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NEW WAYS OF ASSESSING THE WATER RESISTANCE OF MILITARY UPPER LEATHER*

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ABSTRACT

A new simple and compact tester for measuring the resistance of upper leather to water penetration is introduced. Three commercial leathers for military boots, each treated with silicone in a different way, were examined on this tester. Measurements were also made using slurries of sand or mud in place of water. The specimen served as a trough to hold the water or the slurries. Other specimens of the same leather were tested on the Maeser Tester in the conventional manner and also with the specimen acting as a trough. A single specimen underwent five tests, allowing adequate recovery times between them. The results were used to compute medians and ranges rather than means.

The water absorption of the silicone-treated leather was also determined. A conventional method was used in a slightly modified form. This property was also measured five consecutive times. The results served for the computation of medians and means.

In most instances water resistance and water absorption decreased with repeated flexing. The number of flexes until leakage and the degree of water absorption depended mainly on the type of silicone treatment. Data collected in this way are of great significance for the selection of the proper upper leather for the standard and tropical boot of the Armed Services. Evidence is presented which suggests the need for greater uniformity and the desirability of striving for economy in silicone treatments of leather.

INTRODUCTION

The Quartermaster Research and Engineering Center in Natick is engaged in testing the direct-molded sole process for military footwear. The

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molding of a rubber sole to the uppers eliminates the most important source of wet feet, the entry of water through the welt seams. Once a boot can be made in which sole and upper are not stitched together, comfort will be enhanced by making the upper leather water-resistant.

The Dow Corning Company supplies a silicone for making upper leather water-resistant. The product, a methylpolysiloxane, is available in an organic solvent under the trade name "Sylmer" (1*a*)*. This material can be applied in two ways, to both leather surfaces and to the grain surface only. When the treated leather is worn grain out, both treatments enhance resistance to water penetration. However, there is a significant difference between them. When both surfaces of the leather shed water, the leather will not be capable of absorbing foot perspiration. For comfort's sake boots made from such leather should be leather-lined, as many are which are manufactured commercially.

A lined boot is expensive and the lining also usually has a shorter service life than the whole boot. Therefore, military boots are not lined; if they are to have silicon-treated uppers this treatment should be on the grain surface only. Such upper leather would be highly resistant to penetration by water from the outside, but it would remain absorptive to foot perspiration. Such leather is especially well-suited for the vulcanized combat boot.

Leather treated with silicone on both sides also has a place in military footwear: it can be used in the tropical boot which is in part made of cloth and is not supposed to keep water away from the foot. Ordinary leather soaks up water when it gets wet and gradually becomes very boardy. The leather on the dry boot can be so hard and boardy that the soldier cannot slip it on without first wetting it again. A silicone treatment, it is hoped, can prevent this stiffening by keeping the water out. Here a low water absorption on both leather surfaces is important. To obtain it, a silicone application to these two surfaces or a full immersion in a silicone bath is called for.

The two-fold purpose of a silicone treatment requires two different methods of testing the leather in the laboratory: one method which measures resistance to water penetration from the grain side, and one method which measures total water absorption. The former should give higher results with leather treated on the grain surface only; the latter should give the lowest results with leather treated on both surfaces or by immersion.

A number of machines have been constructed for measuring resistance to water penetration while the leather specimen is flexed to simulate actual conditions of wear. Among these, the Maeser machine, the Bally Penetrometer, and the Dow Corning Tester are the best known. They were used in various studies dealing with the dynamic testing of silicone-treated upper leather

*The mention of specific brands or companies is not to be construed as an endorsement by the U.S. Army of these brands or companies over those not mentioned.

(2–5) and are also discussed in the *Handbook on Chemistry and Technology of Leather*, Volume III (1*b*). However, these sources do not distinguish between the two possible methods of application in the tannery and do not furnish data on the water-absorptive ability of the treated leather.

A further investigation seemed desirable in the light of the military interest in silicone-treated leather. In the present study of water resistance, for the first time, modes of application will be distinguished, and their effect on water absorption will be considered. Moreover, the question will be answered whether alternating periods of flexing in water and of drying-out influence water resistance and whether it is influenced by the presence of a slurry of sand or soil, both of which are likely to occur as often as plain water.

For answers to these questions, the Maeser and Dow Corning testers, in which the leather is flexed while dipping into a water-filled tray, are not well suited. A more versatile arrangement has the leather itself serve as a trough. Hopton, it seems, was the first to come upon this idea, but he filled the trough with water alone, not with sand or soil slurries (6).

The Maeser and Dow Corning testers would also allow the specimens to be inverted. However, if any experiments on inverted leather specimens have been conducted with these testers, they apparently were never published.

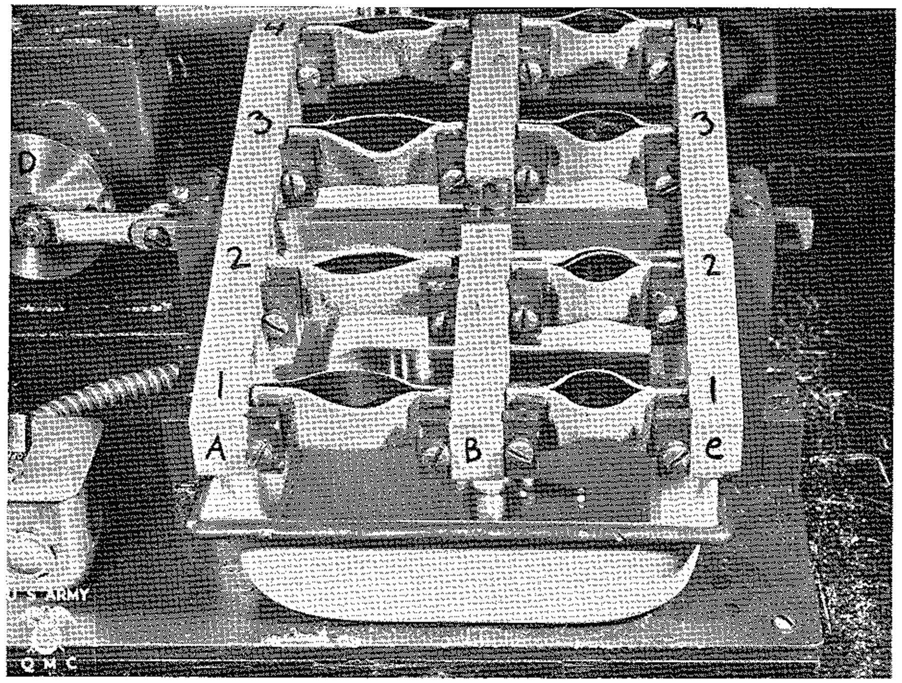

FIGURE 1.—Frontal view of Q.M. Water Penetration Tester.

The Natick Laboratories have used a machine based on Hopton's principle for a number of years. This so-called QM Tester is described in the Appendix. Fig. 1 shows the tester, with leather specimens mounted at its eight stations. Its construction is so simple that any machine shop can build it. It has three other advantages: it requires much smaller leather specimens than the testers now in use; it can accommodate 6 or 8 units on a platform smaller than that for a single unit of the Maeser machine; the specimens are easy to mount and to remove.

For assessing the new QM Tester correctly, the Maeser machine, the only other type available for this study, was run both ways, i.e., with water outside, as is usually the case, and also with water inside. The tests using slurries of sand or soil, however, were conducted on the QM Tester only.

EXPERIMENTAL PART

Tannery A supplied two lots of Sylmer-treated upper leather, one consisting of 8 sides treated on the grain surface only, and one consisting of 7 sides treated on both sides. Chemical and physical data, mostly supplied by the manufacturer of these leathers, are shown in Table I. The water resistance tests were conducted on specimens of a one-square-foot area cut out next to the official test area where the analytical sample had been removed previously.

TABLE I

CHEMICAL AND PHYSICAL PROPERTIES OF SYLMER-TREATED COMBAT BOOT SIDE UPPER LEATHER

Properties	Sylmer Treatment: One-Sided (on grain) Tannery A	Two-Sided Tannery A	Two-Sided (Secotan) Tannery B
a. Chromic oxide, %	5.6	5.9	
b. Chloroform extract, %	11.3	15.2	8.2
c. Unidentified balance*, %	10.7	7.4	
d. pH	3.3	3.3	3.3
e. Shrinkage temperature, °C.	106 (104–109)	110 (108–112)	
f. Stitch tearing strength, lb.	92 (72–118)	107 (65–116)	
g. Water vapor permeability, g/m²/day			
at 23°C. and 50% R.H.	195 (185–210)	112 (90–135)	220
at 38°C. and 95% R.H.	1200 (1170–1240)	900 (765–1100)	1340

*Briefly called tannin in specification for this leather (MIL-L-3122), but actually including all anions in chrome complex and unextractable portion of grease and silicone.

NOTE: *a*: % on hide substance basis
b, c, g: % on dry basis
e, f, g: means of measurements on five different sides except in third column, since two sides only from Tannery B were available. Ranges are shown in parenthesis.

Tannery B supplied Sylmer-treated leather for six pairs of boots which were dismembered for other purposes. This leather was of special interest, since it was the product of the Secotan process. Test specimens were cut out of the vamps to measure the resistance to water and to a soil slurry. A few important properties of this leather are also listed in Table I.

ANALYTICAL METHODS

The methods used for obtaining the figures of Table I are listed in Federal Specification KK-L-311, as methods 2151, 6311, 6515, 6621, 7011, and 8011.

TESTING FOR RESISTANCE TO WATER PENETRATION

The following testers were employed:

1. Two Maeser machines (Federal Specification KK-L-311, method 8021.1) using rubber wedges; rate: 153 flexes per minute.

2. The QM Tester (described in Appendix); rate: 92 flexes per minute (60% of rate of Maeser machines), closely corresponding to the military marching rate.

Also needed was an ohmmeter (V.O.M. Multi-tester, Simpson, or equivalent), set for D. C. and for a resistance of 10,000 ohms, with two leads. The end of one lead is pointed and is used to probe the dry (flesh) side of the specimen for water penetration. The other lead ends in an alligator clamp, which in the conventional Maeser test is clipped to the tank but which in any test where the leather specimen itself holds the water is fastened to the specimen so that the clamp dips into the water.

Sand and soil.—The sand was the fraction obtained by screening through numbers 16 and 30 of the U. S. Standard Sieve Series. The sand was obtained from a quarry near Natick, Mass. The particle size of the sifted sand varied from 0.0232 to 0.0469 inches (0.59 to 1.19 mm).

The soil was an unsterilized soil used time and again for soil burial tests.

Sand and soil were discarded after each run.

Method—The following quantities of water, sand, and soil were used in the tests with the water inside the pockets found by the specimens when fastened in the tester.

	Water ml.
Maeser Tester	35
QM Tester, water alone	6
QM Tester, slurry of sand or soil*	5

*10 g., air-dry, added before the water.

The water resistance of the leather from Tannery A was tested in five different ways:

A. On the Maeser machine
   1. In the conventional way
   2. With the water inside the pocket

B. On the QM tester
   3. With the water inside the pocket
   4. With a sand slurry inside the pocket
   5. With a soil slurry inside the pocket

The leather of Tannery B representing the Secotan process was tested by methods B3 and B5 only.

Each leather specimen was tested five times, with recovery times usually of three days between each test. During this time the leather specimens remained in a room conditioned at 70°C. and 50% relative humidity.

The flexing was briefly interrupted when the specimens were probed for a possible leak. A specimen which had begun to leak was removed. However, if no leak appeared, the specimens were flexed 10,000 times before the test was ended. All readings were rounded to the next lowest multiple of 10.

TESTING FOR WATER ABSORPTION

The following equipment was used:

1. Museum jar No. 5, inside diameter at bottom 3½ x 2¾ inches; height, 6½ inches.

2. Shaking Machine, reciprocating, stroke 1½ inches, adjusted to 60± 5 strokes per minute.

Method: Testing and calculation of results followed method 8111 of the Federal Specification KK-L-311. No correction for water-soluble material was applied. However, a number of refinements were introduced:

(*a*) The specimen size was increased to 3 x 2 inches.
(*b*) Specimens were weighed to nearest 0.001 g.
(*c*) Specimens of the same type of leather were immersed together.
(*d*) The volume of the distilled water was equal to 10 ± 0.5 times the weight of the specimens.
(*e*) The jar with the specimen was shaken at the rate of 60 ± 5 strokes per minute.
(*f*) Each leather specimen was tested five times, with recovery times usually of three days between each test.

RESULTS

Resistance to water penetration.—Tables II to V show the results of the tests measuring water resistance. To reduce the size of these tables, the figures for water penetration are shown for three of the five consecutive runs to which each specimen was subjected, i.e., for the first, third, and fifth run only. Tables II to IV show the median and mean values and the ranges; Table V shows only the medians.

The test sides were numbered in the order in which their water resistance in the Maeser machine increased when they were tested in the conventional way, i.e., with the outside of the pocket dipping into the water. Consequently, the ranking changes for each successive run.

TABLE II

SYLMER TREATMENT OF THE GRAIN SURFACE OF COMBAT BOOT UPPER LEATHER
FLEXES TO INITIAL WATER PENETRATION*

On the Maeser Tester

	Conventional (Water *Outside*)				Experimental (Water *Inside*)		
Side No.	1st Run	3rd Run	5th Run	Side No.	1st Run	3rd Run	5th Run
1	2640	1470	1450	1	1640	920	650
2	3040	2030	**2040**	2	1800	1490	650
3	3530	2410	2520	4	2380	**1830**	1940
4	**3970**	**2240**	1600	5	**2830**	1520	750
5	4260	1390	1220	3	4860	1840	**1140**
6	10000+	4960	5680	7	6020	7920	4350
7	10000+	10000+	10000+	6	7820	5770	1880
Mean value	5350+	3500+	3500+		3910	3040	1610
Range	7360+	8610+	8780+		6180	7000	3700

On the QM Tester (Water Inside)

	Without Sand				With Sand		
Side No.	1st Run	3rd Run	5th Run	Side No.	1st Run	3rd Run	5th Run
2	1580	1430	1080	2	960	1570	1730
1	1750	1930	870	1	1750	3300	1770
5	3170	**2640**	**2040**	4	2920	4400	6720
3	**4440**	3120	2700	5	**3030**	3190	2040
4	4850	1780	1640	3	5170	**4030**	**4590**
7	4850	10000+	10000+	7	10000+	10000+	10000+
6	10000+	9380	9850	6	10000+	10000+	10000+
Mean value	4380+	4330+	4030+		4830+	5210+	5260+
Range	8420+	8570+	9130+		9040+	8430+	8270+

*Median values in bold face type.

Where the tables record flexes of 10,000 without leakage, a plus sign is attached not only to the figure 10,000 but also to the values for the median, the mean, and the range, all based on one or more of these truncated measurements.

TABLE III

TWO-SIDED SYLMER TREATMENT OF COMBAT BOOT UPPER LEATHER
FLEXES TO INITIAL WATER PENETRATION

On the Maeser Tester

	Conventional (Water Outside)				Experimental (Water Inside)		
Side No.	1st Run	3rd Run	5th Run	Side No.	1st Run	3rd Run	5th Run
1	1050	1080	900	1	660	620	650
2	1100	970	770	4	1170	790	440
3	1320	1240	450	7	1300	1250	540
4	1340	850	380	8	1660	720	1000
5	1780	1080	990	6	1830	1210	670
6	3670	2010	610	3	2030	2220	1070
7	5400	2230	1100	2	2110	1880	1270
8	7290	5550	3060	5	2330	2420	1200
Median value	1560	1160	830		1750	1230	820
Mean value	2870	1880	1030		1680	1220	850
Range	6240	4700	2680		1670	1800	830

On the QM Tester (Water Inside)

	Without Sand				With Sand		
Side No.	1st Run	3rd Run	5th Run	Side No.	1st Run	3rd Run	5th Run
1	450	300	310	1	440	300	310
4	550	380	380	8	580	620	630
7	1020	590	520	7	620	380	520
2	1080	510	460	4	750	690	880
8	1120	770	880	2	1020	510	650
6	1630	320	480	5	1580	510	420
3	1660	1310	680	3	2080	1310	1680
5	1670	750	390	6	2100	1290	950
Median value	1100	550	470		880	500	640
Mean value	1150	620	510		1150	700	760
Range	1120	1010	570		1660	1010	1370

TABLE IV

SYLMER TREATMENT OF COMBAT BOOT UPPER LEATHER
FLEXES TO INITIAL WATER PENETRATION
IN PRESENCE OF A SOIL SLURRY

On the QM Tester (Water Inside)

Sylmer Treatment	On Grain Surface			Sylmer Treatment	Two-Sided		
Side No.	1st Run	3rd Run	5th Run	Side No.	1st Run	3rd Run	5th Run
1	5050	3640	2110	3	2590	2820	1880
6	5780	4620	4450	8	2620	1880	1980
5	?	4400	6130	4	3680	2150	2000
2	6320	3870	5900	7	7020	2840	2030
7	8050	4260	3180	5	7020	3340	3960
3	10000+	5080	1390	1	7350	1880	2090
4	10000+	10000+	6010	6	9010	4040	2030
				2	10000+	3290	2420
Median value	6320	4400	4450		7020	2830	2030
Mean value	7530+	5120+	5120		6160+	2780	2300
Range		6360+	4740		7380+	2160	2080

TABLE V

SYLMER TREATMENT OF SECOTAN-PROCESSED COMBAT BOOT UPPER LEATHER
FLEXES TO INITIAL WATER PENETRATION

On the QM Tester (Water Inside)

	Water				Soil Slurry		
Sample No.	1st Run	3rd Run	5th Run	Sample No.	1st Run	3rd Run	5th Run
1	1830	1380	1260	2	5370	890	1100
2	4440	1110	3690	4	6050	1200	800
3	5290	4810	4140	5	9270	1500	1260
4	5930	3890	2580	3	10000+	3740	2190
5	8170	1210	1470	7	10000+	10000+	3020
6	5510	3480	2570	6	10000+	8870	7320
7	10000+	6730	10000+	1	10000+	8000	10000+
8	10000+	6180	10000+	8	10000+	10000+	10000+
Median value	5720	3680	3130		10000+	4750	2600

A diagram illustrating the nearly universal decline in the median values for water resistance with periodic testing is shown in Fig. 2. The mean values are less suitable for graphic presentation, since too many of them include at least one truncated value, i.e., a value obtained by breaking the test off after 10,000 flexes.

Adding up the total number of flexes per side in the tests reported in Tables II and III, we obtained the figures of Table VI. These begin with the lowest and end with the highest figure, regardless of the numbers assigned to the sides originally.

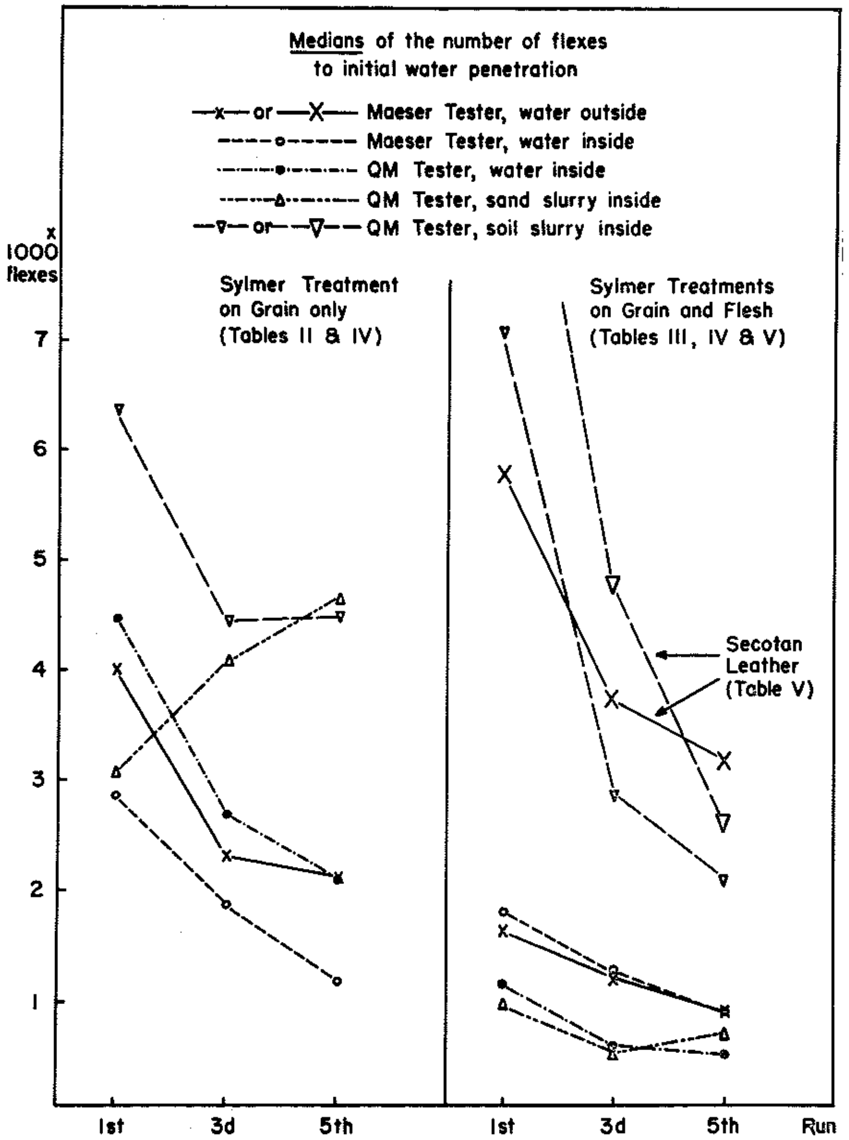

FIGURE 2.—Results obtained on Q.M. Water Penetration Tester.

TABLE VI

SUM OF FLEXES TO INITIAL WATER PENETRATION IN TESTS OF TABLES II AND III

Side No.	One-Sided (Grain) Treatment	Side No.	Two-Sided Treatment
2	19,400	1	7,070
1	20,140	4	8,600
5	28,080	2	12,330
4	36,270	5	15,120
3	40,350	7	15,470
6	95,340+	6	16,770
7	103,140+	3	17,050
		8	23,880
Median value	36,270		14,540
Mean value	48,960+		15,300

TABLE VII

RANK CORRELATION COEFFICIENTS BETWEEN NUMBER OF FLEXES TILL LEAKAGE IN THE TESTS INDICATED AND TOTAL NUMBER OF FLEXES TILL LEAKAGE IN ALL TESTS*

For Leather With a One-Sided Sylmer Treatment (Tables II & VI)

	1st Run	3rd Run	5th Run
Maeser Tester, conventional	.82	.68	.75
Maeser Tester, water inside	.89	.96	.57
QM Tester, water	.93	.54	.93
QM Tester, sand slurry	.93	.39	.96
Critical value (95% confidence level)	.71		

*Except test using soil slurry.

Table VII shows the rank correlations between the flexes until leakage in the four test methods of Table II and the sum total of flexes recorded in Table VI. These rank correlations exist for the Sylmer-treatment on the grain only. No similar rank correlations were found for the treatments on both sides.

Water absorption.—Table VIII shows the results for water absorption by leather of Tannery A. Again each specimen was tested five consecutive times, with adequate recovery times between testing. Table VIII shows only the results of the first, third, and fifth runs. The side numbers are the same as before.

TABLE VIII

WATER ABSORPTION BY IMMERSION AND ON FLESH SIDE (PERCENT BY WEIGHT OF THE LEATHER)

Side No.	One-Sided (Grain) Treatment 1st Run	3rd Run	5th Run	Side No.	Two-Sided Treatment 1st Run	3rd Run	5th Run
1	47	42	36	1	12	8	5
2	43	38	27	2	17	8	6
3	39	35	24	3	32	21	10
4	45	37	28	4	15	9	6
5	49	45	49	5	20	10	12
6	38	28	29	6	14	8	4
7	36	31	21	7	18	9	7
–				8	16	9	6
Median value	42	37	28		18	10	6
Mean value	45	37	31		17	9	7

DISCUSSION

Water-resistant leather of Tannery A.—One lot of this leather was Sylmer-treated on the grain only, the other on grain and flesh. Leather of different resistance to water penetration and with different water-absorptive properties was produced. The results of the tests concerned with water resistance in presence of water or of slurries of sand and soil are presented in Tables II to IV. The median values shown in these tables are graphically presented in Fig. 2. Those obtained with a Sylmer treatment on the grain and flesh are shown on the right; those obtained with a Sylmer treatment on the grain alone are shown on the left. The graph shows at a glance that all median values except those where sand was used in the QM Tester decrease from the first to the fifth run. It also is obvious that the two-sided treatment generally gives lower median values than the grain treatment.

It is desirable to obtain a single figure indicating how the various test conditions compare with each other. To obtain such a figure, average the three medians for each test condition and express the resulting means in percent of the means for the conventional Maeser test. The following figures are obtained:

	Grain Treatment %	Two-Sided Treatment %
Maeser, conventional	100	100
Maeser, inverted	70	94 (65)
QM Tester, water alone	110	60
QM Tester, sand slurry	*	57
QM Tester, soil slurry	184	335

*Deleted because water penetration rate rises rather than falls.
Figure in parenthesis is the mean value.

The figures reveal these facts:

1. Inverting the leather in the Maeser Tester reduces the number of flexes to leakage by 30 to 35%. In the two-sided treatment the median values do not confirm this observation, but the mean values do, and these can be used here instead since no truncated figures were obtained here. Hopton stated (5) that penetration time is cut in half by inversion, but his estimate apparently is exaggerated.

2. On the QM Tester water penetration through leather with a grain treatment is about the same as in the conventional Maeser test, but water penetration through leather treated on grain *and* flesh is 40% faster.

3. A sand slurry, although causing an irregular increase in water resistance of the grain-treated leather, as already mentioned, does not differ from water alone in its action on a two-sided treatment. We don't believe that this is a freak result but find it difficult to explain.

4. A soil slurry, simulating the action of mud, prevents water from penetrating leather, regardless of treatment, for a much longer time than any other test condition.

Water-resistant leather of Tannery B.—This leather has been oiled sparingly by the SECOTAN process and contains only 8% chloroform extract, including the silicone (Table I). Examination was limited to the QM Tester filled with water or "mud".

The medians obtained under these two test conditions are shown in the right portion of Fig. 2, since the Sylmer treatment penetrated the leather from both sides, grain and flesh. At a glance, it is apparent that initial water resistance is very high, but the decline in subsequent test runs is steep, especially where "mud" is used. Therefore, in the latter case, after the fifth run, the median number of flexes to leakage is close to that of the two-sided treatment of Tannery A. By contrast, at the same time, penetration by water alone is still nearly seven times higher.

Variations between sides.—Extreme variability in the water resistance of silicone-treated side upper leather comes as no surprise. In a previous paper (3) an attempt was made to continue flexing to leakage even with the most impervious specimens. Some of them required over a million flexes on the Maeser Tester, running for more than 6 days at the speed of 195 flexes per minute. The number of specimens that leaked below 10,000 flexes was very small, especially among those taken from the official test area, as is the case in the present study. Not only does it appear impractical to extend flexing beyond the 10,000-mark, but it is obviously unnecessary to provide for a water resistance much beyond the limits of a reasonable test for it. Instead it seems more economical to strive for uniformity in the application of silicones whether the treatment is applied to the grain or to both sides.

The question, then, is this: How much variability is found in the two lots of Tannery A of which one had been intentionally prepared for high water resistance and the other for low water absorption?

For an answer one has to look only at Table VI. Here the variations between sides in each of the two types of leather become apparent. As pointed out before, the figures of Table VI represent the sums of the number of flexes until leakage for the twelve test runs of Tables II and III. The test runs of Table IV with a soil slurry are omitted because of the great changes in water resistance caused by mud.

Table VI shows not only the range typical for the water resistance of seven or eight sides supposedly treated in the same manner but also the enormous difference between the two kinds of application in the number of flexes until leakage occurs.

Where ranges are large, rank correlations are more probable than in small ranges. Therefore, rank correlations can be calculated between Tables II and VI but not between Tables III and VI, i.e., they are restricted to leather treated on the grain. The correlation coefficients are shown in Table VII. They are highest for the first run and seem to be consistently higher for the QM tester than for the Maeser Tester. This observation can be interpreted as favoring the QM Tester for evaluation of water resistance. A high correlation coefficient also means that the sides with the lowest and highest water resistance can be reliably sorted out by a single test with specimens from the official test area. The very same sides are the poorest and the best tested by every method: i.e., No. 1 and 2 are low and No. 6 and 7 are high in water resistance every time. The same does not hold true of the sides treated on grain and flesh as a closer study of Table III reveals.

A comparison of the ranges in Table III can also be interpreted as favoring the QM Tester, because the ranges generally are narrower with this tester than with the Maeser Tester.

Water absorption of leather from Tannery A.—Water absorption is important for comfort because leather that absorbs water can pick up foot perspiration when the man is under stress. Water vapor permeability is then too slow, even though it may be sufficient to transmit moisture to the outside after the stress has subsided. One would expect that different techniques of applying silicone would affect water absorption, but to what degree has not been studied heretofore.

Table VIII fills this gap. The figures presented in this table show the following:

1. A grain treatment preserves high water absorption.
2. A treatment on grain and flesh reduces water absorption to a level that would affect foot comfort in all-leather boots.

3. Repeated wetting and drying leads to a gradual decrease in water absorption.

After five consecutive wettings the leather treated on the grain has a water absorption of about 25–50% as compared with 40–100% for untreated leather of the same kind. Measurements of untreated leather (not shown in Table VIII) are taken from our unpublished experiments.

A fully Sylmer-treated leather, as Table VIII shows, may after some wear have a water absorption of about 10%. If such leather is used intentionally to prevent the uppers from soaking up water, as in the tropical boot, no objections can be raised. In this boot the quarter is made of nylon cotton duck so as to keep the feet as cool as possible in the climate in which they are worn. No attempt is made to keep water out if one steps into water. In fact, two tiny holes near the arch provide for drainage. Clearly, leather in the tropical boot functions as a sheathing only. Sometimes the boot may be in contact with water for days on end; but whenever an opportunity arises for the upper to dry out, the amount of water to be removed from the leather parts should be so small that the evaporation process should take no more than a few hours.

SUMMARY AND CONCLUSIONS

The present investigation of silicone-treated leathers distinguishes for the first time between several modes of silicone application. At the same time it was aimed at testing the permanency of the treatment in presence not only of water but also of wet sand and of mud. To this end the resistance to water penetration in these media was retested five consecutive times. As an additional means of distinguishing between the silicone treatments, water absorption was measured.

The conventional water penetration testers were not considered adequate for the testing program set forth in this study. Instead a new, simpler, and more compact tester was used. This machine, built at QM, is better suited for testing the behavior of leather toward sand and soil slurries because the leather forms a cup holding the water or the slurries. Moreover, mounting and removing the specimens are fast and easy. No leakages occur, as is often the case with the Maeser machine.

There is one more feature to the QM Tester that may prove to be the most important in the long run; this is the desirability of testing at a large angle of flex which in the past could not be obtained with any instruments except Baumann's Penetrometer (4). Figure 3 illustrates the angle of flex obtained with the QM Tester. The angle of flex is determined by the compression in the length of the specimen forming the cup. This compression reaches about 20% with the QM Tester. For other testers either the angle of flex or the compression, or both, are known, as shown in Table IX. Evidently the Penetrometer can be operated under milder, and the Hopton Tester under more severe, flex conditions than the other testers. The QM Tester stands between the Maeser Tester and the Penetrometer.

For the two types of leather tested, the measurement of both water resistance and water absorption convincingly proves that the end results depend on the skill of the tanner who uses the Sylmer treatment. By applying silicone to the grain side alone he can produce highly water-resistant leather without sacrificing water absorption from the flesh. By applying silicone to both grain and flesh he can produce leather that will not absorb water without being particularly resistant to water penetration.

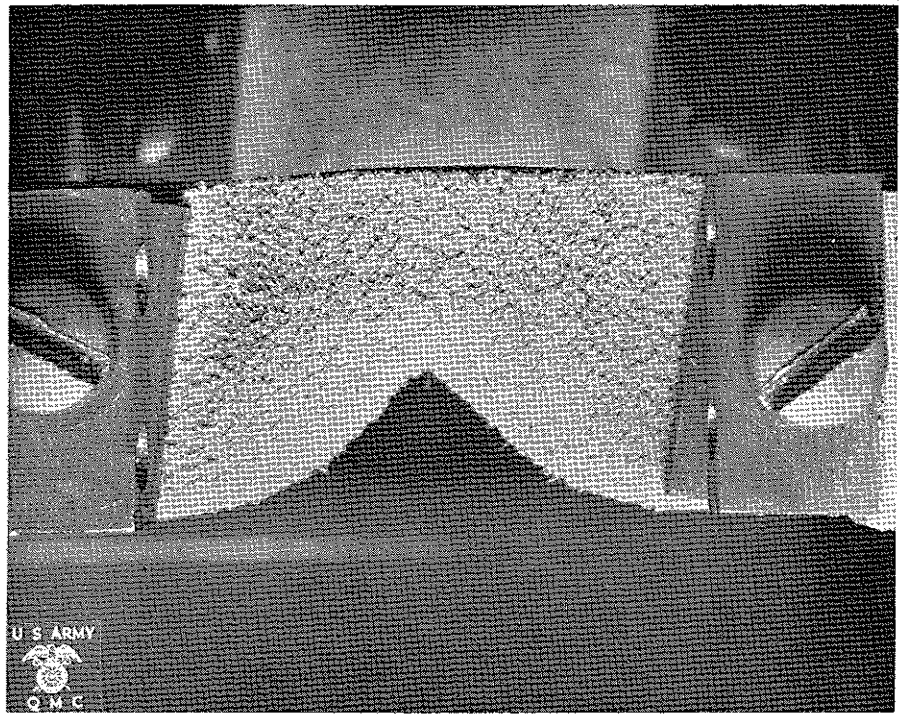

FIGURE 3.—Angle of flex on Q.M. Water Penetration Tester.

The surprising result of repeating the tests with these leathers was that both water resistance and water absorption gradually decreased with one exception: flexing the grain-treated leather in a slurry of sand caused water resistance to increase. The general result suggests that the silicone gradually penetrates into the interior of the leather, thereby coating more fibers and so preventing them from absorbing water; but at the same time, it spreads itself so thin that more water can pass through the interstices. The result with a sand slurry, however, is difficult to explain; possibly the sand grinds

up the pigment in the leather finish and pushes it so deep into the grain layer that the passage of water is eventually blocked.

A second type of Sylmer leather produced in combination with the SECOTAN process was also examined. This leather, treated by immersion, initially was very resistant to water penetration but showed sharper declines than the other kinds of treated leather. We believe that the water resistance of the SECOTAN leather is unnecessarily high and that a saving in the quantity of silicone employed is possible. We are supported in this assumption by the recent British experience that uppers with 2½% silicone by weight gave "generally excellent results" (7). It almost goes without saying that avoidance of wetting agents and emulsifiers in all stages of leather manufacture probably allows great savings in silicone and may also contribute to greater uniformity.

TABLE IX

ANGLE OF FLEX AND COMPRESSION OF WATER RESISTANCE TESTERS

Name of Tester	Angle of Flex (degrees)	Compression (%)	Reference
Hopton		60	(6)
Dow Corning	25	32*	(2)
Maeser	57	**	(2)
Baumann		5†	(3)
QM	84	20	

*Calculated from photograph on page 391, Ref. 2; in tentative method of the American Society for Testing Materials, 40%.
**Cannot be computed because one of the clamps moves below the horizontal while specimen is flexed.
†Lowest compression possible; others: 7.5, 10, and 15%.

The leather industry should welcome an inexpensive tester which will enable the laboratory to test quickly and, more important, in greater numbers than heretofore possible the various ways of applying silicones and the possible influence of fatliquors, mordants, and other agents upon the ultimate water resistance of Sylmer-treated leather. While the investigation has not been extended to cover any other leather treatments, for instance, with Bavon or Scotchgard, the QM Tester should be of great value also for users of these and similar materials whose effect on leather is even less known than is the effect of silicone.

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APPENDIX

Description of the QM Water Penetration Tester.—The tester with 8 stations, shown in Fig. 1, requires a 1-HP motor for operation. The speed reduction unit and the motor can be seen in the left lower corner of Fig. 1. The mechanical reset counter is still farther to the left and is not shown. It is activated by a ¾″ long prong fastened to the revolving disc D of Fig.1. Attached to this disc is an eccentric with a short link connecting with the shaft of the tester. This shaft is square in Fig. 1, but it could as well be round.

Building a tester identical with that of Fig. 1 requires only a few critical measurements. These are the following:

1. *Distance between the arms A, B, and C in Fig. 1.* Arm B is mounted on the shaft; A and C are fastened to supports which in turn are mounted on the platform. The distances between A and B and between B and C are 70 mm. when the eccentric on disc D forms a 90% angle with the shaft. After a quarter turn of disc D, in either direction, the shortest and longest distances of A and C from B are reached: these are 65 and 75 mm., respectively.

2. *Size of rectangular brass plates* bolted to the arms A, B, and C for holding the specimens. Each plate is 25 x 12.5 x 4 mm. and is recessed 0.5 mm. in the arm to which it is bolted. Altogether there are 32 such bolts, 4 being necessary to hold one specimen, as Fig. 1 shows. Each of the 16 bolts held by the frontal plates, all visible in Fig. 1, goes through to a movable brass plate 25 x 12 x 4 mm. Each end of the specimen is set between this plate and a fixed rear plate. The maximum distance between one of these movable plates and the fixed rear plate is 13 mm. With the specimen in place the distance is reduced by tightening the bolts with a screw driver until the specimen is held tightly by the two plates.

The following measurements, while not critical, are of interest to anyone who wants to copy the QM Tester:

1. Slope of arms A, B, and C to facilitate access to the bolts in the brass plates holding the specimens. In Fig. 1, the difference in height between the bolts of station 1 and those of station 4 is 65 mm.

2. Distance between stations makes the QM Tester a truly compact apparatus; the 3 arms A, B, and C are each 225 mm. long, and the 2 pairs of specimens in Fig. 1 on either side of the central shaft are 60 mm. apart.

Sample sizes compare as follows:

Tester	QM	Penetrometer	Maeser	Dow Corning
Dimensions (std. sample), inches	2 x 2.9375	2.95 x 2.36	3.875 x 4.5	4 x 4
Deviations allowed, inches	±0.0625	none	±0.0625	±0.125
Area (std. sample), sq. inches	6	7	15.5	16

Testing method.—Any kind of automatic end point detection was discarded in favor of probing the specimens continuously with the leads of an ohmmeter. This method was found to be reliable and well adapted to the QM Tester with its eight stations. Every specimen can be tested in a few seconds. A mirror placed underneath helps to detect any moist spots as soon as they appear and also to locate the exact spots where there is constant bending and where penetration is most likely to occur. The enamel tray shown in Fig. 1 serves conveniently for catching the water that may be lost when a leaking specimen is removed.

DISCUSSION

Malcolm Battles (A. C. Lawrence Leather Co.): I would like to thank Dr. Seligsberger for outlining the requirements of the military and for his evaluation of the various leathers. One question, Dr. Seligsberger: What do you think are the advantages of this method of testing over the other devices already available?

Dr. Seligsberger: In the first place, I think that we use much less time in mounting the samples and in taking them off. For testing we simply use the ohmmeter which we think is reliable. We have eight stations on one platform. I don't think the Maeser Test, for instance, can compete, timewise, with this test.ng.

Mr. Battles: As a result of the work, have you established limits which you consider acceptable for performance?

Dr. Seligsberger: We have not come to anything definite about that. We just wanted to know how two different treatments, which we obtained from the Industry, would compare. We have however, established 30% as the maximum water absorption for treated leather for the tropical boot. We do not intend to test this leather on the Maeser Tester, or on our tester, because the water resistance there, in the sense of resistance to penetration, is immaterial, as I pointed out in my paper.

DR. CASSEL (National Bureau of Standards): Perhaps I should have been able to get this from the data, but is the variability of this test method reduced over that of the Maeser Test? In other words, the problem there seemed to be the variability from one sample to another. Is the reproducibility better with this test machine?

DR. SELIGSBERGER: I don't think I should say that this is so, because we have only tested one kind of leather, i.e., Sylmer leather, from two different tanneries. I would say we would have to have much more material to come to a definite conclusion on that.

DR. NEHER: On these one-side versus two-side treatments, you had much better results from the one-side treatment. Do you know what the level of the silicone treatment for those two types of treatments was?

DR. SELIGSBERGER: I don't know the level. I simply left it to the tannery. The tannery did not intend to make the leather with the two-side treatment resistant to water, in the Maeser or in our tester. Their intent there was to produce a leather with a low water absorption. This is what I wanted to show—that you can produce two different kinds of leather by s milar treatments, by technical know-how.

DR. VON FUCHS: My first comment is in connection with the statement made by Dr. Cassel. He mentioned that leather is not uniform in its water resistance after treatment. I claim—and I have plenty of evidence—that the cow is just as waterproof in its neck and belly as it is in its back. So I think that is a myth. The cow does not know it. Let's forget about water-repellent leather and think about fatliquoring, and you will eliminate the whole problem.

One more point: I would like to ask Dr. Seligsberger after this meeting, and I ask him now publicly, to extend his investigation into ASA. He will find it worth his while.

MILTON BAILEY (U. S. Navy Research and Development Facility, Brooklyn, N. Y.): I would like to congratulate Dr. Seligsberger on a very interesting presentation. One of the questions which occurs is a method of end point determination by the ohmmeter method. It appears that this would not be much better than using your eyesight for determining water penetration. Could you tell us something about it?

DR. SELIGSBERGER: Usually the operator, when all eight stations are occupied, is very busy running the ohmmeter over the samples, and he usually discovers a leak first with the ohmmeter, and then after making 50 flexes more, it will become visible in the mirror. So I would say that the ohmmeter is a great help, but then, of course, these were combat boot leathers which are not dyed through.

When we deal with leather which is black and dyed through, we cannot see the leak and have to have the ohmmeter.

MR. BAILEY: Another question on your data on silicone maxima. I know that the Navy has been purchasing the water-resistant leather, both ASA- and silicone-treated, and has had a very high requirement, considerably higher than that which would be indicated by your investigation. Rationalizing, or trying to reconcile that with some of your results, I would say there is considerable variation between the various machines. I wonder if you can suggest why your machine is lower than the commercial results?

MR. BATTLES: I will answer that for you. We produced these two experimental lots for Dr. Seligsberger, and these were not commercial treatments. There were requirements that the leather be compatible with the direct-molded sole construction, and it did not permit the use of silicone in the same manner or quantity that would be used in your fleet shoe leather. This was special leather and was not intended to have high values.

DR. SELIGSBERGER: We feel that in general we do not actually need leather with water-resistance figures which had been quoted before, particularly in connection with the paper of Dr. Neher. We just feel that when we have perhaps 4000 flexes, we have attained very good water resistance.

The question is, how do we translate our laboratory findings into practice? Do we really want 100,000 flexes in the laboratory? We have to stop the test somewhere, and we thought that stopping at 10,000, and considering 4000 already an appreciable water resistance, would be adequate.

MR. BATTLES: I would like to terminate that discussion with a suggestion. I would like to suggest that Dr. Seligsberger or Mr. Bailey or someone else arrange to have a rather large test run to correlate the various methods of testing with actual performance. This has never been done. We talk about where the cut-off point should be, but we don't really know.