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Office of The Quartermaster General
Military Planning Division
Research and Development Branch

TEXTILE SERIES - REPORT NO. 46

Aug. 1947

THE TREATMENT OF ARMY SOCKS FOR SHRINK RESISTANCE

BY THE QUARTERMASTER CORPS

Prepared jointly by
the Staffs of the Harris Research Laboratories
and the Textile Research Laboratory of the Research and Development Branch
located at
the Philadelphia Quartermaster Depot

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FOREWORD

This report on shrink-resistant treatment of Army wool socks was prepared in part at the end of the war as a history of Quartermaster work on the prevention of shrinkage of wool. While originally intended primarily as a summary of the detailed data for our own records, it was later considered that it should be made public as soon as it was possible to prepare the material in proper form for public release.

The extent of the accomplishment of the Army Research Program on wool shrinkage can best be judged by the fact that this was the first time that an entire industry has ever produced a shrink-resistant wool item in this country. The relative ease with which the program was accomplished may give the misleading impression that the problem of overcoming the felting shrinkage of wool presents no difficult technical or production problems. Actually the success of this work was in considerable measure due to the exceptional cooperation received from a great many people in industry, and to the able leadership provided by Dr. Milton Harris, at the time on the staff of the Textile Foundation, who was in charge of all technical aspects of the project, and Captain Harry F. Clapham, who administered the project in our office. While it is not possible to mention here all of the individuals who contributed to this accomplishment, this report could scarcely be released without mention of some of them.

First of all, there was Mr. Kenneth Marriner, then Head of the Wool Branch of the War Production Board, who early in 1943 encouraged our office to make the effort to solve this problem despite the fact that we were then at war and the industry had never been able to solve the problem in time of peace.

Then there was the Textile Foundation which made available the services of its research staff located in the National Bureau of Standards, which included, in addition to Dr. Milton Harris, Mr. Arthur Smith and Mr. Daniel Frischman, and later Mr. Arnold Sookne. Mr. Smith's services became available through his release from the North Star Woolen Company where he had been employed up until the time this work was started, and where he had gained considerable preliminary experience in connection with research by that company in this field.

The work of the Quartermaster Board under Colonel Max Wainer, President of the Board, constituted not only a major contribution to the wool shrinkage program but also to the whole subject of field testing. The testing techniques employed and the organization of personnel for controlled testing along these lines made possible not only the determination of the direct value of shrink-resistant treatment to the Army and to the public, but also provided means for evaluation of the effectiveness of laboratory and pilot plant work and for ascertaining the effect of various treatments upon wear. Major Thomas J. Dempsey, Captain James D. Finley and Corporal Julius ("Socks") Schneider, were the principal members of a large staff which collaborated with our office in carrying forward this program.

In industry there were two individuals whose assistance to our office was particularly outstanding: Mr. Richard Thompson, President of the Sulloway Hosiery Mills, Franklin, New Hampshire, and Mr. William Gosch, Nolde and Horst Company, Reading, Pennsylvania. In addition, many other firms having processes for the treatment of wool freely made available their knowledge, laboratories and technical personnel to try out the application of their processes on Army socks.

Within the Quartermaster Corps there were, in addition to Captain Clapham, Major Donald C. McLeod, who was in charge of the Hosiery Section in the Research and Development Division at the Philadelphia Quartermaster Depot, and Lt. Colonel Frank M. Steadman, in charge of that Division which carried the responsibility for arrangements for the procurement of test samples and coordination with the Procurement and Inspection Services.

This report was prepared by various members of the staffs of the Harris Research Laboratories, where this study is currently being continued, and our own Textile Research Laboratory, located in the Philadelphia Quartermaster Depot, including Mr. Louis I. Weiner, who is at present the Project Manager on this research project, and Mr. Norman Roberts, Historian for the Laboratory.

This report is released with some reservations with respect to making the test data public for, although the actual names of processes have been omitted, some identification can, of course, be made from the nature of the treatments. It has been pointed out to us that in a number of cases improvements have since been made in the techniques or products which would give better results than we obtained in the trials during the war. However, the data being released were those obtained in careful application trials and it is believed that the general aspects of our tests and research upon which our program was based should become available to the public.

Public release is being made at this time in view of the widespread interest which has developed in the whole subject of the shrink-resistant treatment of wool and the evident fact that the American wool manufacturing industry is now on the point of reaching out in an earnest effort to overcome this greatest limitation of the usefulness of the wool fiber.

S. J. KENNEDY
Research Director
For
Textiles, Clothing and Footwear

August 1947

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SECTION A

THE PROBLEM OF WOOL SHRINKAGE IN MILITARY ITEMS

Since man first clothed himself, wool has been one of the major materials used for body protection, felts made from wool being among the earliest forms of cloth. Through the years the technology of fabricating wool into woven materials, knit goods, and felts has advanced from the production of coarse homespuns to the manufacture of the fine woolens and worsteds we know today.

One of the reasons for wool's early acceptance as a clothing material has been its ability to "full" or "felt". This property, though even today little understood from a scientific standpoint and explained only by theories, made it possible for loosely woven or knitted materials to be closed up into tight dense fabrics under the influence of heat and moisture. Though this tendency to felt is desirable and essential in the production of some kinds of woolen materials, it also creates the hazard of shortening the useful life of items made from them by possible further felting if the garment is subjected to washing. The inability of wool to retain its original size after repeated washings has been recognized for years as its principal limitation, and the literature reveals many attempts that have been made to overcome this undesirable characteristic.

In military items this felting characteristic presents much more of a disadvantage than to civilians. In the first place it must be regarded as a virtual certainty that under some conditions every item of the soldier's clothing must be laundered. Despite the extent to which dry cleaning plants were provided overseas, there were many occasions when there was no choice but to wash everything a man brought back from a combat mission. Some kinds of soil cannot be effectively removed by dry cleaning. While that applies to civilian clothing to some extent, it is true many more times over for the grime of battle. The so-called wool-laundering formula, as will be shown in this report, is no preventative to felting - at best, it simply prevents the action from proceeding as fast as it might do under less careful laundering.

A further greater hazard in military clothing lies in the fact that the American soldier uses considerably more wool in his clothing than he did as a civilian. His socks, winter underwear, and shirts are made from wool. Even though these items as supplied during the war were made from a wool-cotton blend, the percentage of wool was adequate to insure the retention of the essential military characteristic of wool - its resilience when wet. The problem of preventing shrinkage is accordingly one of much greater magnitude, and it cannot be avoided by simply turning to some different material as a civilian can well do.

At the opening of World War II the lack of prior commercial research on wool shrinkage in this country and the absence of available processes in the industry generally prevented the Quartermaster Corps from specifying the obvious requirement that all of its wool items should be treated to prevent shrinkage. The best that could be done under the circumstances was to direct that mild laundering procedures should be followed on items where washing was required, and in the case of one or two fabrics, to specify a dense weave and a clear surface that would not give the wool an opportunity to start the felting process.

That considerable losses were being incurred to the Government from wool shrinkage was evident fairly early in the war. The nature of these losses, and the way in which wool shrinkage contributed to waste of military clothing, became more clearly evident only as our research proceeded.

The extent of these losses to the Government came into sharp focus in 1943 after the using Arms and Services had requested that the issue of the cushion sole sock be extended to the whole Army. This item had been developed in 1943 for issue to jungle troops. Its unbalanced construction presented an opportunity for rapid felting, not only in the loosely knitted body of the sock, but also in the foot, which is made by knitting in an extra all-wool terry yarn. Because of the free floating of the yarn, felting of the wool starts readily. Reports from the field stated that although the sock, when new, was greatly superior to any which had been available previously, it became unwearable after the first or second laundering under field conditions. Corroborating such complaints was the fact that comparative wear tests which were undertaken at the Quartermaster Board, Camp Lee, Virginia, could not be completed because the socks had shrunk after a few launderings to such an extent that they could no longer be fitted on the man participating in the experiment. The inability of such an otherwise desirable item to retain its size and shape after a comparatively few launderings indicated an urgent need for the development of a shrink-resistant process that could be adopted quickly by the entire industry.

While the emphasis in such consideration was placed upon socks, in view of the fact that the cushion sole sock was new to most of the industry and its large scale production would require extensive machinery conversion, as well as the application of such a treatment, it was recognized that the problem was also common to Army underwear, shirts, sweaters, and to a lesser extent to uniform fabrics.

In retrospect, the economic losses suffered because of failure to prevent wool shrinkage on all of these items appear to have been very large. The monetary loss was not all, however. There was also a loss in fighting efficiency resulting from uncomfortable or unprotective or unwearable garments. Then too there was the increased strain upon industrial production and military transportation and distribution caused by the need for more frequent replacements.

SECTION B

ATTEMPTS TO IMPROVE THE WEAR CHARACTERISTICS OF ARMY SOCKS

1. Early Attempts To Increase The Wear of Socks

The start of the Army research program on shrink resistance of wool began with attempts early in 1943 to deal with the apparent rapid rate of replacement of Army socks. Procurements of the standard issue Sock, Wool, Light, were scheduled during 1943 at around 5,000,000 pairs per month. Even after allowing for filling the supply pipe line, it appeared that part of this requirement arose from a very short service life. Reports from training centers confirmed this.

Shortly after the war started the National Association of Hosiery Manufacturers had suggested that the Army revise its specification to provide a high-spliced heel and double sole; i.e., to run in an extra reinforcing yarn in the high heel and in the non-reinforced part of the sole. No action was taken on this, in part, because a number of individual manufacturers when approached on the matter, had objected that it would take more yarn and interfere with their scheduled deliveries, and in general questioned the value of such a move.

In January 1943 a meeting was held with representatives of the industry to consider the adoption of such a change in the specification. An alternate type was then added to the specification providing for this reinforcement, and all manufacturers present were urged to offer this type on a forthcoming procurement. None of them did so however.

2. Initiation of a Comparative Wear Test at The Quartermaster Board

It was apparent that the industry itself did not know how much such reinforcement would add to the wear of socks. It was, accordingly, decided to run a wear test at the Quartermaster Board, Camp Lee, Virginia, to find out whether the extra wear would more than offset the extra cost and extra yarn supply that would be needed. In planning the test a number of additional variations in construction were also included, especially the alternate types of socks, wool, light, which the merino yarn shortage had made it necessary for the Quartermaster Corps to accept. These included particularly socks knitted with one end of 10's carded underwear yarn, and yarn spun on the French system. Also included for purposes of comparison were the Socks, Wool, Cushion Sole, and the Socks, Wool, Heavy. A complete list of the types of socks prepared specially for this test and shipped to the Quartermaster Board in June 1943 is shown in Table I.

TABLE I

TYPES OF SOCKS PROVIDED FOR COMPARATIVE WEAR TEST AT THE QUARTERMASTER BOARD

Code No.	Type	Treatment	Leg and Foot: Yarn	Leg and Foot: Size	Fiber Content	Spinning System	Heel - Toe Reinforcement	High Spliced Heel Double Sole
1	Sock, Wool, Light	Standard	2 ends	20's combed	50% cotton-50% wool	Cotton	50/2 Cotton CPM	None
2	" " "	None	" "	30's	" " " "	French	" " "	"
3	" " "	"	1 end	10's carded	" " " "	Cotton	" " "	"
4	" " "	"	2 ends	20's combed	" " " "	"	Spun Nylon 32's Cotton count	"
5	" " "	"	" "	" "	" " " "	"	Filament Nylon	"
6	" " "	"	" "	" "	" " " "	"	50/2 Cotton CPM	40/2 Cotton CPM
7	" " "	"	" "	" "	" " " "	"	Spun Nylon	Spun Nylon
8	" " "	"	Core yarn		" " " "	Cotton core Bradford Wrapper	50/2 Cotton CPM	None
9	" " "	"	2 ends	20's	50% wool-50% spun rayon	Worsted	" " "	"
10	" " "	"	" "	"	" " " "	Silk	" " "	"
11	" " Cushion Sole	" (10" high)			50% wool-50% cotton			
12	" " "	" (14½"high)			" " " "			
13	" " "	"	Core yarn		" " " "			
14	" " Heavy	" (3¼ lb.)			25% cotton-75% wool			
15	" " "	" (3 lb.)			" " " "			
16	" " "	" " "			50% " 50% "			
17	" " Medium	" (2 lb.)			" " " "			
19	" " Light	Experi-mental shrinkproof	2 ends	20's combed	" " " "	Cotton	50/2 Cotton CPM	None
20	" " Cushion Sole	Experi-mental shrinkproof			" " " "			
21	" " Medium	None (2½ lb.)			" " " "			
22	" " Light	$Ca(OCl)_2$ Inhibitor Process	2 ends	20's combed	" " " "	"	" " "	"

The test procedure which the Board planned to use for the evaluation of these socks, and which was followed throughout the subsequent testing, was as follows. For test subjects, arrangements were made to use enlisted men in the Army Service Forces Replacement Training Center, and officer candidates of the Quartermaster School. Test personnel were then divided into groups of 50 men. Each man was issued two pairs of socks, consisting of one pair of each of two different types. As the companies were deactivated the socks were reissued to men in new companies who required the same size socks. Each pair of socks was worn two days, and then laundered in a field laundry using the standard wool laundering procedure. To assure equal wear conditions, half of the men in each group wore one type of socks, while the remaining half wore the other type. With the initial appearance of a failure in the foot or ankle area, the socks were withdrawn from the test and the location, type and cause of failure were recorded, together with the number of days worn. The test was continued until all of the socks had failed. An analysis was then made of all failures and their locations to determine the comparative wearing qualities of the various types.

The shrinkage of the socks was usually measured after the first and third laundering and every third laundering thereafter until the socks were withdrawn from the test. Graphical analysis of the data was made to show the cumulative number of socks failing based on days' wear (Figure 2) and also the average number of days that each type of sock was worn before the appearance of a failure (Figure 3). Percent shrinkage was plotted against number of launderings to indicate the degree of dimensional change which had occurred.

Shortly after the test had begun, the Quartermaster Board advised the Research and Development Branch that it would be impossible to run the test on the cushion sole socks, because after the first two or three washings in the mobile field laundry, they had become unwearable.

As a result of this finding, two actions were taken. The Board was advised to give a deferred priority to the testing of the heavier weight socks for the time being, and to expedite their test on the Socks, Wool, Light. Also plans were laid to start a straight laundry test without wear to determine the extent of shrinkage on the light wool and cushion sole socks resulting just from laundering, and which operations in the field laundering procedure were principally responsible for felting of the wool.

3. <u>Quartermaster Board Study of the Causes of Shrinkage</u>

Since this test did not contain the wear cycle, but only involved laundering and drying, it could be run concurrently with

Fig. 1

EFFECT OF 18 LAUNDERINGS UPON THE ELASTICITY OF SOCKS CUSHION SOLE UNTREATED the wear test just referred to above, and its results could be expected in a very short time. Actually the test got under way shortly after a conference in mid-October at which the plan of the test was agreed upon. Findings were reported back early in December.

The test plan, briefly, provided for 12 launderings by the so-called wool laundering formula, with withdrawal of certain socks after each operation, viz., sudsing, rinsing, extracting and tumble drying. The first three types were air dried. Various controls were set up to insure comparability of results. Measurements of the amount of shrinkage were made after 1, 3, 5, 8 and 12 launderings by the ruler and sock board methods.*

The findings of this test showed that the greatest amount of shrinkage occurred during the first laundry operation, sudsing. After 12 launderings, for example, light wool socks which had shrunk 23.9% during sudsing lost only 5.2% more by rinsing, extracting and dry tumbling combined. For an equivalent number of launderings, cushion sole socks shrank 33.2%, of which 28.6% was accounted for by the sudsing operation alone. (See Figures 1, 2 and 3).

It had been thought that some of the excessive felting came from the dry tumbling operation, and that perhaps some change in that procedure might provide a means for reducing the degree of felting that was occurring in field laundering. Since it was now evident that the sudsing operation was the principal point at which felting occurred, it was clear that there was little that could be gained by attempting to change the laundering process.

Around the middle of December 1943 at a conference with representatives of the Quartermaster Board, evaluation of two additional types of socks by this laundry method was requested.

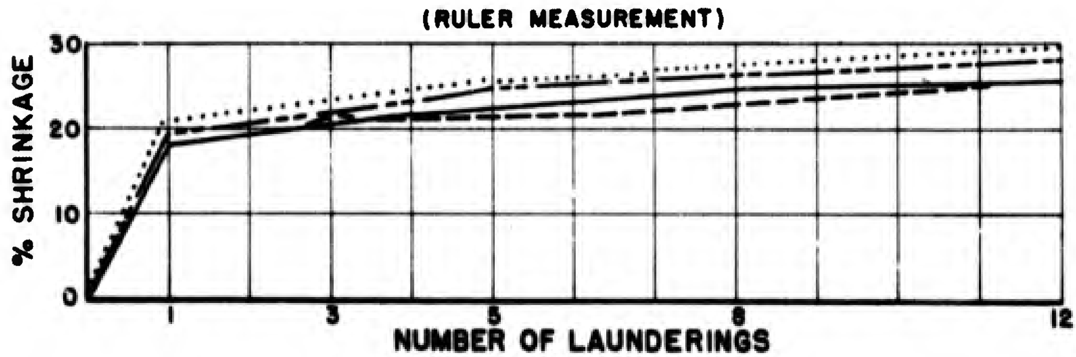
One of these types consisted of 4 pairs each of Socks, Wool, Light, and Socks, Wool, Cushion Sole, treated, in the laboratory by an enzyme process. The results of this test of the enzyme process were not particularly conclusive, except that they showed that even by this severe test of 12 consecutive launderings in the mobile laundry, socks which had been shrink resistant treated did not shrink as badly as non-treated. By the sock board method of measuring, the treated light wool socks after 12 launderings had shrunk only 11.5% as compared with 26.1% for the control, and the treated cushion sole socks 17.6% as compared with 30.2%.

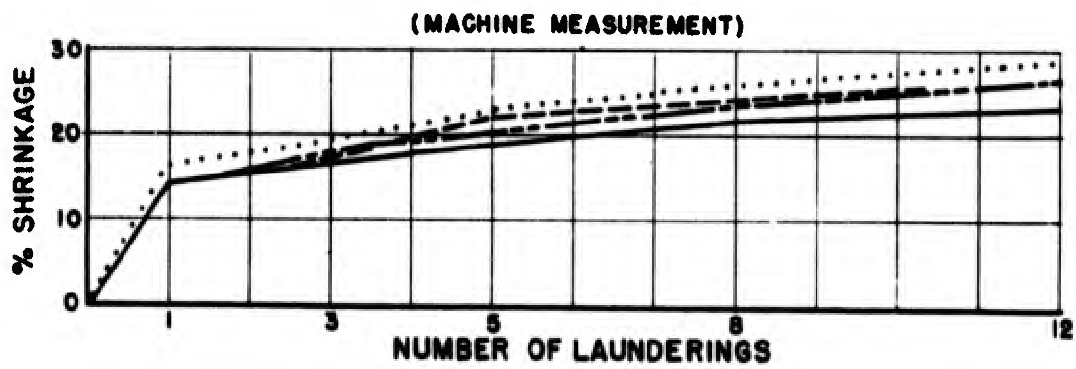
The other consisted of socks made from coarser grades of wool than had previously been specified, which it was believed would reduce

*See page 23.

Figure 2
AVERAGE CUMULATIVE SHRINKAGE OF SOCKS
WOOL, LIGHT, O. D.

TUMBLING ··············· EXTRACTING — — — —
RINSING — — — - - SUDSING ————





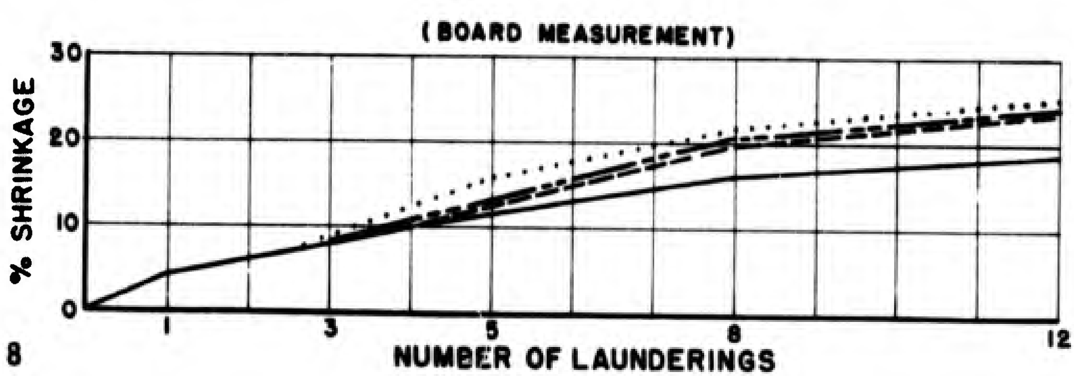


Figure 3

AVERAGE CUMULATIVE SHRINKAGE OF SOCKS, WOOL, CUSHION SOLE.

TUMBLING ----------
RINSING ————————
EXTRACTING ——— ———
SUDSING ——-—-——

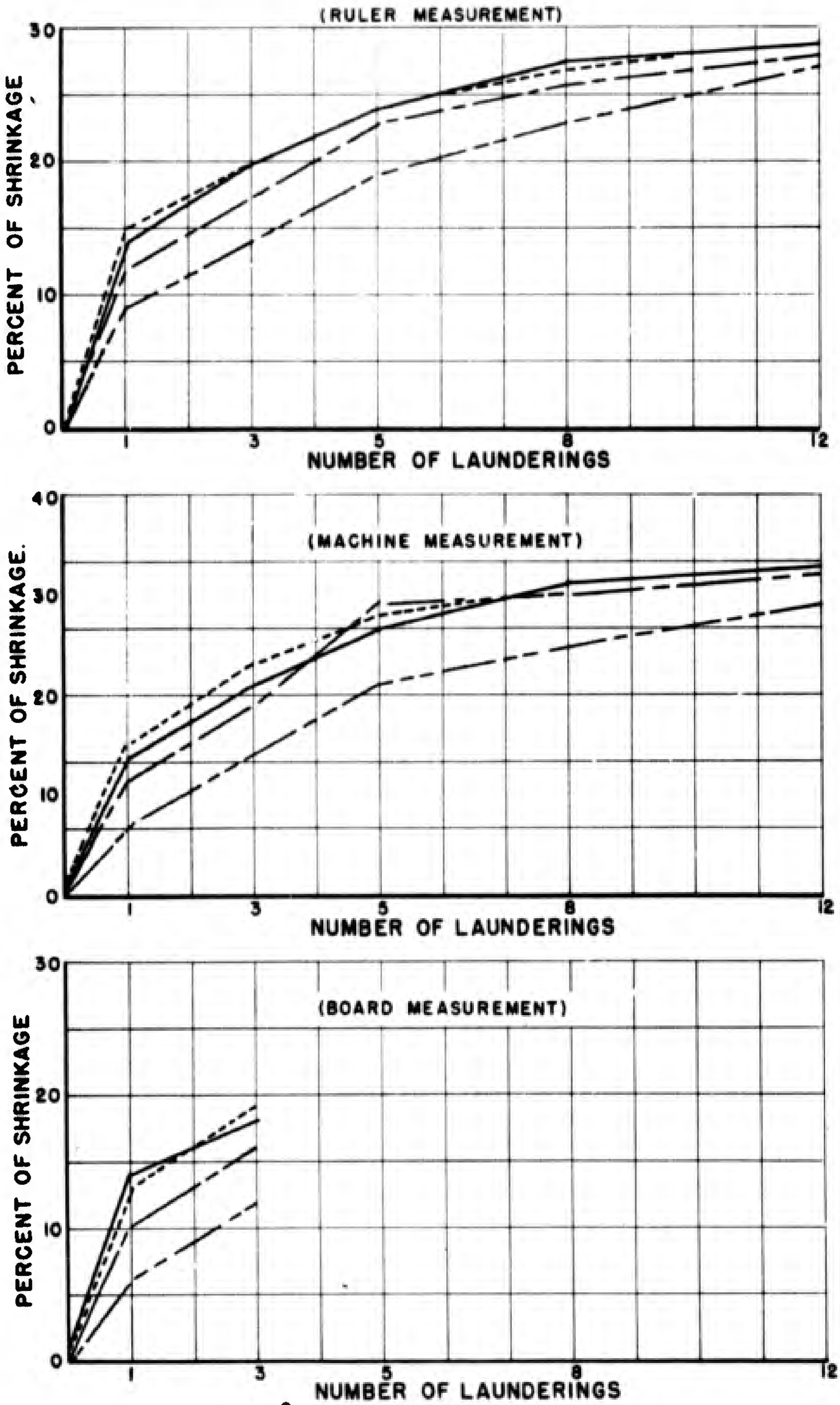


Figure 4
CUMULATIVE PERCENTAGE OF FAILURES OF SOCKS, WOOL, LIGHT.

CONTROL TYPE ————
EXPERIMENTAL TYPE - - - - - -

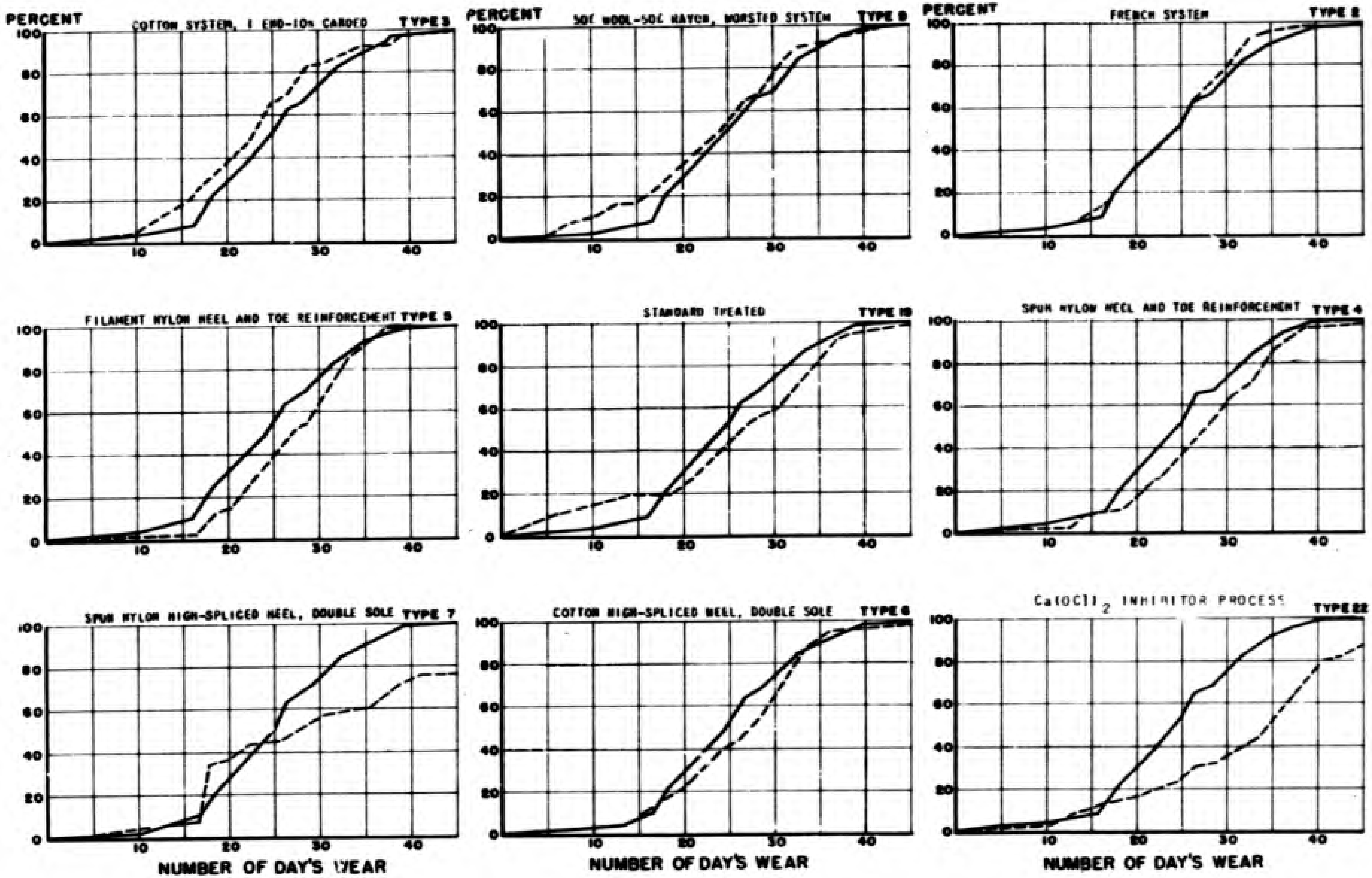
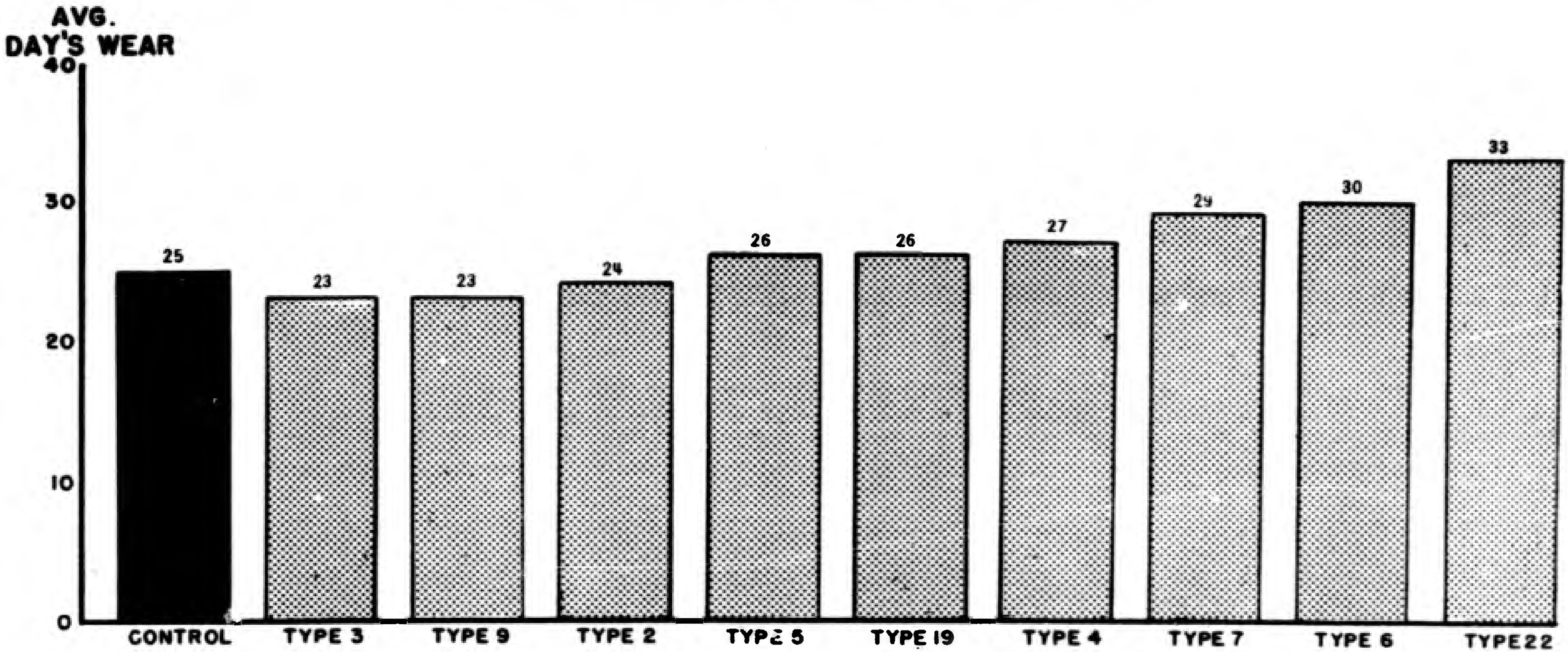


Figure 5

AVERAGE DAY'S WEAR OF SOCKS, WOOL, LIGHT.



LEGEND

TYPE	DESCRIPTION	TYPE	DESCRIPTION
CONTROL	STANDARD, COTTON SYSTEM	6	COTTON, HIGH-SPLICED HEEL, DOUBLE SOLE
2	FRENCH SYSTEM	7	SPUN NYLON HIGH-SPLICED HEEL, DOUBLE SOLE
3	COTTON SYSTEM, 1 END-10s CARDED	9	50% WOOL-50% RAYON, WORSTED SYSTEM
4	SPUN NYLON HEEL AND TOE REINFORCEMENT	19	STANDARD TREATED
5	FILAMENT NYLON HEEL AND TOE REINFORCEMENT	22	$Ca(OCl)_2$ INHIBITOR PROCESS

the amount of felting. At a conference in October 1943 with representatives of the wool yarn and hosiery industry, it had been agreed to call for 56/60's grade of wool in the body of the cushion sole sock, and 50/56's in the all-wool terry yarn, in place of "not coarser than 60's" as had previously been specified. The test, however, was made on both the light wool socks and the cushion sole socks, with both of them made from 56/60's grade of wool in the body yarn.

The laundry test on socks made from the coarser grade of wool did appear to warrant the change in specifications that had been made. By the sock board method of measurement, the light wool socks made from 56/60's grade of wool had shrunk only 11.6% as compared to 22.5% for the control, and the cushion sole socks only 17.9% as compared with 27.0%. It was evident from this test, however, that the use of a coarser grade of wool did not provide an adequate means for controlling shrinkage.

4. Results of the Comparative Wear Test

By mid-December the results of the wear test on the light wool socks were known,* and were presented informally to the Research and Development Branch. The test did show that socks with the high-spliced heel and double sole were superior to the existing item without those features, but much more important, it showed that the most effective way to increase the life of wool socks was to reduce the felting and shrinkage of the wool.

Figure 4 and Figure 5 show the wear life data on 9 types of sock, wool, light, which were included in this test at the Quartermaster Board. Thus Type 6, with cotton yarn reinforcing in the high heel and double sole, showed 20% more wear than the standard (30 days as compared with 25), and Type 7, with a reinforcing yarn in these areas spun from nylon waste, ran an average of 29 days. This sock would have worn longer except for faulty construction, as the rib top was too tight and tears developed at that point. It is significant that a fifth of all socks of this type were still in use after 45 days, when the test was discontinued.

Socks made from one end of 10's carded yarn, (Type 3) which had to be accepted as a substitute for two ends of 20's combed merino yarn, and socks made from a blend of 50% wool and 50% rayon (Type 9) were significantly inferior with only 23 days average wear each. The location of failures was also significant as is shown below in Table II.

*The formal report was submitted under date of 25 January 1944.

TYPE 10

TYPE 8

Fig. 6

EFFECT OF 3 LAUNDERINGS UPON LENGTH OF SOCKS WOOL LT.

TABLE II

PERCENTAGES OF FAILURES BY LOCATION

	Heel							
Type	Above Reinf.	On Reinf.	Toe	Sole	Instep	Ankle	Leg	Rib
1	45.3	25.8	18.0	3.8	0.0	0.0	0.8	6.3
2	22.5	21.7	15.0	1.7	0.0	0.0	1.6	37.5
3	45.6	21.6	12.8	13.6	3.2	0.0	0.8	2.4
4	56.6	15.1	11.3	4.7	1.9	0.0	0.9	9.5
5	55.9	15.0	3.1	2.4	0.8	0.0	2.4	20.4
6	0.0	66.2	19.8	8.3	1.7	0.0	0.0	14.0
7	1.1	13.6	13.6	0.0	0.0	1.1	9.2	61.4
8	WITHDRAWN		----	---	---	---	---	----
9	16.1	27.3	13.3	11.2	2.8	0.0	11.2	18.1
10	WITHDRAWN		----	----	---	---	----	----
19	45.6	21.6	12.8	13.6	3.2	0.0	0.8	2.4
22	28.8	26.0	13.5	21.1	6.7	1.0	2.9	0.0

Note: Types 8 and 10 had to be withdrawn because of excessive shrinkage after three launderings that made it impossible to wear them. (See Figure 6)

The most significant feature of this test was the clear evidence that socks treated for shrink resistance outwore any other socks not so treated. Two types of shrink resistant socks were included in this trial - Types 19 and 22. Type 19 was an early trial and the results were not particularly significant. Type 22, however, was a trial lot treated by the calcium hypochlorite inhibitor process which came to be permitted on contract deliveries of cushion sole socks by the first contractors to be converted over. On Type 22 the average wear was 33 days as compared with the 25 days of the standard, or an increase in wear life of 32%. Moreover a number of the socks were still in use at the end of the 45th day.

This factor of shrinkage was carefully explored from a number of different angles because of the heavy shrinkage which it had been shown occurred in the field laundries. A test was made to determine the average number of days wear when socks were worn on a one day wear-and-laundry-cycle and laundered by different methods, and also the amount of shrinkage resulting from such different methods of laundering. The results are shown in Table III.

TABLE III

SHRINKAGE AND DAYS OF WEAR OBTAINED WITH DIFFERENT METHODS OF LAUNDERING

	Hand Laundering	Field Laundering	Post Laundering
1st Laundering	10.41 %	15.11%	15.66%
3rd Laundering	9.47%	15.88%	16.18%
5th Laundering	9.03 %	16.59%	16.75%
Average days of wear	25.0 days	22.5 days	20.4 days

Here it was evident that the greater wear of the hand-laundered socks arose from the smaller amount of shrinkage obtained by gentler methods of laundering.

Another test showed that when socks were worn for two days and then laundered, they wore longer than if laundered after each day's wear - 23.0 days for two day's wear, as compared with 20.4 days for one day's wear before each laundering. This again showed the influence of shrinkage in laundering upon ultimate wear.

Before the test was actually completed it had become evident to personnel of the Quartermaster Board who were conducting the test, that a principal cause of wear in untreated socks was the decrease in their size resulting from felting shrinkage, the shifting of the point of wear above the reinforced area to the high heel, and the increase in tension at the principal points of wear. The final results of the tests bore out these conclusions. Meanwhile, the decision had been made to adopt a shrinkproofing process as soon as possible, and to require the high heel and double sole reinforcing on future deliveries of the Sock, Wool, Light.

5. Initiation of Wool Shrinkage Research

Early in 1943, when consideration was being given to the problem of wear of socks, a survey was made of the possibilities of adopting some process for making Army wool items shrink resistant. Various individuals and firms who were familiar with the technology involved and the different available treatments were consulted. Representatives of the British wool industry were included, and a consultant of the Research and Development Branch was sent to England in the Spring of 1943 to make a detailed study of the methods employed there to obtain shrink resistance of wool.

Further study of the process most favorably regarded and most widely used in Great Britain, a dry chlorination process, indicated that its immediate use on industry-wide basis in this country was not feasible. It necessitated the use of certain equipment, not too elaborate, but very difficult to obtain in the face of higher priorities from other military requirements. It also required certain "know-how" and the use of technically trained men, who were not then available in the hosiery industry, and in the face of Selective Service policies, clearly could not be made available.

When the report came in from the Quartermaster Board in August 1943, that the cushion sole socks had had to be taken out of the test because they became unwearable after the second or third laundering, it was realized that a solution to the problem of felting shrinkage on wool socks had to be found at once.

The matter was presented, in accordance with standing procedure in the Research and Development Branch, to the Committee on Quartermaster Problems of the National Research Council. It was recommended to the Committee that a research project be arranged with The Textile Foundation in order to obtain the services of Dr. Milton Harris as the leader of the project for the study of this problem. Through the cooperation of all concerned a contract under the National Research Council with The Textile Foundation was quickly signed and work was commenced.

By the time of the December 13, 1943 meeting with the Quartermaster Board, progress had been made in further surveying the field and narrowing down the lines of investigation. The process for treating wool socks used by the Sulloway Hosiery Mills, Franklin, New Hampshire, appeared to offer the most promising line of investigation. However, there were two other processes along quite different lines, which it was felt should also be investigated immediately. These were an enzyme process and one based upon the use of alcoholic potassium hydroxide.

Arrangements were accordingly made with the Sulloway Hosiery Mills for a trial application of all three processes. The objective was to obtain some practical experience with them, and also to get some socks for evaluation of the treatments by the Quartermaster Board. This trial run was made around Christmas 1943, and the socks were sent at once to Camp Lee.

This experimental run demonstrated that even in the absence of adequate test procedures which could be included in a specification, the process was sufficiently controllable to warrant its use in procurement. Accordingly, a few weeks later arrangements were made with the Sulloway Hosiery Mills to renegotiate their contract to permit their changing over to production of shrink resistant treated socks.

This action was followed shortly afterward by conversion of the plants of W. B. Davis & Sons, Fort Payne, Alabama, and Nolde & Horst Company, Reading, Pennsylvania. The procedure in each case was to make a demonstr ion run, and to check the resulting product in the laboratory by the best means available at the time to determine the degree of shrinkage control and the extent of damage to the wool fiber.

Partly because of the convenience of the Nolde & Horst plant to the Philadelphia Quartermaster Depot, and also because of the availability there of the required equipment, as well as the exceptionally cooperative attitude of this firm, arrangements were made with Nolde & Horst to utilize some of its facilities for pilot plant operation in the further study and improvement of this and other processes for wool shrinkage control.

6. First Quartermaster Board Evaluation of Treated Socks

The socks which had been treated at Sulloway just before New Year's Day 1944 were added as additional types to both tests being run at the Quartermaster Board: the laundering test, and the wear test, as described above. They included both Socks, Wool, Light, and Socks, Wool, Cushion Sole, and were carried under the code numbers shown in Table IV.

TABLE IV

ADDITIONAL TYPES OF SOCKS PROVIDED FOR THE COMPARATIVE WEAR AND LAUNDERING TESTS AT THE QUARTERMASTER BOARD

Code No.	Type	Treatment	Grade of Wool	Spinning System	High-Spliced Heel and Double Sole
27	Socks, Wool, Light	None	56/60's	French	2 ply CPM
28	Socks, Wool, Cushion Sole	None	56/60's	French	" " "
29	Socks, Wool, Light	Enzyme	60's	Cotton	" " "
30	" " "	$Ca(OCl)_2$ Inhibitor Pro.	"	"	" " "
31	" " "	Alcoholic KOH	"	"	" " "
32	" " "	None (Control)	"	"	" " "
33	Socks, Wool, Cushion Sole	Enzyme	"	"	---
34	" " "	$Ca(OCl)_2$ Inhibitor Process	"	"	---
35	" " "	Alcoholic KOH	"	"	---
36	" " "	None (Control)	"	"	---

In the laundering phase of the test, the procedure was the same as had previously been used except that it was decided to increase the number of launderings and take measurements also after the 15th and 18th launderings.

The results of the laundering phase indicated that we still had a long way to go to get satisfactory shrinkage control. Most of all they showed that a more satisfactory method of measuring shrinkage had to be found. Neither the ruler nor the sock board methods of measurement seemed to be telling the story of what was actually occurring. They did not agree with each other, and the sock board method seemed to lean too much to the judgment of the operator (See Figure 7). Work was accordingly expedited which led later to the development of the Schiefer Machine.

The results of the laundering test showed that shrinkage control was being effected, but not as much as had been hoped for. The socks that had been treated by the alcoholic potassium hydroxide process seemed to be the best of the three treated types. The Socks, Wool, Light, treated by this process, when measured by the ruler method after 18 launderings, showed a shrinkage of 20.6%, but only 8.7% by the sock board method. The Socks, Wool, Cushion Sole, treated by this process showed a shrinkage of 15.2% by the ruler method after 18 launderings, and 13.0% by the sock board method.

The enzyme treatment seemed to give about as good results on the Socks, Wool, Light, but not nearly as good on the Socks, Wool Cushion Sole. In fact the amount of shrinkage of these enzyme treated cushion sole socks was so great they could not be pulled over the sock boards.

The calcium hypochlorite inhibitor process gave only fair results. It was possible to get these socks over the sock boards, but the degree of shrinkage on the cushion sole socks, 21.7%, was certainly excessive.

It must be pointed out that this part of the test was concerned solely with laundering of the socks, also that this was the first plant trial application on the three processes.

In addition to this laundry phase there was a wear phase as had been conducted on the earlier tested types. The results of this test were as follows:

TABLE V

AVERAGE DAYS OF WEAR AND SHRINKAGE

ADDITIONAL TYPES OF SOCKS LISTED IN TABLE IV

	Percent shrinkage	Average Days Wear
Socks, Wool, Light		
1 (Standard)	20.87	22.3
25 (Same as 27 but cotton spun)	14.38	21.3
27	16.67	24.2
29	19.54	27.0
30	17.74	28.1
31	18.34	32.8
32 (Control)	19.90	27.3
Socks, Wool, Cushion Sole		
26 (Same as 28 but cotton spun)	11.96	35.5
28	13.61	*
33	14.44	36.6
34	13.85	37.8
35	11.79	40.6
36 (Control)	14.87	25.1

*Withdrawn after 14 days wear because of excessive shrinkage in the top and leg.

This test afforded an opportunity to make a new run on the standard sock, Type 1, which previously had shown 25 days of wear. In this test a re-run gave 22.3 days. Similarly, Type 32 was presumably a duplicate of Type 6, which had previously shown 30 days of wear. This showed just about the same percentage reduction in amount of wear as Type 1, which would indicate harder wear in some way by this group of men. This seemed to indicate that variations did exist between trials, and that a group of socks tested at one time could not be compared exactly with socks tested at other times.

Several interesting conclusions seemed warranted from this test. From a study of the location of failures, it was apparent that the greater durability of Type 32 as compared with Type 1 lay in the high spliced heel reinforcement, rather than the double sole.

Similarly the socks made of 56/60's grade of wool did not wear quite as well as socks made with 60's grade - 24.2 days on the light-weight sock as compared with 27.3. (Both had the high spliced heel and double sole reinforcement). The comparison could not be made on the cushion sole sock because of forced withdrawal of Type 28.

Socks made of yarn spun on the French system seemed to shrink slightly more than those made from yarn spun on the cotton system.

As to the effect of the shrinkage treatments upon wear, the results, as in the laundering phase, were disappointing. Only the alcoholic potassium hydroxide process gave a clear indication of increased wear, 32.8 days as compared with 27.3 days for the control.

The fact that Type 36, an untreated cushion sole sock, could be worn to failure, whereas that had not formerly been possible, may be attributed in part to the fact that a much tighter specification had been drawn up, requiring, among other things, a specified number of courses in the leg and foot, and a generally tighter construction.

Subsequently a group of both types of socks were admitted to the test, made from wool treated by a dry chlorination treatment. This wool actually was finer than 60's, about 64's grade. The results of trial run indicated shrinkage of around 18% and wear of 30 to 33 days.

7. Further Evaluation of Treated Socks

In considering all of the foregoing data, account should be taken of the fact that up to the time of conclusion of these tests no satisfactory technique had been developed for differentiating between felting shrinkage and relaxation shrinkage. Consequently, the figures represent total shrinkage which was all the Board was prepared to measure at that time.

Direct comparison also cannot properly be made between shrinkage figures of cushion sole and light wool socks, since they were later shown to have different relaxation shrinkage characteristics.

A further factor which began to demonstrate itself and which tended to influence significantly the validity of further testing at the Board, was the increasing number of failures of test socks at the looping line across the toe. Reinforcement of the high heel, and reduction of shrinkage was apparently causing much higher percentage of failures to occur at the remaining weak point in the sock.

Thus, by the middle of 1944 the evaluation of shrink resistant processes in the laboratory had progressed to a point where it was desired to try out a number of variations of the process most generally being used, as well as some other processes, to see if laboratory conclusions could be verified by field trials. The results of these tests were generally inconclusive, largely due to this factor of the shifting of the point of wear to the looping line.

On one such test of treated cushion sole socks, the untreated control type showed 17.5% of its failures at the looping line, whereas the treated types showed 31.7%, 26.9%, 30.6%, 27.4%, 34.0%, 39.8% and 35.2%. Since failure at the looping line had nothing to do with the characteristics being tested, it was apparent that measurement of average number of days of wear was not going to be a valid test method for comparison of variations in treatment upon wear expectancy.

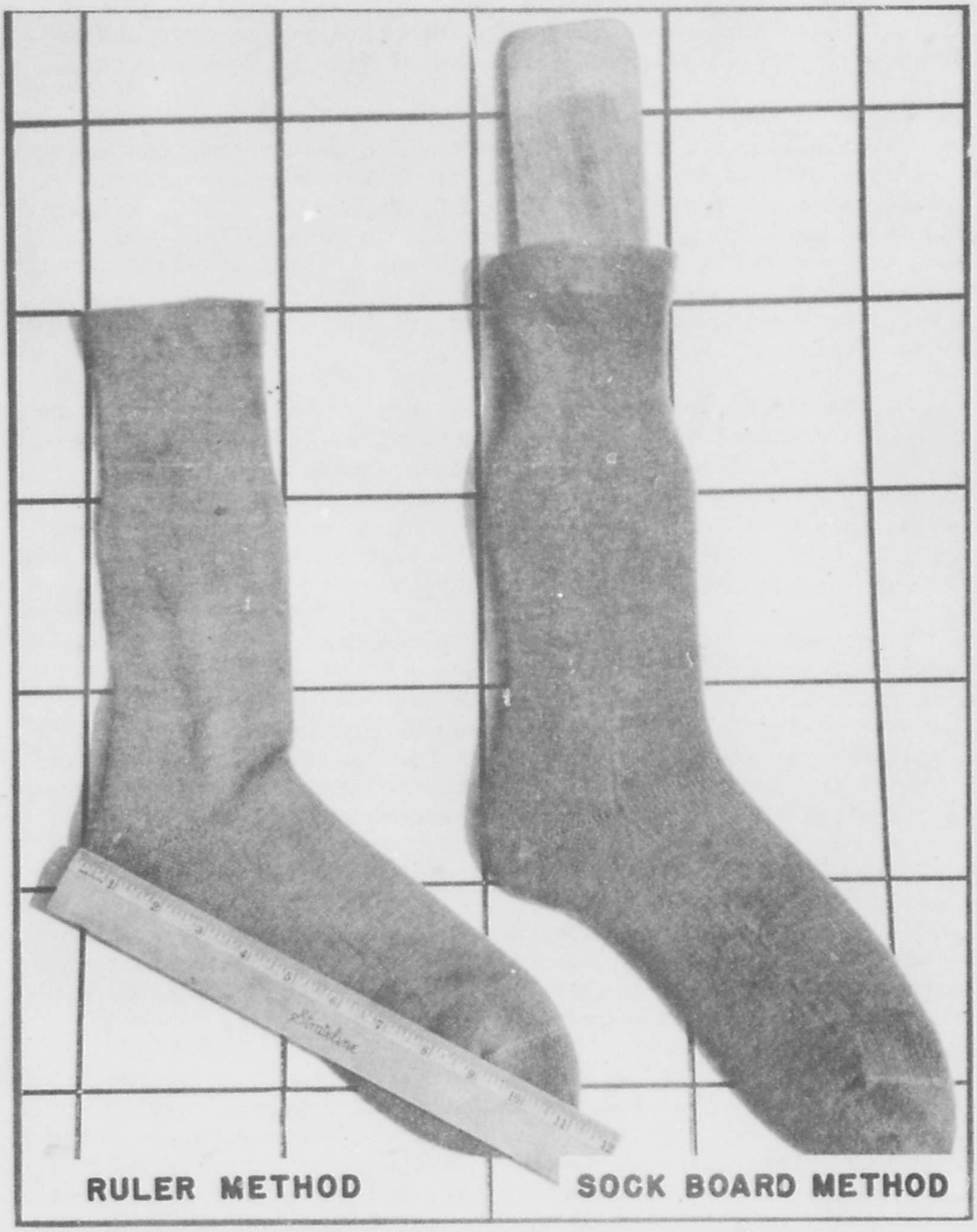
The simple measurement of failures, which had quite evidently given valid results in the early comparative wear tests, no longer was adequate, now that the socks no longer shrank significantly. Furthermore, it became evident as the results of these tests came in, that even though it was a cushion sole sock on which evaluation was desired, it would have been better to have used a sock with less protection at the points of wear for the types of evaluation sought.

At about the same time that it was becoming evident that the wear test technique of the Board was not going to give desired data on refined types of treatment, the laboratory research program had made very significant progress in developing research tools of much greater precision. Accordingly, after the beginning 1945, further sock tests for Camp Lee were held in abeyance and work was concentrated upon the laboratory phases of the research project.

8. Development of a Cotton Sock With Wool Cushion Sole

Among the various experiments in sock construction which were tried was one that held considerable interest. This was the development at the suggestion of Quartermaster Board personnel of a sock with an all-cotton body and a wool cushion sole.

The test of these socks demonstrated good wear characteristics for a heavy all-cotton sock which did not shrink appreciably, even though the wool terry yarn in the foot felted progressively. These socks had the disadvantages, however, of lack of elasticity and the loss of the resilience of the wool fiber, and hence were considered as an alternate only in case of a shortage of wool.



On a size 11 sock the foot measures 11 inches from the top of the toe through the gore of the heel to a point in back of the heel.

A size 11 sock fits smoothly, without undue stretch, over a size 11 sock board.

Fig. 7

METHODS OF MEASUREMENT

SECTION C

DEVELOPMENT OF TEST METHODS

It was apparent from the start that a performance specification would be needed in Quartermaster procurement of wool items with a shrink-resistant finish. Accordingly, one of the most important aspects of the early work in the research program was the development of test methods.

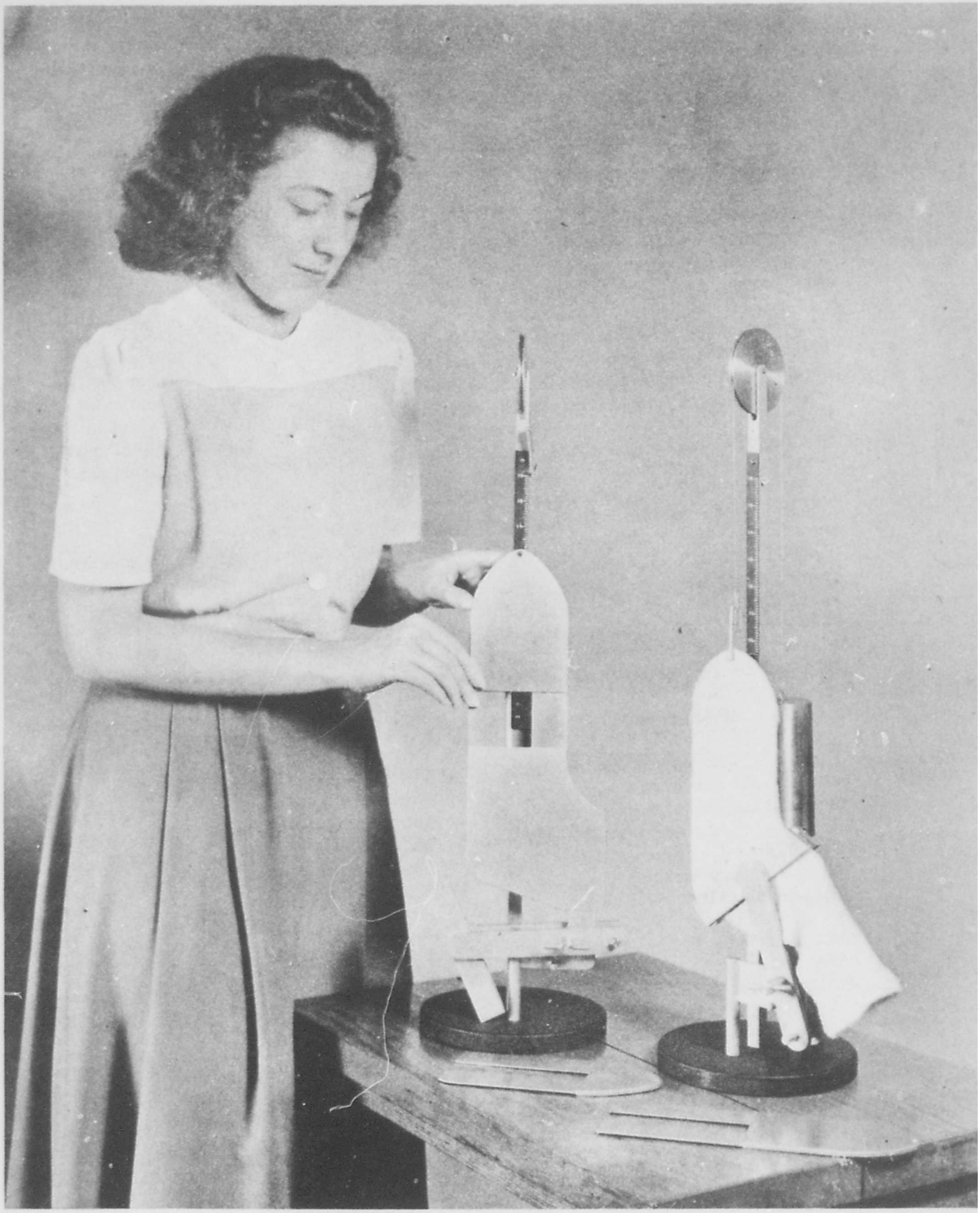
It is well known that many, if not all, of the processes for reducing the tendency of wool to shrink and felt also cause a certain amount of fiber modification. Accordingly, one of the most important problems in applying any such treatment was to determine the point at which the benefits of shrink resistance would be offset by the disadvantages of reduced strength and elasticity which might result from excessive fiber modification.

Therefore, it was essential to have adequate methods of measuring both shrinkage control and fiber damage in order to compare the effects of various treatments and to establish a method for controlling each process. Thus, two of the first problems for the laboratory research phase of the program were the development of a standard method of measuring felting shrinkage, and the evaluation of various tests for wool fiber damage to select those most applicable for each type of treatment.

1. Measurement of Shrinkage.

The exact measurement of knitted fabrics is difficult because slight differences in tension cause considerable variations in result. In the case of irregular shaped articles, such as socks, the problem is especially difficult, and it is important to have a reliable and reproducible standard method for determining size. The customary method used in the hosiery industry has been to measure the distance between the heel and toe with a ruler while the sock lies on a flat surface. It was found, however, that different operators did not secure the same results even on the same socks when this method was employed. An alternative method was the sizing of socks on standard sock boards, but this also was not reliable because it involved too much judgment of the tension of the sock on the board on the part of the operator. (Figure 7)

Another method was sought, and under the direction of Dr. Herbert Schiefer of the National Bureau of Standards, a sock



Fiqure 8

SCHIEFER SOCK MEASURING DEVICE.

measuring device was developed. The present form of the device is illustrated in Figure 8. The metal foot form is made in two pieces and is mounted so that the toe portion will slide out to allow elongation of the sock. The sock is put on the form, clamped in position across the gore line, and a five-pound load is applied to the foot by attaching the weighted cord to the hole in the toe plate. Thus the length of the sock under a definite load can be read directly from the scale. The measurements obtained in this way proved consistent and showed little difference between operators.

In addition to the difficulty of obtaining accurate measurements on socks, the problem of differentiating between relaxation shrinkage and felting or fulling shrinkage also had to be considered. Relaxation shrinkage is the shrinkage which occurs when woolen socks are wet out, and is the result of the relaxing of mechanical tensions set up during fabrication and finishing. Fulling or felting shrinkage on the other hand is the damaging shrinkage that occurs during washing from the starting of the felting action of the wool.

To achieve the ultimate from the experimental program and to properly evaluate shrinkage control experiments, it was necessary to distinguish clearly between relaxation shrinkage and felting shrinkage. As a first step in analysis socks were accordingly soaked in water at 95-104° F for two hours and allowed to dry at room temperature on a horizontal wire screen before they were first measured for size.

The actual felting-shrinkage test was carried out as follows: The socks were given a two-hour washing in a running suds* of neutral soap and 0.2% sodium carbonate (on the weight of the solution) at 140° F., followed by two rinses at 50° C. A 24x20-inch cylinder Najort washer, with a speed of 32 r.p.m., reversing every 5 cycles, was used. The test load was four pounds, and the ratio of bath to goods was 15 to 1. The water level was kept only two inches above the inside of the cylinder so that the socks were subjected to considerable mechanical action during the washing.

*A running suds is just visible on the side of the laundry wheel when it is turning away from the operator.

The laundry time for the all-wool socks had to be reduced to one hour, for when washing was continued longer than this the socks shrank so much that they could not be measured on the Schiefer device. The calculations for shrinkage were made according to the following formulas:

$$\text{Relaxation shrinkage (\%)} = \frac{L_O - L_R}{L_O} \times 100$$

$$\text{Felting Shrinkage (\%)} = \frac{L_R - L_W}{L_R} \times 100$$

where L_O is the original length of the sock, L_R is the length after relaxation, and L_W is the length after washing.

2. Estimation of Fiber Damage

Numerous tests for detecting and estimating damage to wool fibers have been suggested, but the majority of them have a limited range of usefulness, or are tedious and time-consuming. Therefore, many tests were investigated in an effort to find simple, reproducible, quantitative measurements which could be used for routine control work, and which would correlate with the data from the actual wear tests.

a. Loss of Weight. This is perhaps the simplest method of measuring wool damage, as it involves only determining the oven-dry weight of the sample before and after it has been treated. This loss of weight was considered significant when it was greater than 1%. A large loss in weight indicates appreciable damage resulting from actual degradation of the protein molecule; the smaller molecular weight degradation products are more soluble than the intact protein.

b. Alkali Solubility. It is known that treatments with halogens, peroxides and other oxidizing agents increase the susceptibility of wool to attack by alkalies largely by splitting the disulfide cross-linkages of the wool structure. Thus, solubility in alkali may be used as a measure of this type of wool degradation, and actually such a test, called the alkali-solubility test, has been extensively used in the wool industry. The usefulness of such a test is indicated by the fact that in some cases which have been investigated, a relationship between alkali solubility and wear has been established. Thus, for example, it has been shown that there is a fairly close correlation between the alkali solubility and the wear index of carpets made from wools which had been treated with different concentrations of sodium hypochlorite.

The alkali solubility is defined as "the percent loss in weight of one gram of wool which has been kept in 100 ml. of N/10 NaOH for one hour at 65°C., rinsed and dried". It is calculated from the formula:

$$\frac{W_0 - W_t}{W_0 F} \times 100 = \text{Alkali solubility (\%)}$$

where W_0 is the oven dry weight of the original sample, W_t is the oven-dry weight of the treated sample, and F is the fractional wool content of the sample. In this way all values are expressed on the basis of 100% wool.

3. The 30% Index

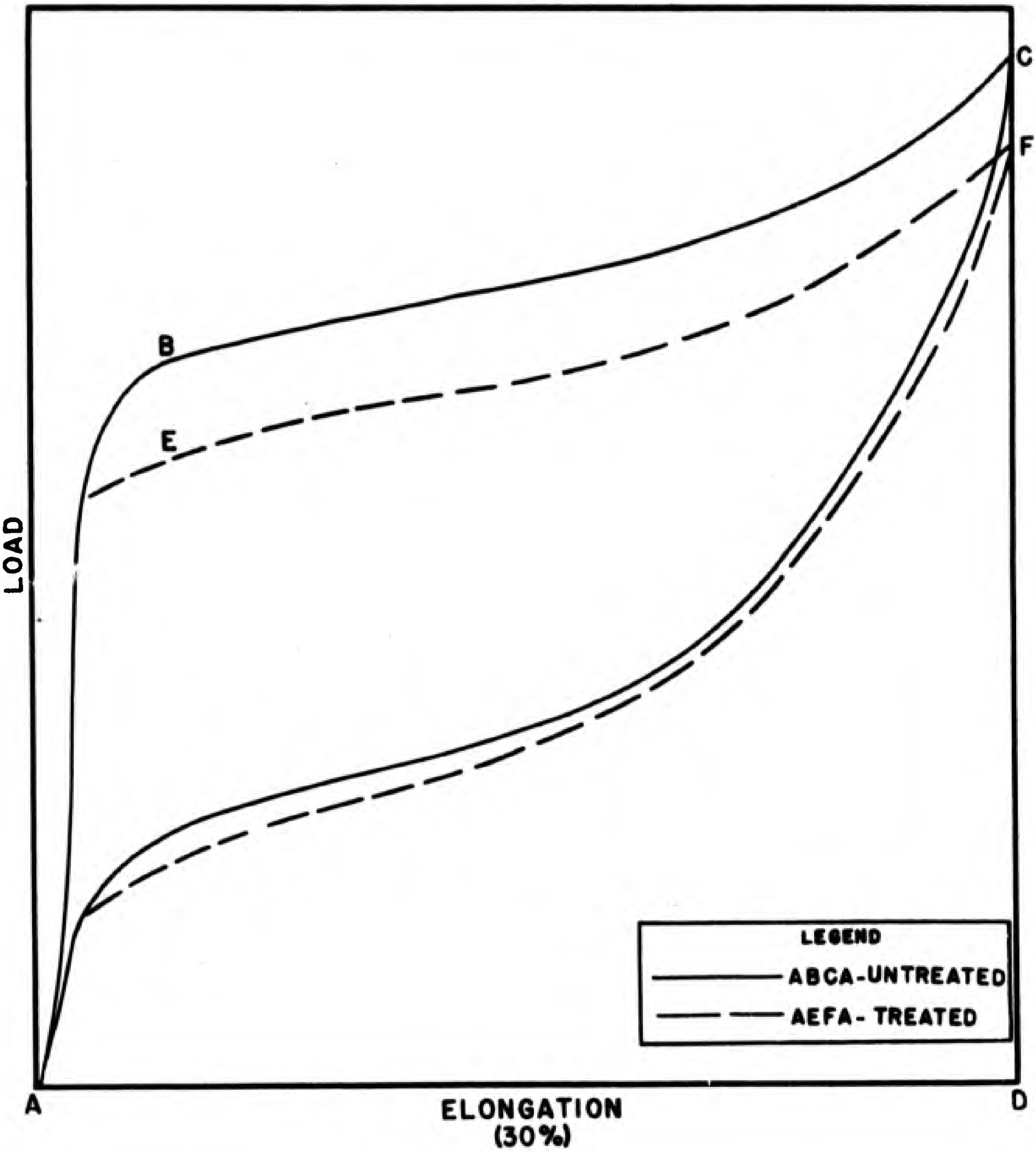
Resiliency and elasticity are undoubtedly the most important properties of wool fibers and contribute much to the desirability of wool for many items of clothing. Since these properties may be adversely affected by chemical treatments, it was necessary to ascertain whether any of the shrink-resistant treatments produced harmful effects. Fortunately an autographic stress-strain balance had been developed by Sookne and Rutherford for studying the mechanical properties of single fibers and preliminary experiments indicated that this apparatus would be useful in securing quantitative information on the extent of modification of wool fibers during shrink-resistant treatments.

The tests were made by mounting a single fiber between two glass hooks about two inches apart, soaking the fiber in distilled water for 24 hours, stretching it, while wet, to 30% of its original length, and allowing it to recover. The elongation and recovery curves of the fiber were recorded. The fiber was then inclosed in a perforated Saran capsule and processed with socks during treatments at the pilot plant. After the treatment, the fiber was removed from the capsule and again stretched to 30% of its length. The ratio of the work required to stretch the treated fiber to the work required to stretch the untreated fiber is known as the "30% index".

Fiqure 9

STRESS-STRAIN CURVES OF SAME UNTREATED & TREATED WOOL FIBER ELONGATED TO 30%.

$$30\%\ \text{INDEX} = \frac{AEFD}{ABCD} = 88\%$$



A typical set of curves is shown in Figure 9, where the solid line represents the original fiber and the dotted line represents the same fiber after treatment. In this particular case the ratio of AEFD to ABCD is 88%, but for undamaged fibers the ratio is seldom below 99%.

This measurement affords a very sensitive method of detecting physical changes in fibers, but it does not indicate what chemical action has taken place, nor does it predict the wearing qualities. These factors must be determined by correlation with other tests. Furthermore, the test requires highly specialized equipment and trained operators, which means that it is useful only as a research tool and not as a routine laboratory check.

4. Nitrogen, Total Sulfur, and Cystine Content

A decrease in the nitrogen, sulfur or cystine content, and especially the last, is indicative of oxidative damage to the wool. The analyses were made by standard methods, using the Mease method for total sulfur, the Sullivan method for cystine, and a micro-Kjeldahl method for nitrogen.

5. Surface Scale Structure

It has been suggested frequently that the felting properties of wool are closely related to its scale structure, and that the shrinking and felting characteristics of wool are reduced by those processes which alter the scale structure. The theory has been advanced that the fibers become slippery so that it is no longer possible for them to migrate and interlock with each other. Preliminary investigations revealed that direct microscopic observations of the scales may lead to confusing results, and accordingly comparisons of scale structure were made on transparent fiber casts rather than on the fibers. The casts were prepared by placing the treated fibers between sheets of ethylcellulose, which were then warmed under slight pressure. Typical scale structures are illustrated and discussed later.

6. Frictional Properties

The fact that the outer layer of wool fibers is composed of overlapping scales, each with its free end pointed toward the tip of the fiber, explains why wool normally exhibits a highly directional friction effect. That is, when the coefficient of friction is determined by rubbing the fiber from the tip toward the root end a higher value is obtained than when the fiber is rubbed in the other direction. It has been suggested that the felting properties of normal wool are due in part to its high directional friction effect, which allows the fibers to migrate and interlock with each other during the felting process. Excessive chlorination also has been shown to remove the surface scales, leading other workers to suggest that the mechanism of chlorination is to cause the fiber surface to become so slippery that fiber migration, and consequently felting, is greatly reduced. To test this theory, a special instrument was devised for measuring the static coefficient of friction of single fibers. The fiber, with a 400-mg. weight at one end, was placed over a horizontal rod covered with wool felt, and the other end of the fiber was attached to a chainomatic loading device. Thus, the fiber was held taut and the load was applied gradually until the fiber just started to move across the felt. Calculations were made according to the following formula:

$$\text{Static coefficient of friction} = 0.733 \log_{10} \frac{T}{T_o}$$

where T is the total weight acting on the chain side of the fiber and T_o is the weight applied to the other side.

Two coefficients were obtained for each fiber; one obtained by attempting to move the fiber from tip to root (or against the scales) and one by attempting to move the fiber from root to tip (with the scales). The former gives a larger coefficient. A directional coefficient may then be calculated by subtracting the lower value from the higher value.

Two additional and more useful values, the friction index and the friction ratio, may be calculated by the following expression:

$$\text{Friction index } (\%) = \frac{F_{HT} - F_{LT}}{F_{HO} - F_{LO}} \times 100$$

$$\text{Friction ratio } (5) = \frac{F_{HT} + F_{LT}}{F_{HO} + F_{LO}} \times 100$$

where F is the static coefficient of friction, H indicates the high value and L the low value, O is the original untreated fiber, and T is the treated fiber. The former represents the change in the directional friction effect and the latter the change in overall frictional properties of the fiber produced during treatment of the fibers.

7. Further Exploration of Test Methods

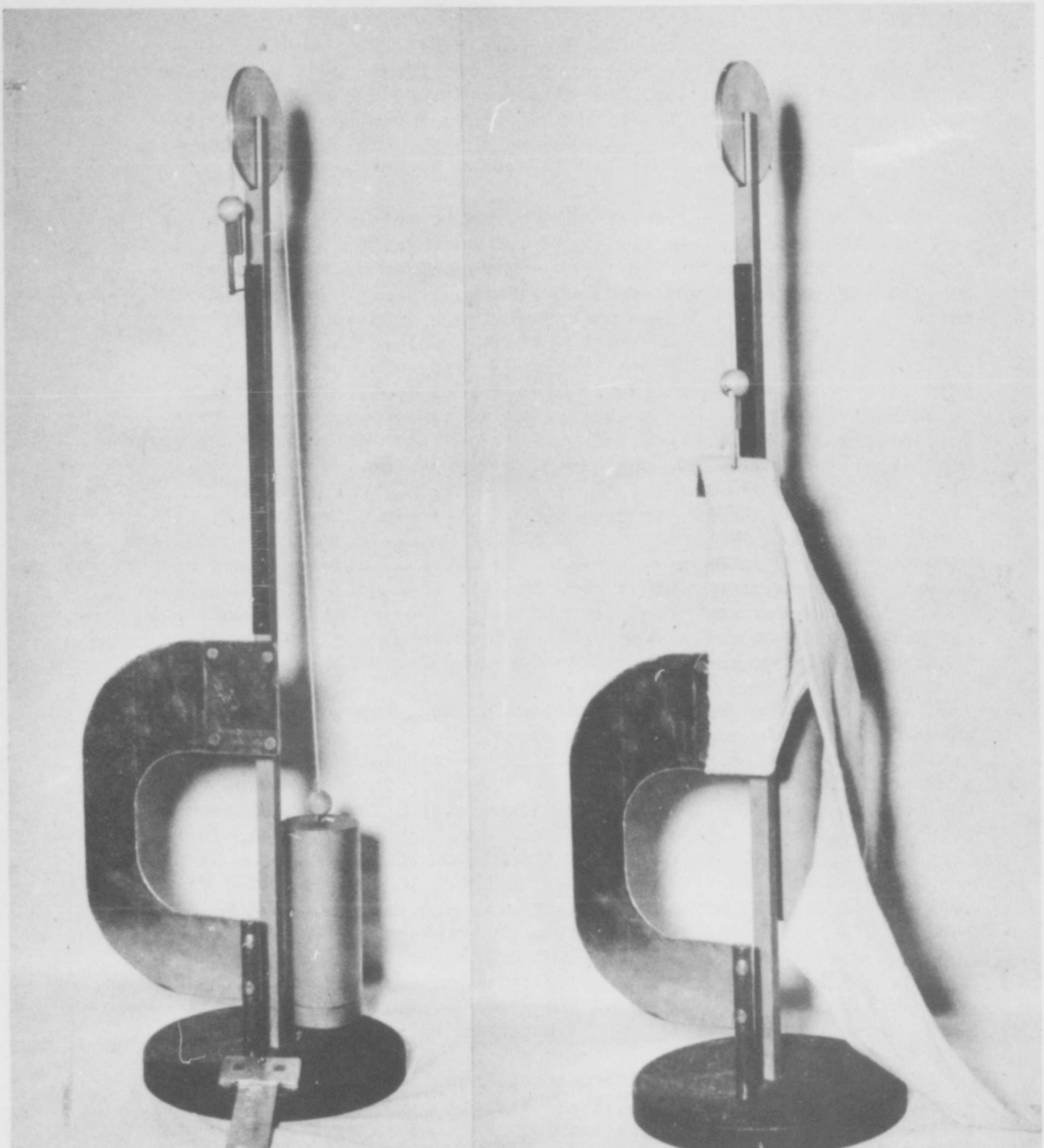
In an attempt to obtain a more satisfactory method of measuring shrinkage of socks than was accomplished by the Schiefer machine and to obviate the lack of correlation of the ruler, sock board, and Schiefer machine techniques, study was continued at the Textile Research Laboratory located at the Philadelphia Quartermaster Depot, to improve the previously developed procedures.

Two basic approaches were taken in this work. The first was an attempt to measure shrinkage volumetrically by filling a sock with small glass marbles both before and after washing and determining the shrinkage by count of the marbles. The second method sought to take linear measurements in different directions under constant load to determine shrinkage across the sock or lengthwise along certain predetermined axes. The necessity for this latter method was indicated by previous spot investigations which had shown that lengthwise shrinkage as determinable by methods then existing was not always equivalent to what occurs in other critical directions, such as, for example, cuff width.

In the marble technique, sock size was determined by the number of marbles required to fill a sock under controlled conditions without producing excessive stretch. Results obtained by this method, however, were not found to be reproducible inasmuch as the weight of the marbles caused variable stretching in spite of all precautions. Similar unreliable results were noted when steel shot was used, or when the volume of the sock was measured by inflation.

The other method of determining shrinkage of socks has shown considerable promise. In essence, it represents a modification of the Schiefer device and permits the measurement under tension of dimensions other than foot length. The apparatus, termed the Houchins Modification, was developed at the Textile Research Laboratory located at the Philadelphia Quartermaster Depot. In the Houchins apparatus, the foot form and clamps of the Schiefer device are replaced by a curved bracket, as in Figure 10, by which the dimensions of even highly shrunk socks can be measured. An auxiliary form is also available which permits measurement of the width of the sock from the instep to the heel. The sock is so positioned that the heel fits over the upper portion of the frame with the gore in line with the center of the instrument, and the width is then read directly from the scale as shown in Figure 11.

Preliminary laboratory tests have indicated that there is a close correlation between the results obtained with the Houchins Modification and the Schiefer machine, so that the latter instrument is considered adequate for production control. However, the Houchins device should prove useful for detailed studies, particularly when improper knitting results in inadequate elasticity in some parts of the sock.



Fiqure 10

HOUCHINS' MODIFICATION OF THE SCHIEFER MACHINE(WIDTH MEASUREMENT)

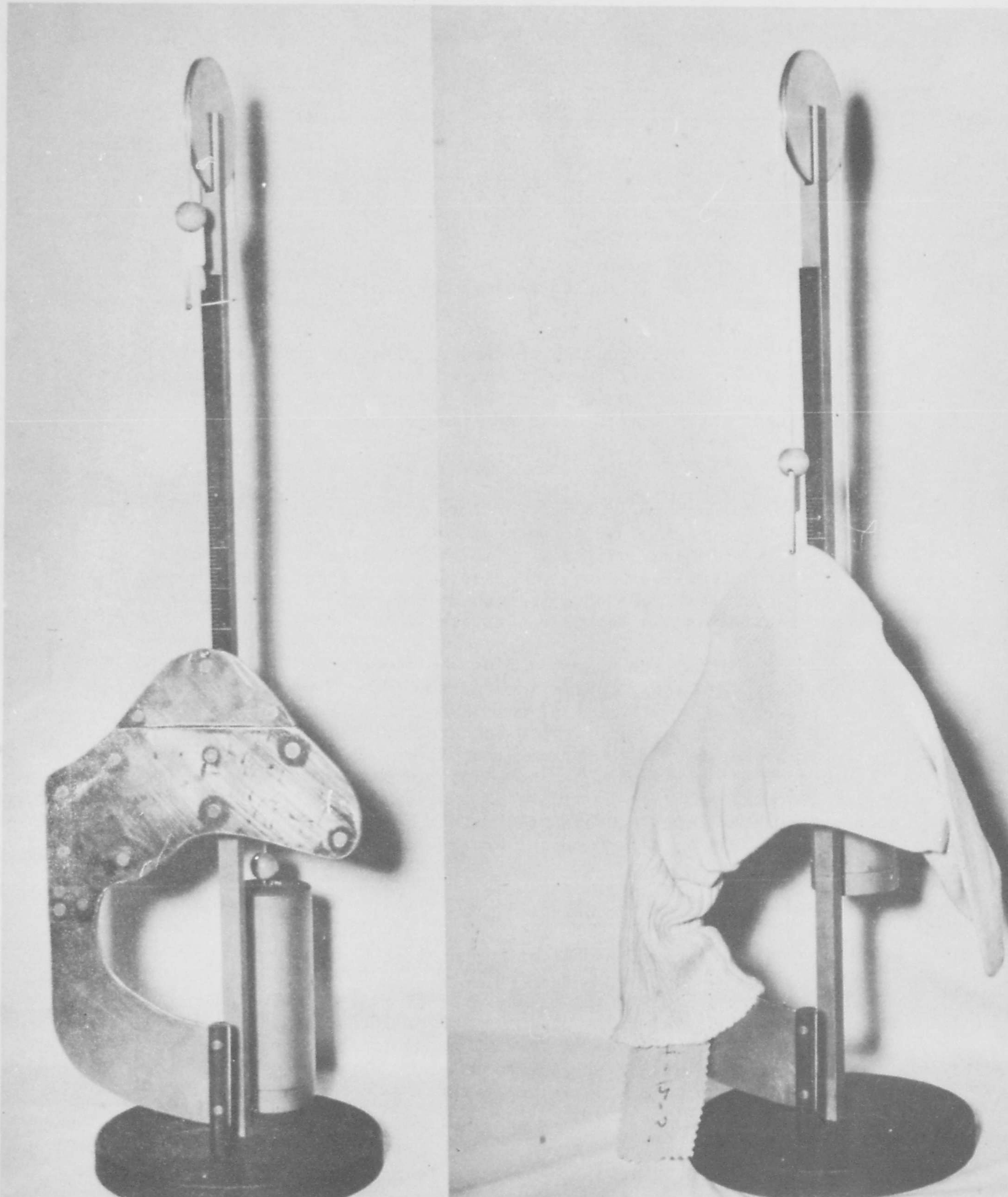


Figure II
HOUCHINS' MODIFICATIONS OF THE SCHIEFER MACHINE.
(INSTEP MEASUREMENTS.)

SECTION D

LABORATORY INVESTIGATION OF TREATMENTS TO PREVENT SHRINKAGE OF WOOL

The processes available to the Quartermaster Corps at the start of its research program were of four main types:

a. Halogenation
b. Resin
c. Alcoholic potassium hydroxide
d. Enzyme

The wet halogenation processes, of which there are many variations, are relatively simple and effective, but require careful control. However, since as has already been pointed out, they had the important advantage of being applicable in the currently available types of hosiery dyeing machinery and therefore were a logical starting point for the research program. Since wet chlorination processes had been used successfully by a few manufacturers of wool knit goods, these were selected for immediate investigation. The study of other types of treatments, which had the disadvantages of requiring specialized equipment or of requiring careful control to prevent excessive fiber damage, was delayed until later in the program to permit complete concentration on obtaining a workable process for application at the earliest possible time.

The immediate objectives of the laboratory research program involved standardizing, controlling and improving any of the known processes or the development of a more suitable process. In order to make all tests and experiments comparative, a lot of 200 dozen pairs of socks, all from the same source, was set aside for experimental work at the laboratory and pilot plant. The work discussed below is concerned largely with the practical aspects of these processes, such as shrinkage control, extent of modification of the fiber, etc. The more fundamental aspects of the process are discussed in Section E.

a. Halogenation Processes

(1) Calcium Hypochlorite Inhibitor Process

This process could be operated in ordinary wool dyeing machinery and was the first treatment to be investigated. A treatment involving use of 4.5% of calcium hypochlorite* (on the weight of the socks) was arbitrarily selected as a preliminary standard treatment and was conducted as follows:

*The calcium hypochlorite contained 70% of available chlorine.

Three dozen pairs of socks (3400 g.) were placed in a Smith-Drum machine containing 96 liters of water at 25° C. and 34 g. of a wetting agent stable to chlorine. In a separate container, 153 g. (4.5%) of calcium hypochlorite and 51 g. (1.5%) of the inhibitor were dissolved in 4 liters of water.

This solution was added to the bath in the machine at a constant rate over a period of 20 minutes, the machine was run for 10 minutes and then 153 g. (4.5%) of sulfuric acid in 4 liters of water was added over a period of 20 minutes, so that the pH decreased at a uniform rate. After 10 minutes a further running, 53 g. (1%) of sodium bisulphite was added, the machine was run an additional 5 minutes, rinsed, and dyed. Active chlorine and pH determinations were made at 5 minute intervals during the addition of the chlorine.

A large number of variations of the above-described process were studied in order to determine the effect of temperature, the effect of varying the proportions of different reagents, and the effect of varying the manner of adding the reagents. The results of these studies are summarized in Table VI.

Apparently the rate of adding the sulfuric acid was one of the most critical of the factors investigated. When the sulfuric acid was added in a 30 second period, the 30% index of the fiber decreased and the alkali solubility increased. These results indicated unnecessary injury to the fiber, although the amount of shrinkage was practically unchanged. However, the chlorine could be added in a 30 second period without causing the results to differ from those obtained by the standard method. In this connection it is interesting to study Figure 12 which shows the rates of reaction of chlorine for various modifications of the calcium hypochlorite inhibitor process.

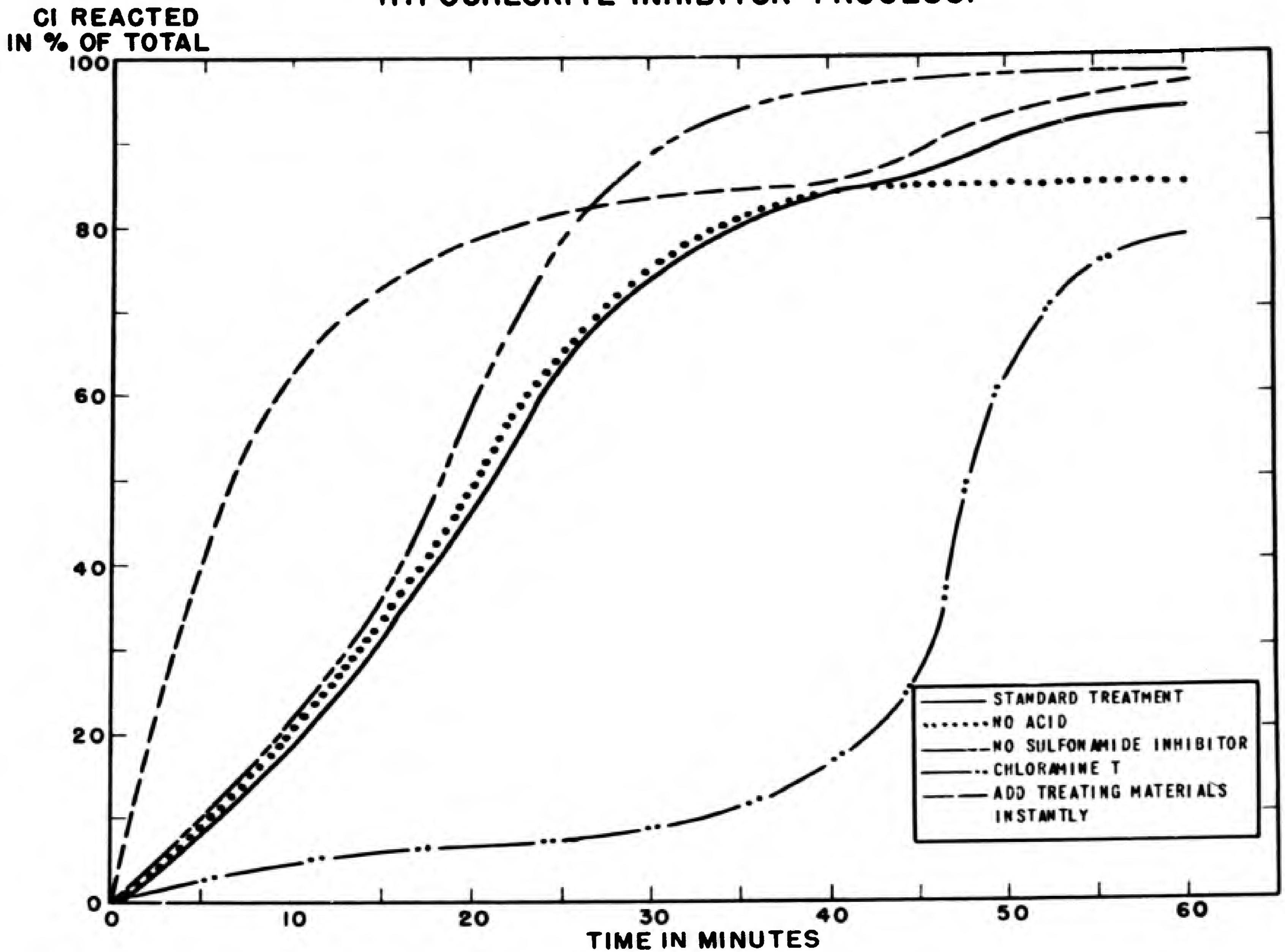
TABLE VI

Effect of Variations in the Calcium Hypochlorite Inhibitor Treatment Applied to Cushion-Sole Socks

Treatment	Shrinkage %	Alkali Solubility %	30% Index %
Untreated	23	16.0	99
4.5% Calcium Hypochlorite Inhibitor at 15°C.	11	17.5	92
4.5% Calcium Hypochlorite Inhibitor at 25°C. (Standard)	11	17.0	93
4.5% Calcium Hypochlorite Inhibitor at 35°C.	8	18.2	91
4% Calcium Hypochlorite Chloramine T	11	17.9	93
4.5% Calcium Hypochlorite Inhibitor, added instantly	10	17.6	91
Standard treatment, but acid added instantly	10	18.6	88
Chemically equivalent amounts of Calcium Hypochlorite and Inhibitor	7	24.6	94
Chloramine T and acid	7	23.2	94
Calcium Hypochlorite and acid	8	14.8	94
Calcium Hypochlorite	8	14.9	94

Figure 12

RATE OF CHLORINE REACTION FOR MODIFICATIONS OF THE CALCIUM HYPOCHLORITE INHIBITOR PROCESS.



Theoretically, calcium hypochlorite reacts with the inhibitor to form Chloramine T, which then decomposes with a gradual liberation of chlorine. However, calculations showed that the above amount of inhibitor used was sufficient to combine with only 13% of the hypochlorite present. When chemically equivalent amounts of hypochlorite and inhibitor were used, the results were almost identical with those obtained by the use of Chloramine T alone, indicating that the chloramine is actually formed in the process. Surprisingly, however, hypochlorite alone, or hypochlorite and acid, gave as good as or better shrinkage control and apparently caused less damage than any of the calcium hypochlorite inhibitor treatments. Furthermore, the rate of reaction in the latter treatments was practically the same as it was when hypochlorite alone was used (see Figure 12). These results suggested that worthwhile reductions in chemical costs might result from a further investigation of the hypochlorite reaction itself.

(2) Controlled Chlorination Process

Hypochlorite treatments of several concentrations were first investigated using calcium hypochlorite*. In these tests the calcium hypochlorite was added over a period of 20 minutes in a buffered solution, and the machine was run for 10 minutes. One percent sodium bisulfite was then added, and the socks were rinsed and dried as usual. The results of these tests are shown in Table VII.

It should be pointed out that when alkaline hypochlorite is used alone, the wool is yellowed. However, this did not prove a handicap for Army socks dyed Olive Drab.

TABLE VII

Effect of Controlled Chlorination Treatments Applied to Cushion Sole Socks

Treatment	Shrinkage %	Alkali Solubility %	30% Index %	Loss of Weight %
Untreated	23	16.0	99	--
3% Calcium Hypochlorite**	8	13.2	98	2.0
4.5% Calcium Hypochlorite	6	13.8	97	3.8
8% Calcium Hypochlorite	5	14.8	96	8.0
12% Calcium Hypochlorite	5	18.6	92	8.6

In every case, the shrinkage control was as good as, or better, than that obtained with the inhibitor process described in Section a

*The calcium hypochlorite used contained 70% of available chlorine.
**On the weight of the socks.

above. With the 12% calcium hypochlorite the alkali solubility was high, but the 30% index indicated little damage. The loss of weight was high for both the 8% and 12% treatments, but these concentrations appeared unnecessarily high as little improvement in shrinkage control was obtained by using more than 4.5% calcium hypochlorite on the weight of the socks (7% on the weight of the wool).

Although the treatment involving the use of 4.5% calcium hypochlorite offered a simple, effective and inexpensive solution to the problem of producing shrink-resistant wool socks, numerous other halogenation processes were studied and evaluated in order to determine their advantages and disadvantages in comparison with the controlled chlorination process. These are discussed briefly in the Sections that immediately follow, and the results obtained on all of the halogenation processes are summarized in Table VIII.

TABLE VIII

Effect of Wet Halogenation Treatments Applied to Cushion Sole Socks

Treatment	Shrinkage %	Alkali Solubility %	30% Index %
Untreated	23	16.0	99
4.5% Calcium Hypochlorite Inhibitor Process	11	17.0	93
4.5% Calcium Controlled Chlorination Process	6	13.8	97
Acid Calcium Hypochlorite Process	2	16.2	87
Acid Sodium Hypochlorite Process	15	15.6	96
Sodium Hypochlorite plus a protective agent	10	20.2	93
Sodium Hypochlorite Sulfamic acid Treatment	2	24.2	72
Wet Bromination Treatment	-1	24.5	82

(3) Acid Calcium Hypochlorite Process

This process utilized calcium hypochlorite in an acid bath at a low temperature. A 40:1 bath containing 1% HCl (commercial) and 1% NaCl on the weight of the liquor was prepared at 20°C. Then hypochlorite was added over a 20-minute period so that the available chlorine was 3.5% on the weight of the wool. The machine was run for 5 minutes, and the socks were treated with sodium bisulfite, rinsed, treated with a cationic softening agent, rinsed again, and dyed in a normal manner.

This treatment gave excellent shrinkage control, and only a slight increase in the alkali solubility, but caused an appreciable decrease in the 30% index, including decrease in strength of the wool fiber.

(4) Acid Sodium Hypochlorite Process

This process involved immersing the socks in a bath containing 1% of a wetting agent to which was added sodium hypochlorite over a five-minute period to yield 3.2% available chlorine on the weight of the wool. Following this treatment sulfuric acid was added over a five to ten minute period until a pH of 3 was reached. After 25 minutes, the bath was dropped, and the socks were treated with bisulfite, rinsed and dyed. With this treatment is was difficult to secure level dyeing and the degree of shrinkage control was not regarded as satisfactory. However, there was little fiber damage, as indicated by the alkali solubility and the 30% index of the treated fibers.

(5) Sodium Hypochlorite Plus a Protective Agent

This process used sodium hypochlorite in conjunction with wetting and protective agents. A bath containing 10% of a wetting agent on the weight of the socks was put in the machine and mixed for 5 minutes. The socks were then added, the machine was run for 5 minutes, 10% of a protective agent was added, and the treatment was continued for 5 minutes. Sodium hypochlorite was added over a 5 minute period so that the available chlorine was 2.5% on the weight of the wool, the machine was run for 20 minutes, and the socks were rinsed. A pH of 3.5 was maintained throughout the process. In the subsequent dyeing, 5% each of a wetting agent and a dyeing assistant on the weight of the socks were added to the dye bath, and the dyeing was conducted in a normal manner. A final treatment of 1 to 2% of a cationic softening agent was used.

This treatment gave shrinkage control comparable to that of the calcium hypochlorite inhibitor process, and caused only a slight decrease in the 30% index, but it increased the alkali solubility substantially.

(6) Sodium Hypochlorite - Sulfamic Acid Treatment

This process involved a treatment with a compound resulting from the action of sodium hypochlorite with sulfamic acid. In this process, the wool was protected by treatment with formaldehyde. Excellent shrinkage control was obtained by this method, but the fiber modification, as indicated by a very low 30% index and high alkali solubility, appeared to be undesirably great.

(7) Wet Bromination Treatment

This process was the only wet bromination method tested. The treatment was carried out at 17° C. and pH 1.6. The bromine water was fed into the bath at such a rate that the concentration did not exceed 200 p.p.m., and 7% bromine on the weight of the wool was added over a period of 50 minutes. The socks treated by this method did not dye level and the fiber damage was great, as indicated by both 30% index and alkalisolubility tests. However, the shrinkage control was the best of this series.

Summary Comparison of the Halogenation Processes

The comparison of the laboratory results of the evaluation of the wet halogenation processes shown in Table VIII indicates that from the standpoint of shrinkage control alone, several of the other treatments were found to be equal to or more effective than the calcium hypochlorite inhibitor or controlled chlorination processes. However, most of these other processes were considered to be objectionable because of the apparently substantial increase in alkali solubility or reduction in 30% index which they produce, or both. On the basis of the laboratory studies, the controlled chlorination process appeared to be the most desirable because it gave satisfactory shrinkage control and produced less modification than the other halogenation processes.

b. Resin Processes

It was recognized early in the sock treatment program that the lack of suitable treating equipment would seriously limit the value of the several resin processes to the Quartermaster Corps for the immediate production of shrink-resistant socks. However, in order to avoid the possibility of eliminating any known treatment from study in this program, evaluation was made of the existing type of resin processes with respect to their possible application to Army socks.

(1) Resin Process No. 1

In the first process to be tried the resin was applied as a monomer. A 25:1 bath-goods ratio was used, and the socks were treated with an 11.2 percent resin solution, which also contained catalysts for polymerization and softening agents to minimize any boardiness. The socks were agitated in this bath for 20 minutes at 25°C., centrifuged to 110 per cent pick-up, dried to less than 5 per cent regain, and cured on boards for two minutes at 250°F.

The results of this test as shown in Table IX were disappointing in the amount of shrinkage control obtained. Furthermore, the socks were slightly stiffened and became lighter in color as a result of the treatment, although the latter presented no problem since allowance could be made for it during dyeing. No fiber damage was detected in the treated socks.

TABLE IX

EFFECT OF RESIN PROCESSES APPLIED TO CUSHION SOLE SOCKS

Treatment	Resin Content %	Shrinkage %	30% Index %
Untreated	---	23	99
Resin Process No. 1	11	17	99
Resin Process No. 2	15	4	95
Resin Process No. 3	5	1	99

(2) Resin Process No. 2

The second resin process investigated, like the first, employed the resin as a monomer. In the test the socks were first extracted with carbon tetrachloride, dried, and treated for 20 minutes with a 15 per cent resin solution containing catalysts and softening agents. After being extracted to 110 per cent pick-up, dried to 20 per cent pick-up, and boarded, the socks were cured in a raw wool stock drier for ten minutes at 300°F., wet for 20 minutes at 120°F., dried and reboarded.

This process afforded good shrinkage control, but again the socks were slightly boardy and off-shade after treatment. Slight damage to the fiber resulted, but not to an excessive degree.

(3) Resin Process No. 3

The third treatment was of the noncure type, involving the application of a prepolymerized resin which was applied from an emulsion containing 2.5 per cent resin on the wright of the socks. The bath, which was maintained at about pH5, contained 50% anhydrous sodium sulfate. The treatment was conducted at approximately 145°F and the socks were allowed to remain in it until the bath became clear.

Of the three resins evaluated in this test it was found that this latter type, which used the smallest amount of add-on, provided the best shrinkage control and caused the least fiber damage as indicated by the 30% index. The items processed by this method also showed less change in hand than any of the other resin-treated socks.

When it was decided to adopt the controlled chlorination process and convert industry over to its use, it became expedient to concentrate available personnel on the application aspects of that treatment, with the result that further study of the cure type resin treatments was discontinued insofar as socks were concerned. However, it was found that resin process No. 3 was especially adaptable to

TABLE X

EFFECT OF VARIATIONS IN THE ALCOHOLIC POTASSIUM HYDROXIDE PROCESS

Independent Variable	Conc. of KOH	Moisture Content of Alcohol	Temp. of Treatment	Time of Treatment	Shrinkage	30% Index	Loss of Weight	Alkali Solubility	Sulfur Content	Cystine Content	KOH Consumed
	%	%	oC	Min.	%	%	%	%	%	%	mg/g
1. Concentration of KOH	0.4	5	25	30	4	97	0.5	12.4	---	11.4	6
	0.8	5	25	30	2	98	0.6	12.0	---	10.6	14
	1.6	5	25	30	2	96	0.4	11.8	---	10.9	21
	3.0	5	25	30	0	98	0.5	10.2	---	9.2	42
2. Moisture content of Alcohol	0.8	2	25	30	3	100	0.2	11.8	3.40	10.2	--
	0.8	5	25	30	2	98	0.6	12.0	3.23	10.6	14
	0.8	9	25	30	3	97	0.6	9.6	3.10	9.6	42
	0.8	15	25	30	3	88	0.8	9.4	3.03	9.2	53
3. Temperature of Treatment	0.8	5	15	30	4	98	0.4	12.4	3.39	11.0	5
	0.8	5	25	30	2	98	0.6	12.0	3.23	10.6	14
	0.8	5	35	30	4	97	0.6	9.9	2.84	8.1	31
	0.8	5	55	30	4	80	1.8	14.8	2.39	6.1	55
4. Time of Treatment	0.8	5	25	15	4	95	0.5	12.5	----	11.5	5
	0.8	5	25	30	2	98	0.6	12.0	----	10.6	14
	0.8	5	25	50	3	97	0.6	11.6	----	11.0	16
	0.8	5	25	90	2	97	0.6	10.4	----	10.4	30
5. Control	---	-	--	--	23	99	---	12.0	3.44	11.5	--

to certain constructions of 100% wool socks on which the controlled chlorination process could not be used with good results. Accordingly, procurements of these socks, notably those used by the WAC's, were made with the resin treatment applied. Further extensive work in the application of resins to fabrics and other materials was resumed at a later date.

c. The Alcoholic Potassium Hydroxide Process

Preliminary trials of this process, which involves the treatment of the fabrics with an alcoholic solution of potassium hydroxide, were run in the laboratories of United States Industrial Chemicals, Inc., using the following general procedure. Socks, yarn balls, and calibrated fibers were treated with six times their weight of alcoholic potassium hydroxide squeezed to about 200% pick-up, neutralized with alcoholic carbon dioxide, and dried. In general, this treatment gave good shrinkage control and apparently caused little fiber damage. The effects of variation in the concentration of the KOH, the moisture content of the alcohol, and the time and temperature of the treatment were studied, and the results of the tests are shown in Table X.

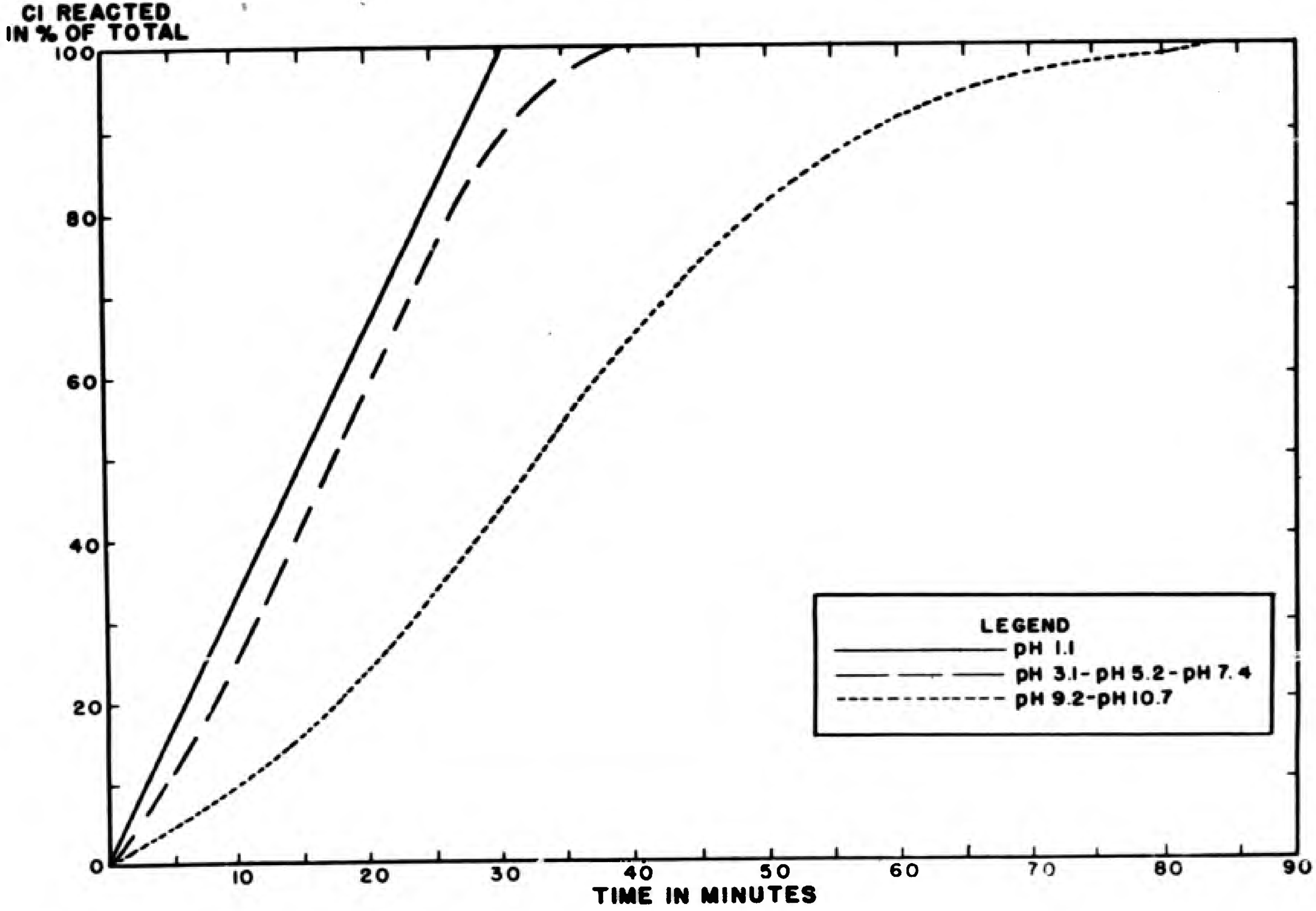
Increasing the temperature of the treatment appeared to cause increased fiber damage without improving the shrinkage control. At a temperature of 55° C. excessive damage was indicated by a low 30% index, low sulfur and cystine content, increased alkali solubility and a greater loss of weight. When the moisture content of the alcohol was 15%, damage was reflected in the 30% index and a somewhat lower cystine content. In both cases the low 30% index was associated with the highest consumption of potassium hydroxide. It is interesting to note that even the most severe treatment did not cause much visible change in the surface scale structure of the fibers.

c. Enzyme Process

This process involved treatment of the socks with an enzyme preparation. The socks processed by this method were rather badly damaged, lost considerable weight and had a 30% index of 85%. Furthermore, they shrank 17%. These results apply only to the particular enzyme process that was investigated, and no general conclusion can be drawn from these data concerning the effectiveness of other treatments of this type.

Fiq. 13

THE EFFECT OF pH ON THE RATE OF REACTION OF SODIUM HYPOCHLORITE WITH WOOL.



SECTION E

STUDIES OF THE FUNDAMENTAL ASPECTS OF SHRINK-RESISTANT PROCESSES

1. Effect of pH on the Chlorination Process

Since the pH of the chlorinating bath appeared to be an important factor in determining the efficiency of shrink-resistant treatments and the amount of fiber damage incurred, a detailed study of the chlorination reaction was made. Wool yarn was treated with buffered baths containing 9% of available chlorine on the weight of the wool. The chlorine was added at a uniform rate over the first 30 minutes and the reaction was continued for 90 minutes. The pH range studied was from 1.1 to 10.7. The rates of reaction shown in Figure 13 suggested that three different types of reaction may occur, each corresponding to a definite pH range. A graphic presentation of the effect of pH on the extent of modification of the wool is given in Figures 14, 15 and 16. In addition, analyses showed that the loss of weight during the treatment increased and the shrinkage control was improved as the pH decreased. The nitrogen and sulfur contents were little affected by chlorination at any pH value.

The data illustrated in Figure 15 further suggested that chlorination causes a weakening or rupture of the disulfide bonds, similar to the reaction which occurs when wool is treated with hydrogen peroxide. It is, evident, therefore, that attack on the disulfide linkage is an important step in at least some of the chemical processes which impart shrinkage resistance to wool.

2. Surface Scale Structure

It has frequently been suggested that the surface scale structure of wool is closely related to its felting properties, and it has been further suggested that chlorination processes are effective in reducing felting because they remove the surface scales. Presumably the fiber is made so slippery that it is no longer able to migrate and become entangled with other fibers.

The influence of scale structure was investigated by microscopic comparison of the surface scale structure of fibers chlorinated at various pH values. The photographs, shown in Figure 17 indicate that chlorination at pH 11, 9 and 7 caused only a slight visible modification of the scale structure. At pH 5 the damage increased rapidly, and at pH 1, practically all semblance of the scales was destroyed. Since other experiments showed that the shrinkage control improved as the pH decreased, a relationship between the scale structure and the felting properties of chlorinated wool is indicated.

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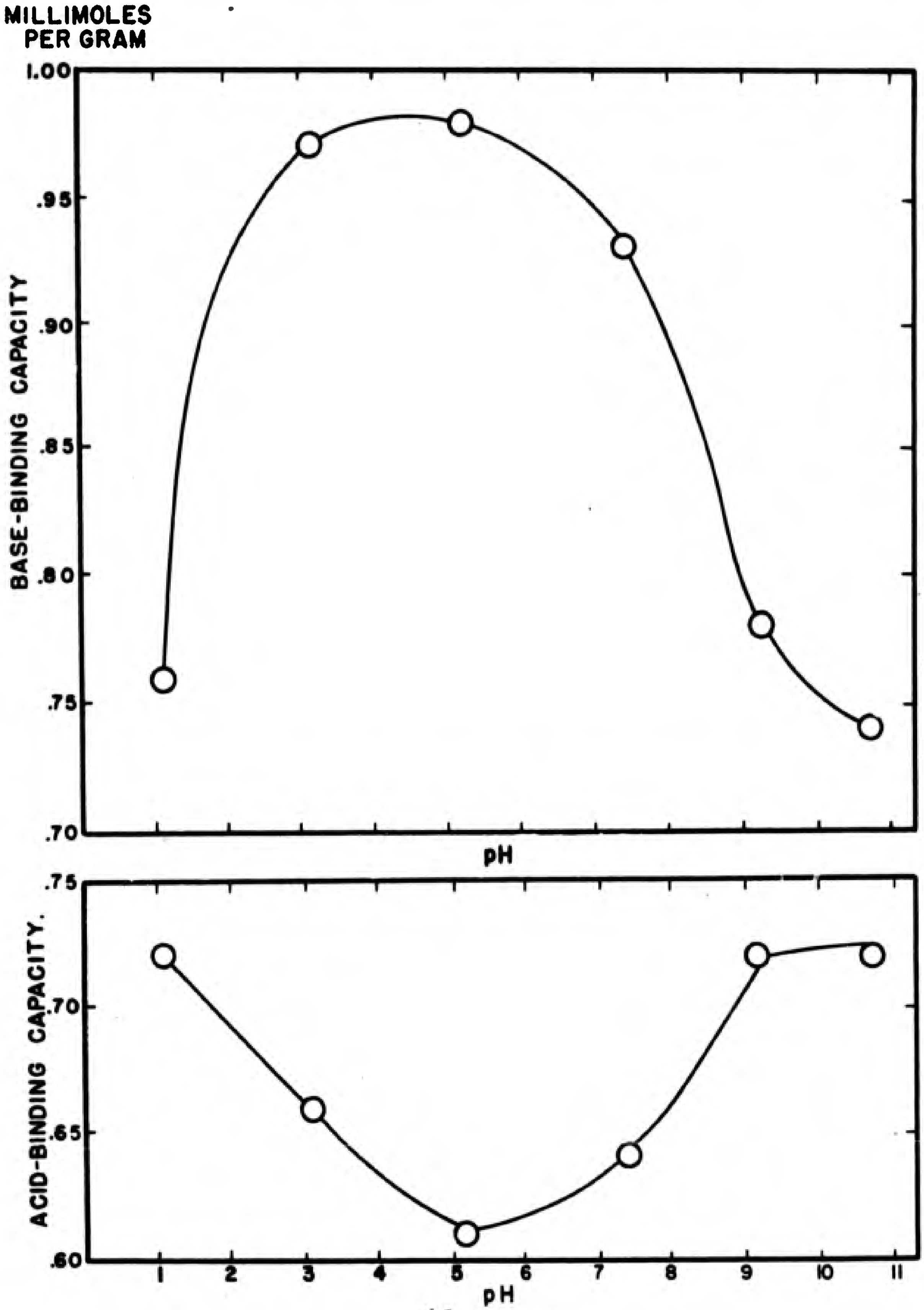
Figure 14
ACID & BASE-BINDING CAPACITIES OF WOOL TREATED WITH 9% CHLORINE AS A FUNCTION OF pH.



Fiqure 15

CYSTINE CONTENT & ALKALI SOLUBILITY OF WOOL YARN TREATED WITH 9% AVAILABLE CHLORINE.

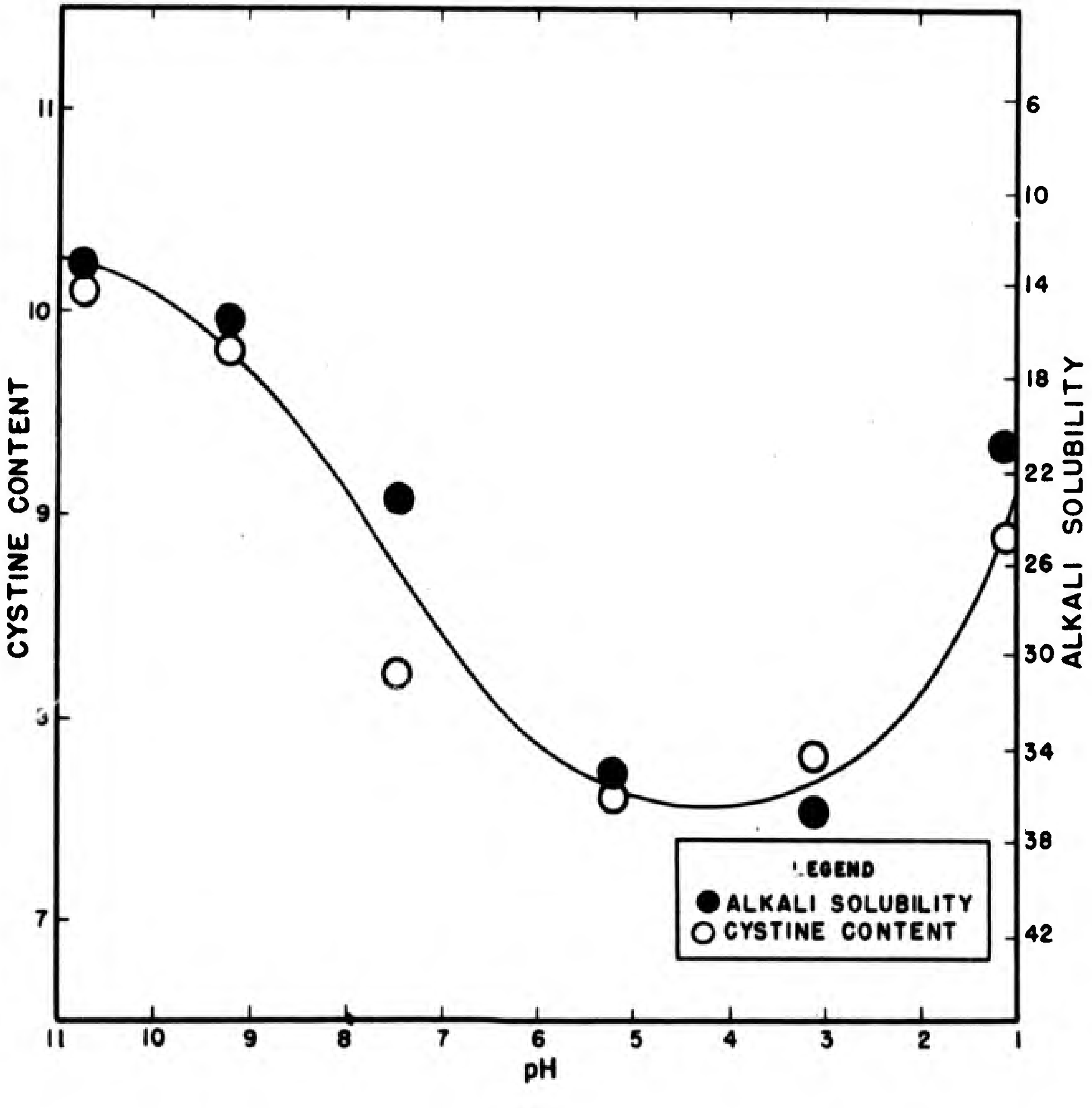
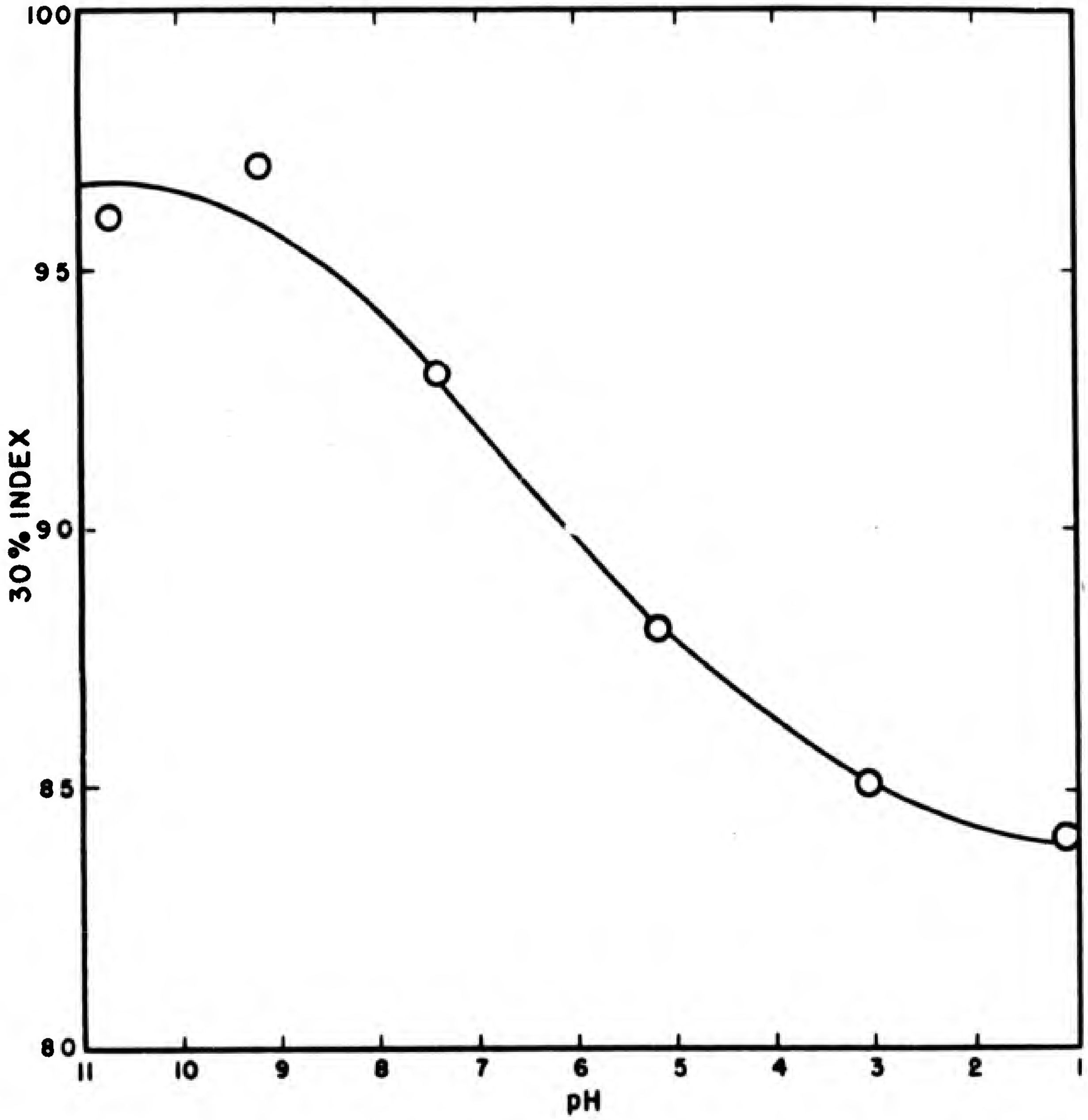


Figure 16

30% INDEX OF WOOL TREATED WITH 9% AVAILABLE CHLORINE AS A FUNCTION OF pH.



However, with other types of shrink-resistant processes the visible scale structure apparently is not so closely related to the felting properties, and it is possible that some other factors may be involved. Thus the photographs in Figures 18 and 18A show that the visible scale structure was not greatly altered by the alkaline hypochlorite treatment, the alcoholic potassium hydroxide process, dry chlorination, and a melamine resin process, yet various degrees of shrinkage control resulted from all of these treatments. When the alcoholic potassium hydroxide process was conducted with alcohol containing 15% water, a large amount of fiber damage was indicated by the 30% index, but still the visible scale structure was changed only slightly. It was concluded that the scale structure might be altered without producing marked visible changes. In order to study this phenomenon further, recourse was had to the direct measurement of surface friction properties.

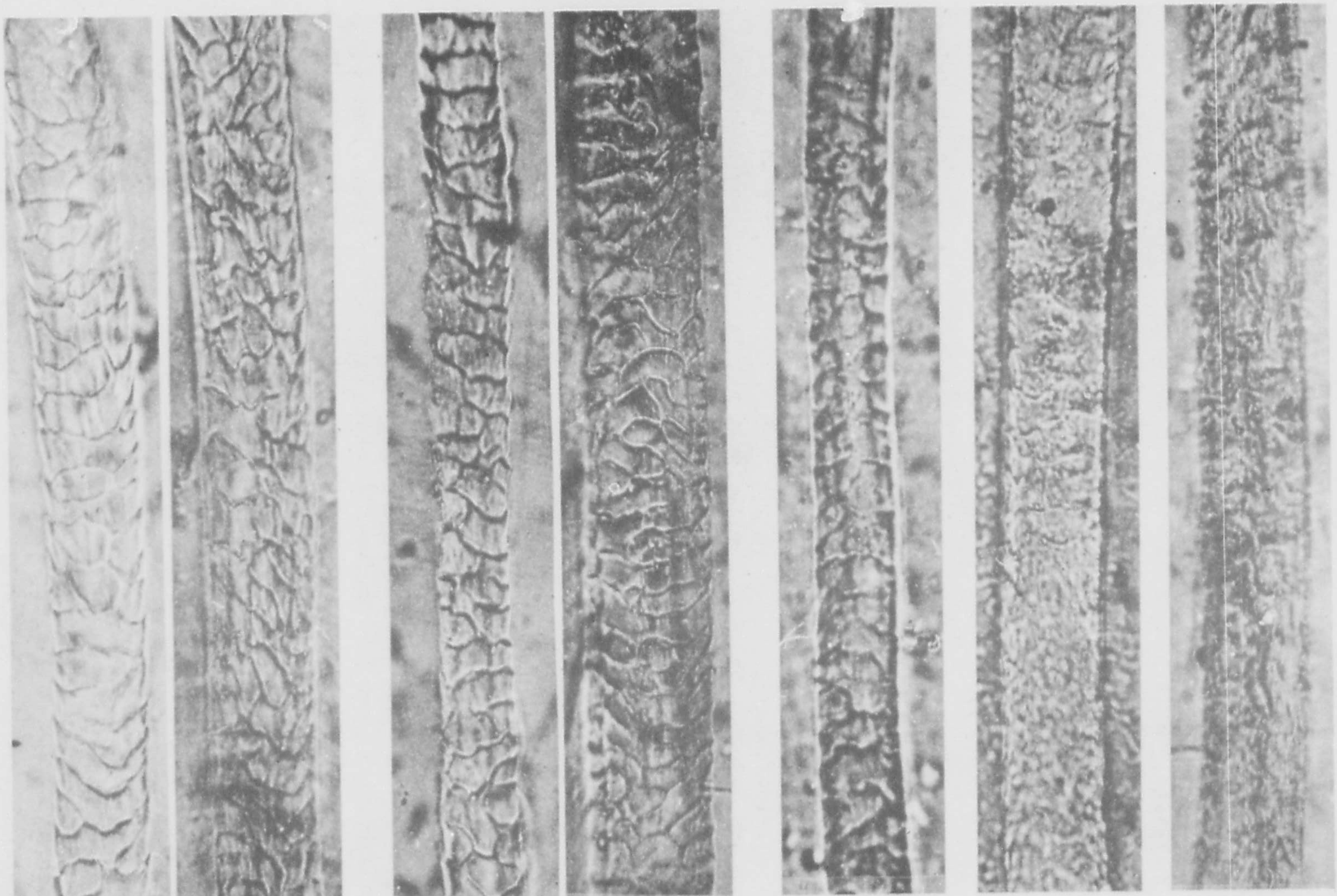
3. Frictional Properties

A recent development in the theory of wool felting is the idea that the directional friction effect, as stated above, is of greater importance than the average overall coefficient. In order to determine the contribution of the directional effect, the maximum and minimum friction coefficients of fibers treated by various processes were determined. From these data the friction ratio and the friction index were calculated according to the expressions on Page 30 and are reported in Table XI. Examination of the data in Table XI shows that the maximum coefficient of friction remained practically constant, but that all the treatments tended to increase the minimum coefficient of friction. Thus, the directional friction effect was reduced, which may be interpreted to mean that treated fibers would tend to move as easily in one direction as in another; in other words, there would be less preferential migration in either direction. The friction index, which may thus be thought of as measure of the case of fiber migration, was decreased by the treatments which gave the best shrinkage control, while the friction ratio, a measure of roughness, was increased slightly.

A noteworthy conclusion to be drawn from these experiments is that, contrary to popular belief, the fiber does not become more slippery as a result of chlorination treatments. Actually, the overall coefficient of friction is increased by all of the shrink-resistant treatments.

4. Relation of Fiber Diameter to Extent of Modification

During some of the early investigations, a number of the preliminary experiments indicated that finer fibers were damaged or modified to a greater extent during chlorination than the coarse fibers.



UNTREATED | TREATED pH 11 | TREATED pH 9 | TREATED pH 7 | TREATED pH 5 | TREATED pH 3 | TREATED pH 1

FIGURE 17
SURFACE APPEARANCE OF FIBERS TREATED WITH CHLORINE AT VARIOUS pH'S
(APPROX. 350X)

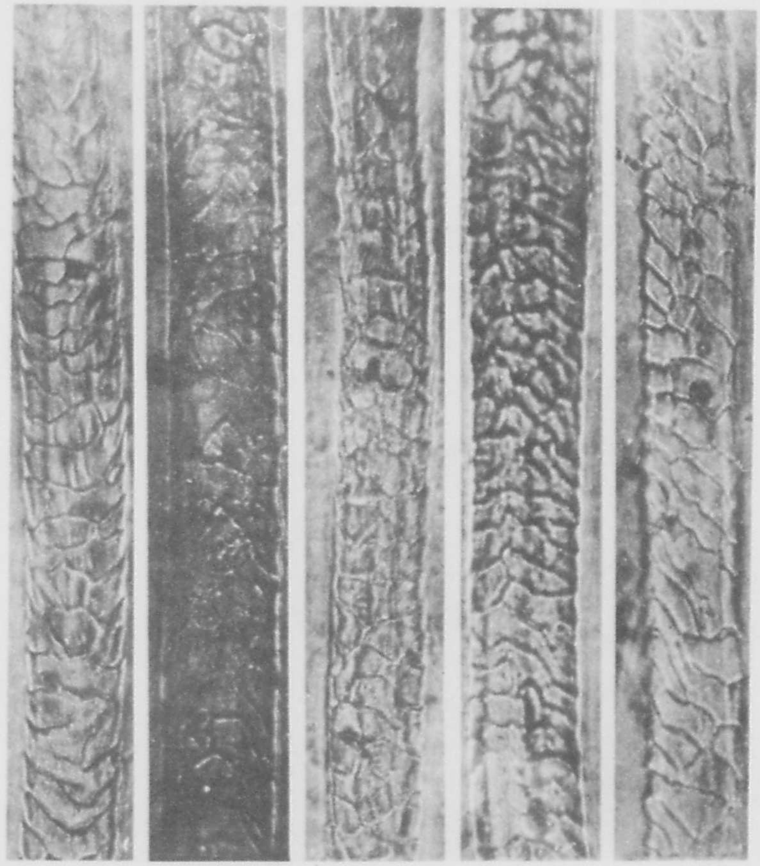


FIGURE 18
SURFACE APPEARANCE OF FIBERS TREATED WITH ALCOHOLIC POTASSIUM HYDROXIDE
(APPROX. 333X)

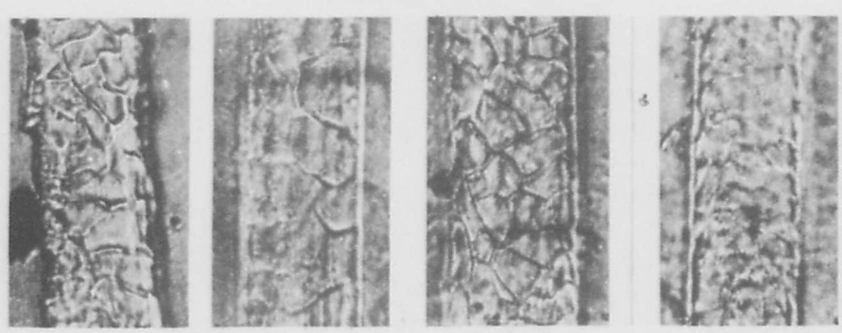
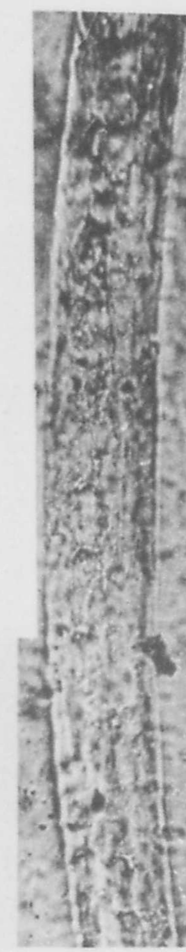




FIGURE 18A
SURFACE APPEARANCE OF COMMERCIALLY TREATED FIBERS
(APPROX. 340X)

TABLE XI

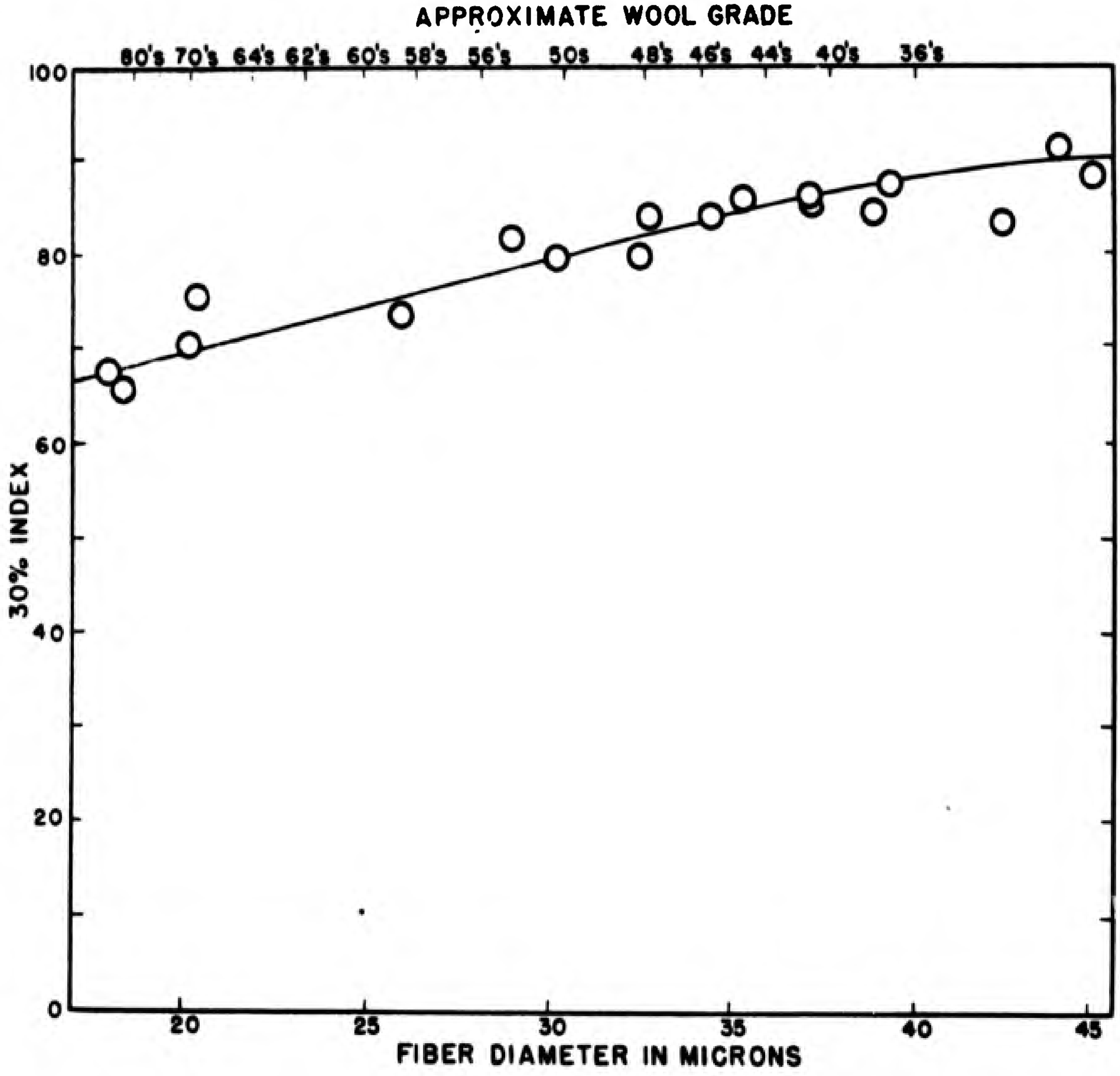
EFFECT OF VARIOUS TREATMENTS ON THE COEFFICIENT OF STATIC FRICTION OF WOOL FIBERS AGAINST WOOL FELT

Treatment	pH	Coefficient of Friction Dry		Wet		Friction Ratio		Friction Index		Shrinkage %
		Max.	Min.	Max.	Min.	Dry	Wet	Dry	Wet	
Untreated	--	0.35	0.21	0.42	0.30	---	---	---	---	23
4.5% Ca $(OCl)_2$	11	.39	.32	.42	.33	127	104	50	92	11
4.5% Ca $(OCl)_2$	9	.39	.34	.37	.33	130	97	36	33	10
4.5% Ca $(OCl)_2$	7	.34	.33	.48	.47	120	132	7	8	-3
4.5% Ca $(OCl)_2$	5	.38	.35	.49	.46	130	132	21	25	1
4.5% Ca $(OCl)_2$	1	.34	.31	.53	.51	116	145	21	17	-2
0.8% alc. KOH, (5% water)	--	.38	.30	.44	.36	122	111	57	67	2
0.8% alc. KOH, (15% water)	--	.35	.31	.42	.36	118	108	28	50	3
Thermosetting Resin No. 1	7	.37	.32	.45	.35	123	111	36	42	17
Dry Chlorination	3	.41	.37	.43	.36	139	110	29	58	*

*No data

Figure 19

EFFECT OF 4% CALCIUM HYPOCHLORITE ON VARIOUS GRADES OF WOOL AS SHOWN BY 30% INDEX.



Accordingly, a series of experiments was undertaken to determine the effect of fiber diameter on fibers ranging from 18.1 to 45.9 microns in diameter. These were chlorinated with 4% calcium hypochlorite on the weight of the wool at pH 1.6 and 25 C., and the data are graphed in Figure 19. Above 25 microns diameter, the relationship between the fiber diameter and the 30% index was almost linear, with the fine fibers showing the greatest amount of damage.

The results of these experiments indicated the necessity for taking due precautions in chlorinating verious grades of wool. Thus, a formula satisfactory for coarse grades of wool might produce sufficient damage in fine wools to make it somewhat unsatisfactory, and necessitate a modification in conditions of treatment for the finer fibers.

APPENDIX

Personnel of the Quartermaster Board who contributed to the Sook Testing Program:

Colonel Max R. Wainer

Major Thomas J. Dempsey
Major Herman A. Gumenick
Captain James D. Finley
Lieutenant Maurice Becker
Lieutenant Albert Hutler
Lieutenant Kenneth Leslie
Sergeant Nathaniel Cohen
Sergeant Robert R. Beers
Sergeant Herbert Cohen
Sergeant Abram H. Feldman
Sergeant Irving J. Fishon
Sergeant Benjamin D. Gaddy
Sergeant George M. Goldman
Sergeant Charles L. Kaufman
Corporal Samuel Epstein
Corporal Theodore Phillips
Corporal Anton Rivlin
Corporal Julius Schneider
Corporal Paul Stocker