such a succession of treatments is important because degradation, which may occur when wool is carbonized, acid-dyed, or acid-fulled, may be greatly accentuated when the material later comes in contact with alkali, as in laundering. Table 2 gives typical results. Because the amounts of soluble nitrogenous materials, which represent partly hydrolyzed protein fragments, that result from each acid treatment are similar for the untreated and the modified wool, it seems likely that about as many peptide chains are hydrolyzed by the acid in one material as in the other, since there is no *a priori* reason for peptide bonds to be stabilized by a reaction involving only the sulfur. The hydrolytic action of a given acid treatment should therefore result in about the same decrease in average molecular weight for each material. The subsequent alkali-solubility test involves breakdown of the disulfide groups of the unmodified wool but not of the *bis*-thioether groups of the modified wool. For these reasons the greater alkali-solubility of the unmodified wool appears to depend on a decrease in molecular weight that results from the rupture both of disulfide cross-links and of peptide bonds.

TABLE 2.—*Action of acids on untreated wool and on modified wool (cystine content 6.5%) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

Wool	Conditions	Alkali-solubility—		Nitrogen liberated in percentage of total Nitrogen
		Before treatment	After treatment	
		Percent	*Percent*	
Untreated	HCl, 0.1 *N*, 65° C, 24 hours	9.5	20.0	2.0
Modified		2.5	6.3	1.7
Untreated	HCl, 0.1 *N*, 65° C, 10 days	9.5	80.0	11.8
Modified		2.5	45.0	11.3
Untreated	H_2SO_4, 0.1 *N*, 65° C, 24 hours	9.5	28.8	2.9
Modified		2.5	9.9	2.5

The carbonizing of wool with sulfuric acid differs from the above treatments in involving baking at a high temperature (about 125° C). The results obtained on subjecting the untreated and the modified wool to a typical commercial carbonizing process are recorded in table 3. The untreated wool, after carbonizing, had a high alkali-solubility, so damage might easily result from laundering or other treatments involving alkali. The alkali-solubility of the modified wool after carbonizing had increased too, but the final value was much lower.

TABLE 3.—*Effect of carbonizing with sulfuric acid on the untreated wool, and on the modified wool (cystine content 6.5%) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

Wool	Alkali-solubility—		Breaking strength [a]—	
	Before carbonizing	After carbonizing	Before carbonizing	After carbonizing
	Percent	*Percent*	*kg*	*kg*
Untreated	9.5	19.4	13.5	13.5
Modified	3.5	11.0	13.0	13.0

[a] 2.54 cm strips, 49 ends.

3. RESISTANCE TO REDUCING AGENTS

Wool is often subjected to the action of reducing agents. For example, wool papermakers' felts frequently come in contact with sulfites. Reducing agents, including dithionites and formaldehyde-sulfoxylates, are used with wool as stripping agents, and dithionites are also used in dyeing wool with indigoid colors. Such reducing agents tend to make wool extremely susceptible to the action of alkali [4]. Reducing agents appear to attack wool mainly by breaking the disulfide linkages of the cystine. Sodium bisulfite, for example, probably reacts as follows [14]:

$$W-S-S-W+NaHSO_3 \longrightarrow W-S-SO_3Na+W-SH.$$

The ionized thiosulfate and mercaptan groups formed by this reaction would be expected to increase the alkali-solubility of the wool. The *bis*-thioether linkages of the modified wools cannot, however, react in this way, so such wools should be far more stable to reducing agents. The results obtained by determining the alkali-solubility of samples of unmodified and modified wool that had previously been treated with reducing agents are recorded in table 4. The modified wool was found in every case to be considerably less affected by the reducing treatment than was the untreated wool.

TABLE 4.—*Action of the reducing agents on the untreated wool and on the modified wool (cystine content, 6.5 percent) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

[For each gram of wool, 100 ml of the indicated reagent was used]

Reagent	Conditions	Alkali-solubility of—	
		Untreated wool	Modified wool
		Percent	*Percent*
None		10.0	2.5
$NaHSO_3$	1%; 100°C; 1 hour	15.2	4.8
$Na_2S_2O_4$	10%; 50°C; 2 hours	39.0	4.5
Na_2SO_2-CH_2O	5% 50°C; 2 hours	13.3	3.7
NaSH	0.2 *N* 50°C; 2 hours	41.5	3.2

4. RESISTANCE TO OXIDIZING AGENTS

Wool comes in contact with oxidizing agents during bleaching with peroxide, during treatment with chlorine, and also in use, through the action of light and air. The effect on wool of certain chemical oxidizing agents is recorded in table 5, where alkali-solubility is again used as a criterion of damage by the oxidizing agents. The results show that the transformation of disulfide groupings to *bis*-thioether groupings diminishes the deleterious effects of oxidizing agents, since, although the alkali-solubilities of both the modified and the untreated wool have increased, those of the modified wool remain low enough to indicate considerable resistance.

TABLE 5.—*Action of oxidizing agents upon untreated wool, and upon modified wool (cystine content, 6.5 percent) prepared by reduction, followed by alkylation with* $(CH_2)_3Br_2$

[For each gram of wool, 100 ml of the indicated reagent was used]

Reagent	Conditions	Alkali-solubility of—	
		Untreated wool	Modified wool
		Percent	*Percent*
None		10.0	2.5
Cl_2	0.01 *N*; 100°C; 1 hour	13.6	6.6
H_2O_2	2 vol; 50°C; 1 hour	15.5	4.0
$KMnO_4$	1%; 35°C; 1 minute	17.5	10.4
$K_2Cr_2O_7$	0.2%; 100°C; 1 hour	11.0	4.6

5. RESISTANCE TO STAINING BY HEAVY METALS

Wool is easily stained by contact with metals, as by the metal fasteners sometimes used with wool clothing. This staining may possibly result either directly from the reaction of the wool with the metal or from the reaction with oxides or salts formed on the surface of the metal. It was found qualitatively that the extent of staining by solutions of certain salts of iron, silver, copper, and lead was considerably greater with the untreated wool than with certain of the modified wools. The results obtained by staining with lead acetate are illustrated in figure 2. The modified wools were stained very much less by a solution of lead acetate than was the untreated wool, and the extent of staining decreased as the amount of the unchanged cystine decreased. Most of the modified wools studied were similar in this respect, but wool prepared by reduction followed by alkylation with methylene bromide, a process that converts its cystine to djenkolic acid (which contains $-S-CH_2-S-$ linkages), was found to be exceptional, since it was stained by lead acetate almost as readily as untreated wool.

6. RESISTANCE TO ENZYMES, MOTHS, AND CARPET BEETLES

Proteolytic enzymes digest wool extensively only after a portion of the disulfide bonds have been broken, although less complete digestion takes place after mechanical injury or after contact with dilute acid for several days [7]. The wools containing *bis*-thioether cross-linkages showed greatly enhanced resistance to digestion, and were not attacked by pepsin even after mechanical injury, or after treatments with acid sufficient to render untreated wool readily digestible. Photomicrographs illustrating the experimental results are shown in figure 3.

Moth larvae, according to Linderstrøm-Lang [6], can digest wool only after breaking its disulfide cross-linkages by the action of a reducing agent present in their intestinal tracts. For this reason it seemed probable that the modified wools containing *bis*-thioether linkages would be far more stable to biological agents than untreated wool, and such stability was actually observed. The new linkages probably interfere with the preliminary reductive step, since *bis*-thioether linkages, as shown above, are very resistant to the action of reducing agents.

A study of the ability of the new cross-linkages to minimize the extent of attack by moths has shown that the modified wools are attacked to a considerably less extent than is untreated wool, and that the resistance increases as the content of unchanged cystine decreases. Table 6 gives the results obtained after the wool samples had been subjected to the action of moth larvae, and the samples are shown in figure 4.[4] The modified materials having cystine contents of 6 percent or less were only slightly attacked, and this attack was mainly around the edges, whereas numerous holes were eaten in the untreated samples. It also appears that reducing the cystine content to 6 percent provides about as much protection as the more extensive treatments. It should be pointed out that the mothproofness produced by the present method is not removed by laundering or dry cleaning, since it is "built into" the molecule as an integral part of its chemical structure.

TABLE 6.—*Action of moth larvae upon untreated and upon chemically modified wools prepared by reduction followed by alkylation with* $(CH_2)_3Br_2$

[Ten larvae were used for each sample.]

Type	Cystine content	Loss in weight
	Percent	*Percent*
Untreated wool	12.2	15.5
Modified wool	10.0	8.0
Do	6.5	.3
Do	4.0	2.9
Do	2.0	.1

TABLE 7.—*Action of larvae of the black carpet beetle on the untreated and on the modified wools prepared by reduction and followed by alkylation with* $(CH_2)_3Br_2$

[Each sample was exposed to 10 larvae for 30 days.]

Type	Cystine content	Weight of excrement
	Percent	*mg*
Untreated wool	12.2	52
Modified wool	10.0	45
Do	6.5	21
Do	4.0	34
Do	2.0	23

Carpet beetles were found to damage both the untreated and the modified wools more extensively than did moth larvae, as table 7 and figure 5 illustrate. Nevertheless, the modified wools were decidedly more resistant than the untreated wool to such attack.

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[4] We thank John A. Levering and J. W. Creely, of the Eavenson & Levering Co., Camden, N. J., for the tests with moth larvae, and A. G. Ashcroft and R. C. Allison, of Alexander Smith & Sons Carpet Co., Yonkers, N. Y., for the tests with carpet beetles.

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WASHINGTON, June 3, 1942.

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[Continued on p. 4 of cover]

[Continued from p. 3 of cover]

MT10. TABLE OF NATURAL LOGARITHMS, VOLUME III:

Logarithms of the decimal numbers from 0.0001 to 5.0000, to 16 places of decimals.
(1941) XVIII+501 pages; bound in buckram, $2.00.

MT11. TABLES OF THE MOMENTS OF INERTIA AND SECTION MODULI OF ORDINARY ANGLES CHANNELS, AND BULB ANGLES WITH CERTAIN PLATE COMBINATIONS:

(1941) XIII+197 pages; bound in green cloth. $2.00.

MT12. TABLE OF NATURAL LOGARITHMS, VOLUME IV:

Logarithms of the decimal numbers from 5.0000 to 10.0000, to 16 places of decimals.
(1941) XXII+506 pages; bound in buckram, $2.00.

MT13. TABLE OF SINE AND COSINE INTEGRALS FOR ARGUMENTS FROM 10 TO 100:

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MT14. TABLES OF PROBABILITY FUNCTIONS, VOLUME II:

Values of these functions to 15 places of decimals from 0 to 1 at intervals of 0.0001 and from 1 to 7.8 at intervals of 0.001.
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Copies of these publications have been sent to various Government depositories throughout the country, such as public libraries in large cities, and colleges and universities, where they may be consulted.

A mailing list is maintained for those who desire to receive announcements regarding new tables as they become available. A list of the tables it is planned to publish will be sent on request.