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This report contains the results of studies performed to evaluate the rot and weather-resistance protection provided by copper-zirconium and Zirchrome as finishes for cotton textiles. Cotton fabrics treated with either copper borate-zirconyl ammonium carbonate (Cu-Zr) or Zirchrome were subjected to rot-resistance and weathering tests. The Cu-Zr finish provided good microbiological protection relative to copper 8-quinoinolate, but there were several instances of loss of protection after leaching or Weather-Ometer exposure and accelerated fabric degradation after weathering.

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The Zirchrome finish, though inferior in microbiological protection and durability of protection to the Cu-Zr finish, was as protective as the MIL-M-46032 cuprammonium finish but caused a large tearing strength loss on application of treatment to cotton osnaburg.

PREFACE

This report contains the results of studies performed to evaluate the rot and weather-resistance protection provided by copper-zirconium and Zirchrome as finishes for cotton textiles. Though the work described in this report was completed essentially prior to 1970 and portions of it have been reported out, the information is considered timely due to a recent renewal of interest in the copper-zirconium finish as a possible replacement for fungicides regarded as hazardous to the environment. This report has been written to provide a complete and integrated summation of efforts carried out.

The authors are indebted to these USDA personnel - Wilson A. Reeves, Albert S. Cooper, Jr., C. James Conner and Norbert W. Berard for technical guidance and coordination of this study with the United States Department of Agriculture. Dr. Leonard Teitell, USA Frankford Arsenal, is to be thanked for exposing samples in Panama Canal Zone. Thanks are also due to Mr. Thomas D. Miles, formerly USA NARADCOM, for supplying some of the tear strength data.

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AN EVALUATION OF SOME ZIRCONIUM-CONTAINING FINISHES AS FUNGICIDES FOR THE PRESERVATION OF COTTON FABRIC

INTRODUCTION

An inexpensive fungal-resistant treatment based on the reaction products of several zirconium compounds has been developed at Southern Regional Research Center, USDA, and is fully described by Conner et al.[1] Briefly, water soluble zirconium compounds were used to solubilize a number of anti-microbial agents. During the cure process, the anti-microbial compounds formed insoluble fungitoxic products with zirconium that were resistant to leaching.

Copper borate, one of the anti-microbials investigated, was solubilized with either zirconyl acetate or zirconium ammonium carbonate and padded onto cotton duck fabric. The cotton duck treated with copper borate-zirconyl ammonium carbonate was more rot-resistant than duck treated with copper 8-quinolinolate at the 0.2% copper level. The copper borate-zirconyl acetate treated fabric, however, was more susceptible to microbiological degradation but good in weathering properties. In short, the weathering and rot-resistance data indicated that these fungicides should be further evaluated relative to copper 8-quinolinolate for potential use in Army applications.

The standard screening procedure used by this laboratory for the preliminary evaluation of potential military fungicides includes the performance of soil burial tests both before and after the standard leaching test and 100 hours of Weather-Ometer exposure. O.D. sateen fabrics which had been treated with copper borate-zirconyl ammonium carbonate and copper borate-zirconyl acetate at comparable wet pick-up levels by Southern Regional Research Center, USDA, were subjected to these tests. O.D. sateen treated with copper borate-zirconyl ammonium carbonate was, in fact, more rot-resistant than the comparable fabric treated with copper borate-zirconyl acetate. After 120 days in soil burial the former fabric retained 83% of its original breaking strength while the latter fabric retained only 22%. Neither the standard leaching test or 100 hours of Weather-Ometer exposure significantly affected the rot-resistance of either fabric. Weather-Ometer exposure, per se, caused an 8%-9% breaking strength loss in the two fabrics. Since the two treatments on the same O.D. sateen base fabric performed equally well during Weather-Ometer exposure, 100 hours was not sufficient to differentiate between the weathering properties of the two treatments.

Another anti-microbial, tetramminecopper carbonate was not as satisfactory as copper borate in soil burial performance. There was a significant difference between sets of the same well-scoured duck treated with either compound in combination with zirconyl ammonium carbonate. After 84 days in soil burial, fabrics treated with tetramminecopper carbonate

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[1] Conner, C.J., A.S. Cooper, Jr., W.A. Reeves, B.A. Trask. Some Microbial Resistant Compounds of Zirconium and Their Effect on Cotton. Textile Res J. 34, 347 (1964).

retained only 45% and 47% of their initial breaking strength, on average. However, fabrics treated with copper borate retained 94%, 91% and 92% following soil burial for 120 days - a considerably longer exposure period. Hence, the fabrics treated with copper borate were more than twice as rot-resistant when the difference in length of soil burial exposure was taken into account. This large difference in performance could not be accounted for by the analytical data obtained from the fabrics.

Primary interest from a microbiological point of view came to be centered on fabrics treated with copper borate and zirconyl ammonium carbonate. Fabrics treated with this combination of compounds demonstrated a high level of rot-resistance and warranted more extensive evaluation including outdoor exposure. This report contains a compilation of laboratory and outdoor exposure data obtained from a series of materials fungus-proofed with the copper borate-zirconyl ammonium carbonate treatment. Also included are results obtained from fabrics prepared by the Zirchrome Process which is a mineral dyeing process for producing weather-resistant fabric. The Zirchrome Process evolved as a consequence of previous work with water-soluble zirconium compounds and anti-microbial agents. Conner et al[2] found that the inclusion of a hexavalent chromium compound under controlled conditions resulted in an insoluble mineral dye which improved the weather-resistance of cotton fabric.

MATERIALS AND METHODS

Fabrics

The fabrics evaluated in this study are listed in Table 1. Fabric 1, a greige duck, which contained 1.03% copper 8-quinolinolate (Cu-8) by analysis was included in this report as a basis for comparing the performance of fabrics treated with copper borate-zirconyl ammonium carbonate (Cu-Zr). Fabric 1 had been treated by the Lowell University Research Foundation with Cunilate 2174 (a 10% active commercial preparation of Ventron Corporation, Beverly, MA) extended in Esso Varsol 1. Fabric 18 was a cotton osnaburg treated with cuprammonium salts in accordance with MIL-M-46032.[3] It was included as a basis for evaluating the performance of fabrics treated by the Zirchrome process because the Zirchrome treatment was originally regarded as a possible replacement for the cuprammonium treatment. Fabric 18 was furnished as disassembled sandbags by the U.S. Army Mobility Equipment R&D Center, Fort Belvoir, Virginia. Hence, the date and place of treatment were unknown.

All fabrics treated either with copper borate-zirconyl ammonium carbonate or by the Zirchrome Process were prepared by the Southern Regional Research Center of the U.S. Department of Agriculture. The copper borate-

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[2] Conner, C.J., G.S. Danna, A.S. Cooper Jr., W.A. Reeves. Novel Mineral Dyeing Process for Improved Weather Resistance of Cotton. Textile Research J. 37,94 (1967).

[3] U.S. Federal Supply Service, "Mildew-Resistant Treatment (For Fabrics) Copper Processes", Military Specification MIL-M-46032, Washington, D.C., U.S. Government Printing Office, 1959.

TABLE 1

Cotton fabrics tested

Fabric[a] no.	Base fabric	Finish	Date & place treated
1	Greige duck	Sol. Cu-8, 1.03%[b]	Nov 64, Lowell Univ.
2	Greige duck	none	-
3	Greige duck	Cu-Zr (0.4% Cu)	Sep 63, So. Reg. Rsch. Cen.
4	Woven awning duck	Cu-Zr (0.4% Cu)	Sep 63, " " " "
5	Vinyl coated stretch broken twill	Cu-Zr (0.48% Cu, 2.3% ZrO_2[b])	Sep 63, " " " "
6	Greige duck	Cu-Zr (0.51% Cu, 3.07% ZrO_2, 0.08% B[c])	Apr 64, " " " "
7	Greige duck	none	-
8	Bleached white duck	Cu-Zr (0.485% Cu, 4.27% ZrO_2[b])	Aug 65, " " " "
9	Bleached white duck	Cu-Zr (0.755% Cu, 4.58% ZrO_2[b])	Aug 65, " " " "
10	Bleached white duck	Cu-Zr (0.52% Cu, 1.84% ZrO_2[b])	Aug 65, " " " "
11	Bleached white duck	none	-
12	Greige osnaburg	Zirchrome (0.45% Cu, 0.65% ZrO_2, 0.63% Cr[b])	Sep 67, " " " "

TABLE 1 (Cont.)

Cotton fabrics tested

Fabric[a] no.	Base fabric	Finish	Date & place treated
13	Greige osnaburg	Zirchrome (0.52% Cu, 0.63% ZrO_2, 0.70% Cr[b])	Sep 67, So. Reg. Rsch. Cen.
14	Greige osnaburg	none	-
15	Scoured osnaburg	Zirchrome (0.48% Cu, 0.81% ZrO_2, 0.69% Cr[b])	Sep 67, " " " "
16	Scoured osnaburg	Zirchrome (0.49% Cu, 0.68% ZrO_2, 0.61% Cr[b])	Sep 67, " " " "
17	Scoured osnaburg	none	-
18	Osnaburg	Cuprammonium (1.75 ± 0.25% Cu[d])	Unknown
19	Scoured osnaburg	Zirchrome (Unknown)	Nov 67, " " " "
20	Scoured osnaburg	none	-

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[a] Fabrics 1, 2, 6, 7 = 334 g/m^2, CCC-D-771B; fabrics 8 to 11 = 334 g/m^2, type III, CCC-C-419a*; fabrics 12 - 20 = 231 g/m^2, class 2, CCC-C-429B.

[b] By analysis.

[c] On the basis of wet pick-up.

[d] **Fabric was prepared to contain 1.75 ± 0.25% Cu in compliance with type III treatment MIL-M-46032 (reference 3).**

***A test fabric designed by Brysson & Markezich[4] to simplify the preparation of ravelled strips for breaking strength measurements.**

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[4] Brysson, R. J., **A.R. Markezich**. New Test Fabric for Tensile Measurements. Textile Res. J. 32, 615 (1962). Letter to the Editor.

zirconyl ammonium carbonate treatment was applied to all the base fabrics listed in Table 1 except cotton osnaburg. The Zirchrome treatment, on the other hand, was applied only to cotton osnaburg because of specific interest in this treatment as a sandbag preservative. All except fabric 6 and fabric 19 were small-scale preparations. Fabric 6, a greige duck, was a 119-metre test run which was scoured prior to treatment. Osnaburg fabric 19, also a large test run, was scoured too. Fabrics 8 to 10 were prepared in an attempt to relate treatment performance during actinic exposure with treatment composition. The base fabric used for this test series was a 334-g/m^2-type III duck, CCC-C-419a.[5] It was boiled off in a 4% caustic soda solution and bleached in a 2% hydrogen peroxide solution immediately after the fabric had been woven. Greige osnaburg fabric 12 and scoured osnaburg fabric 15 were dried four minutes at 120°C and then cured two minutes at 140°C on tenter frames. Greige osnaburg fabric 13 and scoured osnaburg fabric 16 were dried two minutes and then cured two minutes at a gage pressure of 210 kPa. The estimates of treatment level and analytical data contained in Table 1 for fabrics treated either with copper borate-zirconyl ammonium carbonate or by the Zirchrome Process were supplied by the Southern Regional Research Center.

Different specimens of each treated material were subjected to the severe leaching test; i.e. 24 hours at 27°to 29°C and to 100 hours of full cycle exposure in a twin arc Weather-Ometer. These tests were preceded and followed by soil burial testing to measure initial rot-resistance and any loss due to either leaching or Weather-Ometer exposure.

In addition to the above laboratory tests, specimens of fabric 6, a greige duck, were exposed to three different outdoor environments for 12 months. Specimens of osnaburg fabric 19 were exposed at one of the sites for 10 months. At bimonthly intervals specimens of greige fabric 6 were evaluated for changes in copper content, breaking strength, cuprammonium fluidity and rot-resistance. Osnaburg fabric 19 was evaluated only for changes in breaking strength.

The treatments all imparted a characteristic color to the base fabric. Copper 8-quinolinolate imparted a greenish-yellow color, copper borate-zirconyl ammonium carbonate a pale blue tint, Zirchrome a pearl-gray finish, and cuprammonium salts a light brown with a reddish tinge.

Copper content was assayed by the rubeanic acid method described by Kempton et al.[6] Analysis for copper 8-quinolinolate was performed at the Lowell University Research Foundation by the method of Rose et al.[7]

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[5] U.S. Federal Supply Service, "Cloth, Duck, Cotton, Unbleached, Plied-Yarns, Army and Numbered," Federal Specification CCC-C-419a, Washington, D.C., U.S. Government Printing Office, 1961.

[6] Kempton, A.G., M. Greenberger, A.M. Kaplan A Critical Comparison of Available Methods for the Spectrophotometric Determination of Micro Amounts of Copper in Textiles. Textile Res J. 32, 128 (1962).

[7] Rose, A., A.W. Hutchison, J.R. Hayes, I.R. Sharkey. The Estimation of Copper 8-Quinolinolate in Mildewproofed Fabrics. Am. Dyestuff Reptr. 45, 362 (1956).

Breaking strengths were measured on an Instron Tensile Tester Model TT-Cl according to Method 5104.1 of Federal Specification CCC-T-191b[8]. Tearing strengths were measured on an Elmendorf Tear Test Machine according to Method 5132 of Federal Specification CCC-T-191b.[8]

Fluidity measurements were performed as described by Clibbens and Little.[9]

Durability Tests

Outdoor weathering tests were performed at the **NARADCOM exposure site** in Sudbury, Massachusetts and at two Fort Sherman exposure sites in the Panama Canal Zone. The NARADCOM site and one of the Panama sites were unshaded, open field sites. The other Panama site was in a shaded rain forest location. Large swatches of cloth were secured to open-backed racks at the three sites. The racks at Sudbury are of aluminum construction, and samples were tacked to wooden frames that face south at an angle of 0.79 rad from the vertical — the fabrics being a minimum distance of 75 cm from the ground. Fabric samples were attached directly to the aluminum racks at Fort Sherman by either wire and eyelets or slotted angle aluminum. The Fort Sherman frames face south at an angle of 1.05 rad from the vertical.

Weather-Ometer, leaching and soil burial testing were conducted on 25 x 150 mm warp strips in accordance with Methods 5670, 5830 and 5762, respectively, of Federal Specification CCC-T-191b (reference 8). Ravelled specimens were used **whenever possible.**.

RESULTS AND DISCUSSION

Preliminary Physical Measurements

Table 2 demonstrates the effect of treatment on the warp breaking and warp tearing strength of fabrics included in this report. Breaking and tearing strength measurements were performed on all treated fabrics for which an untreated control was available. Cuprammonium treated fabric 18 was also included although no suitable control was available for it. The data indicate that none of the treatments seriously affected the breaking strength of any of the test fabrics. However, the tearing strength data from the Zirchrome treated fabrics were cause for concern because the tearing strengths of the three untreated osnaburg fabrics ranged from 52 to 57 newtons with an average value of 55 newtons for the group while the tearing strengths of the five Zirchrome treated fabrics ranged from 18 to 23 newtons with an average value of 21 newtons. If the losses are calculated as % retention based on the untreated fabric,

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[8] U.S. Federal Supply Service, "Textile Test Methods", Federal Specification CCC-T-191b, Washington, D.C., U.S. Government Printing Office, 1951.

[9] Clibbens, D.A., **A.H. Little.** Shirley Institute Memoirs 15, 25 (1936).

TABLE 2

Effect of treatment on breaking and tearing strength of fabrics

Fabric no.	Fabric description	Breaking strength N	Breaking strength %Ret.	Tearing strength N	Tearing strength %Ret.
1	Cu-8 treated greige duck	592	99	32	100
2	Untreated greige duck (control for fabric 1)	596	--	32	--
6	Cu-Zr treated greige duck	659	101	25	78
7	Untreated greige duck (control for fabric 6)	650	--	32	--
8	Cu-Zr treated bleached duck	481	108	12	92
9	Cu-Zr treated bleached duck	490	110	12	92
10	Cu-Zr treated bleached duck	498	112	12	92
11	Untreated bleached duck (control for fabrics 8, 9, 10)	445	--	13	--
12	Zirchrome treated greige osnaburg	383	94	23*	40
13	Zirchrome treated greige osnaburg	476	116	20*	35
14	Untreated greige osnaburg (control for fabrics 12, 13)	409	--	57*	--
15	Zirchrome treated scoured osnaburg	338	97	22*	39
16	Zirchrome treated scoured osnaburg	405	117	18*	32
17	Untreated scoured osnaburg (control for fabrics 15, 16)	347	--	56*	--
18	Cuprammonium treated osnaburg	392	--	27	--
19	Zirchrome treated scoured osnaburg	343	101	21	40
20	Untreated scoured osnaburg (control for fabric 19)	338	--	52	--

*Data supplied by T. Miles, U. S. Army Natick Research & Development Command.

the fabrics retained only 32% to 40% of their initial tearing strength after treatment by the Zirchrome Process. It appears likely that cuprammonium treated fabric 18 with a tearing strength of only 27 newtons also suffered a reduction in tearing strength as a result of treatment. However, no suitable control was available for estimating the % change. Fabrics treated with copper borate-zirconyl ammonium carbonate lost little tearing strength relative to fabrics treated by the Zirchrome Process. The maximum loss occurred in treated fabric 6 which retained 78% of its initial tearing strength after treatment. Copper 8-quinolinolate treated fabric 1 was unique in that it apparently was the only treated fabric not to lose some tearing strength as a result of treatment.

Copper Borate-Zirconyl Ammonium Carbonate

Rot-Resistance

Table 3 contains the results obtained from laboratory tests performed on the fabrics treated with copper borate-zirconyl ammonium carbonate. Comparable data from greige duck fabric 1 which contained 1.03% copper 8-quinolinolate are included. Fabric 1 lost 17% of its breaking strength following 63 days of soil burial. This performance was not satisfactory in relation to data previously reported in the literature or as experienced in our laboratory. Past work performed in this laboratory by Kempton et al.[10] has shown that 0.50% solubilized copper 8-quinolinolate by analysis protected a 417 g/m^2 cotton duck for approximately 50 days in soil burial. Similarly Klens and Stewart[11] have shown that 0.77% solubilized copper 8-quinolinolate (0.14% copper by analysis) protected a 305 g/m^2 duck for 8 weeks before any loss of fungicidal action was evident. Consequently cotton fabric containing as much as 1.03% copper 8-quinolinolate should last 2 to 3 months in soil burial before losing any breaking strength. It is possible that fabric 1 was not adequately prepared. Changes in rot-resistance after leaching were not measured in this fabric. However, past experience with copper 8-quinolinolate indicates only a negligible loss of fungicide will result during severe leaching exposure.

The test results indicated that the copper borate-zirconyl ammonium carbonate treatment did, in fact, provide good rot-resistance relative to copper 8-quinolinolate. Greige duck, fabric 3 lost significant biocidal action after 60 days of exposure in soil burial. However, the microbiological resistance of the other fabrics was clearly superior to that of fabric 3. Fabrics 8, 9 and 10, which were all prepared from the same Type III duck CCC-C419a, lost little rot-resistance during 120 days of soil burial and were regarded excellent in straight soil burial performance.

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[10] Kempton, A.G., H. Maisel, A.M. Kaplan. A Study of the Deterioration of Fungicide-Treated Fabrics in Soil Burial. Textile Res. J. 33, 87 (1963).

[11] Klens, P.F., W.J. Stewart. New Developments in Textile Preservation. Am. Dyestuff Reptr. 46, 346 (1957).

TABLE 3

Rot-resistance of treated fabrics before and after leaching or Weather-Ometer exposure[a]

	Fabric 1[b] Cu-8 treated greige duck		Fabric 3 Cu-Zr treated greige duck		Fabric 4 Cu-Zr treated woven awning duck		Fabric 5 Cu-Zr treated vinyl coated str. broken twill			
Durability tests performed	Breaking str. N	Breaking str. % Ret.	Breaking str. N	Breaking str. % Ret.	Breaking str. N	Breaking str. % Ret.	Breaking str. N	Breaking str. % Ret.	Clark flex. cm	Clark flex. % Gain
Original + 0 days s.b.[c]	592	100	783	100	917	100	556	100	11.0	0.0
Original + 30 days s.b.	592	100	756	97	912	99	552	99	11.1	0.9
Original + 60 days s.b.	490	83	708	90	881	96	516	93	11.2	1.8
Original + 90 days s.b.	352	59	436	56	837	91	494	89	11.5	4.5
Original + 120 days s.b.			200	26	814	89	320	58	11.5	4.5
Leaching + 0 days s.b.			783	100	934	102	552	99	10.8	-1.8
Leaching + 30 days s.b.			721	92	908	97	507	92	10.9	0.9
Leaching + 60 days s.b.			672	86	846	91	222	40	11.0	1.9
Leaching + 90 days s.b.			329	42	805	86	98	18	11.0	1.9
Leaching + 120 days s.b.			d	d	792	85	80	14	11.2	3.7
Weath-Om + 0 days s.b.	578	98	739	94	890	97	596	107	10.9	-0.9
Weath-Om + 30 days s.b.	565	98	708	96	890	100	552	93	11.0	0.9
Weath-Om + 60 days s.b.	521	90	650	88	841	94	231	39	11.2	2.8
Weath-Om + 90 days s.b.	619	107	187	25	814	91	160	27	11.6	6.4
Weath-Om + 120 days s.b.			d	d	770	87	151	25	11.6	6.4

TABLE 3 (Cont'd)

Rot-resistance of treated fabrics before and after leaching or Weather-Ometer exposure[a]

Durability tests performed	Fabric 6 Cu-Zr treated greige duck		Fabric 8 Cu-Zr treated bleached duck		Fabric 9 Cu-Zr treated bleached duck		Fabric 10 Cu-Zr treated bleached duck	
	Breaking str. N	% Ret.	Breaking str. N	% Ret.	Breaking str. N	% Ret.	Breaking str. N	% Ret.
Original + 0 days s.b.[c]	699	100	481	100	490	100	498	100
Original + 30 days s.b.	681	97	472	98	472	96	481	97
Original + 60 days s.b.	659	94	463	96	467	95	467	94
Original + 90 days s.b.	623	89	463	96	454	93	458	92
Original + 120 days s.b.	596	85	454	94	445	91	454	91
Leaching + 0 days s.b.	668	96	481	100	481	98	494	99
Leaching + 30 days s.b.	650	97	476	99	472	98	485	98
Leaching + 60 days s.b.	596	89	463	96	467	97	481	97
Leaching + 90 days s.b.	565	85	436	91	467	97	463	94
Leaching + 120 days s.b.	383	57	432	90	445	93	378	77
Weath-Om + 0 days s.b.	490	70	392	81	365	74	383	77
Weath-Om + 30 days s.b.	472	96	374	95	360	99	383	100
Weath-Om + 60 days s.b.	334	68	356	91	312	85	383	100
Weath-Om + 90 says s.b.	165	34	347	89	312	85	347	91
Weath-Om + 120 days s.b.	107	22	338	86	276	76	338	88

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[a] The percent retention values after leaching + 0 days soil burial and Weather-Ometer exposure + 0 days soil burial are based on the original fabric as received.

[b] Since soil burial harvests of the Cu-8 treated fabric were performed on a weekly basis, the data shown on the 30, 60 and 90 day lines of original fabric represent actually 28, 63 and 84 days of soil burial, respectively; soil burial was terminated at 84 days. The data shown on the 30, 60, **and 90 day lines of** Weather-Ometer exposed fabric represent 28, 56 and 84 days of soil burial, respectively.

[c] **s.b. = soil burial.**

These specimens were destroyed during soil burial.

In general, the microbiological resistance of fabrics treated with copper borate-zirconyl ammonium carbonate was not significantly affected by either leaching or Weather-Ometer exposure. However, the strength data for vinyl coated fabric 5 indicated that the fungal-resistance of this material was markedly reduced following subjection to either of these tests. Loss of rot-resistance after leaching suggests the treatment was not adequately insolubilized in the material. Furthermore, since the loss of microbiological resistance following Weather-Ometer exposure paralleled the loss of resistance after leaching, both failures could be related in cause. The Clark flexibility data for fabric 5 indicated negligible change during soil burial either prior to or following leaching and Weather-Ometer exposure. The data for greige duck fabric 6, a 119-metre test run, also demonstrated a considerable loss of rot-resistance due to Weather-Ometer exposure. The soil burial performance of fabrics 5 and 6 following Weather-Ometer exposure could not be readily related to either the treatment level or fabric preparation. Both fabrics were judged to be acceptably prepared by the processor. The rapid loss of fungal protection following leaching or Weather-Ometer exposure is an important consideration since it indicated a potential weakness of the treatment to environmental stress under use conditions.

Weather-Ometer Exposure

The data in Table 3 indicated that greige duck fabric 3, woven awning duck fabric 4, and vinyl coated fabric 5, lost little breaking strength as a result of Weather-Ometer exposure. However, greige duck fabric 6, the 119-metre test run, retained only 70% of its breaking strength following Weather-Ometer exposure as compared to 98% for copper 8-quinolinolate treated fabric 1 which was prepared from the same base fabric. Since fabric 7, the untreated control, retained 79% of the original breaking strength, the treatment in fabric 6 was not conferring the protection afforded by copper 8-quinolinolate but was possibly catalyzing degradation of the base fabric during Weather-Ometer exposure.

Several fabrics were prepared in an attempt to relate accelerated degradation of fabric and loss of biocidal action during Weather-Ometer exposure with treatment composition. Three different padding solutions of copper borate solubilized in zirconyl ammonium carbonate with varying concentrations of copper and zirconium were prepared and applied to 334 g/m^2 duck, Type III CCC-C-419a. Table 4 demonstrates the effect of Weather-Ometer exposure on the breaking strength of untreated fabric 11 and treated fabrics 8, 9 and 10. Since the treated fabrics had greater breaking strength than the untreated control, the calculation of breaking strength loss following Weather-Ometer exposure in this case was based on the untreated fabric rather than the original treated fabric to avoid possible exaggeration of the actual Weather-Ometer loss. The treatment in fabric 9 appeared to enhance Weather-Ometer degradation of the base fabric. Since the other two treatments did not show effects significantly different from the untreated control during Weather-Ometer exposure, none of these three treated fabrics demonstrated any evidence of protection during exposure.

TABLE 4

Effect of Weather-Ometer exposure on the breaking strength of 334 g/m^2 type III duck, CCC-C-419a,[a] treated with Cu-Zr at three differing treatment levels

Fabric No.	Treatment level[b]		Breaking strength before 100 hours Weather-Ometer exposure	Breaking strength after 100 hours Weather-Ometer exposure	
	% Cu	% ZrO_2	N	N	% Loss[c]
8	0.485	4.27	481	392	12
9	0.755	4.58	490	365	18
10	0.520	1.84	498	383	14
11	none	none	445	392	12

[a] A test fabric designed by Brysson and Markezich (reference 4) to simplify the preparation of ravelled strips for breaking strength measurements.

[b] By analysis.

[c] Based on breaking strength of untreated fabric 11 prior to Weather-Ometer exposure.

The data in Table 3 indicated that fabrics 8 and 10 performed equally well during soil burial following Weather-Ometer exposure, but fabric 9 was not quite as rot-resistant. Following four months of soil burial, Weather-Ometer-exposed fabric 9 suffered a breaking strength loss of 24% as compared to a loss of 14% and 12% by fabrics 8 and 10, respectively. The enhanced degradation of base fabric and the loss of biocidal action could be related to the significantly higher copper content, 0.755%, of fabric 9 relative to fabrics 8 and 10 containing 0.485% and 0.520% copper, respectively. In summarizing the work of previous investigators, Bayley et al.[12] make mention of the very point that inorganic copper compounds tend to accelerate actinic degradation of cotton fabric. However, this alone does not explain the Weather-Ometer deterioration and biocidal action loss of greige fabric 6 (Table 3) which contained 0.522% copper by analysis. Additional studies are required to clarify this point.

Outdoor Exposure at Three Sites

Differentiation between Actinic and Microbiological Degradation

One hundred nineteen metres of 334 g/m^2 greige duck from the Army supply system had been prepared with copper borate-zirconyl ammonium carbonate for full field evaluation in both tropical and temperate climates at two Panama Canal Zone sites and the local Sudbury, Massachusetts site, respectively. Following treatment, greige fabric 6 contained approximately 0.51% copper, 3.07% zirconyl and 0.08% boron on the basis of wet pickup. Subsequent analysis of the fabric, which indicated the copper content to be 0.522%, verified the add-on estimate. Since greige fabric 6 had demonstrated accelerated degradation and loss of biocidal action during Weather-Ometer exposure, this fabric offered the opportunity for comparison of Weather-Ometer findings with outdoor field data.

Differentiation between actinic and microbiological degradation can be made on the basis of the relationship of the cuprammonium fluidity values to the breaking strength loss. Sunlight and airborne acids will increase both the breaking strength loss and the cuprammonium fluidity, but microbial attack affects only the breaking strength of the fabric. However, the degradative contribution of airborne acids is secondary to the photochemical damage caused by actinic rays. Furthermore, since the three exposure sites are not located in industrial or heavily populated areas where traces of acidic-type substances are found, an increase in both the fluidity and the breaking strength loss can be considered primarily due to actinic radiation.

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[12] Bayley, C.H., G.P.F. Rose, J.B. Clifford, J.D. Cooney. The Effect of Noncellulosic Material on the Actinic Degradation of Cotton Fabric. Part I: Some Copper-Containing Fungicides. Textile Res J. 33, 849 (1963).

The mode of deterioration predominant at each of the three outdoor exposure sites is defined by the data obtained from fabric 7, the untreated control. These data are listed in Table 5 and plotted in Figure 1. The cuprammonium fluidity and breaking strength data indicate actinic activity to be the major cause of deterioration at the two open sites. However, samples returned from the Panama open site did exhibit evidence of some staining which was attributed to microorganisms since stains were not observed in fabric 6, the treated cloth, under comparable conditions. None of the untreated samples exposed at the Sudbury, Massachusetts open site exhibited comparable staining. The microbiological attack on the control sample at the Panama open site, however, was not judged to have significantly affected fabric strength. The good agreement of the fluidity vs. breaking strength data between open sites indicates that the untreated control was degraded primarily by actinic energy at the Panama open site. If microorganisms had significantly damaged the control fabric, the data from this site would have assumed a graphical position somewhere between the data for the Sudbury site, which described solar degradation, and the data for the rain forest describing microbiological deterioration. The lack of increase in the fluidity of the untreated fabric exposed in the rain forest despite significant losses in breaking strength is proof that the mode of deterioration at this site is primarily microbiological. The data from the two Panama sites are in agreement with the breaking strength and fluidity data of Howard and McCord[13] who reached similar conclusions regarding their open and shaded sites in Panama.

It was found that typical organic solvents would not extract the highly insolubilized reaction product of copper borate and zirconyl ammonium carbonate from fabric 6. Solvents listed in ASTM D539-53[14] for sample clean-up prior to fluidity tests were tried without success. Rather than analyze all weathered samples on an individual basis, for extraneous non-cellulosic matter, fluidity measurements were performed on the weathered samples without correcting for the weight of cellulose used in the fluidity test. These data were plotted in Figure 2 against breaking strength losses for samples weathered at both open sites and tested for correlation with the data from Figure 1 describing the actinic degradation of untreated cotton. It was anticipated that any significant shortage of cellulose in the sample weight would result in an increased fluidity value. Hence, the observed fluidity value obtained from treated samples could be somewhat higher than values obtained from untreated samples of comparable breaking strength loss. It was evident from the plot that the fluidity data describing the weathering of the treated fabric were generally comparable to the data derived from the untreated control. At comparable breaking strength loss levels, the difference in one per pascal seconds **(1/Pa·s)** between data for treated and untreated specimens was not

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[13] Howard, J.W., **F.A. McCord.** Cotton Quality Study IV: Resistance to Weathering. Textile Res J. <u>30</u>, 75 (1960).

[14] American Society for Testing and Materials, "Annual Book of ASTM Standards", ASTM Standard D539-53, Philadelphia, Pa., American Society for Testing and Materials, 1966.

TABLE 5

Relationship of cuprammonium fluidity to breaking strength loss for fabric 7 (untreated greige duck) exposed at three outdoor exposure sites

	Open site at Sudbury, MA[a]			Open site at Ft. Sherman, Panama[b]			Rain forest at Ft. Sherman, Panama[b]		
Months	Breaking strength		Fluidity	Breaking strength		Fluidity	Breaking strength		Fluidity
exposed	N	% Loss	1/Pa.s	N	% Loss	1/Pa.s	N	% Loss	1/Pa.s
0	650	0	37	650	0	37	650	0	37
2	627	4	98	561	14	138	650	0	47
4	574	12	138	472	27	224	596	8	40
6	503	23	171	436	33	231	369	43	50
8	312	52	295	356	45	287	196	70	53
10	222	66	317	316	51	283	62	90	56
12	165	75	395	285	56	290	31	95	40

[a] Specimens were exposed outdoors from October 1964 to September 1965.

[b] Specimens were exposed outdoors from December 1964 to November 1965.

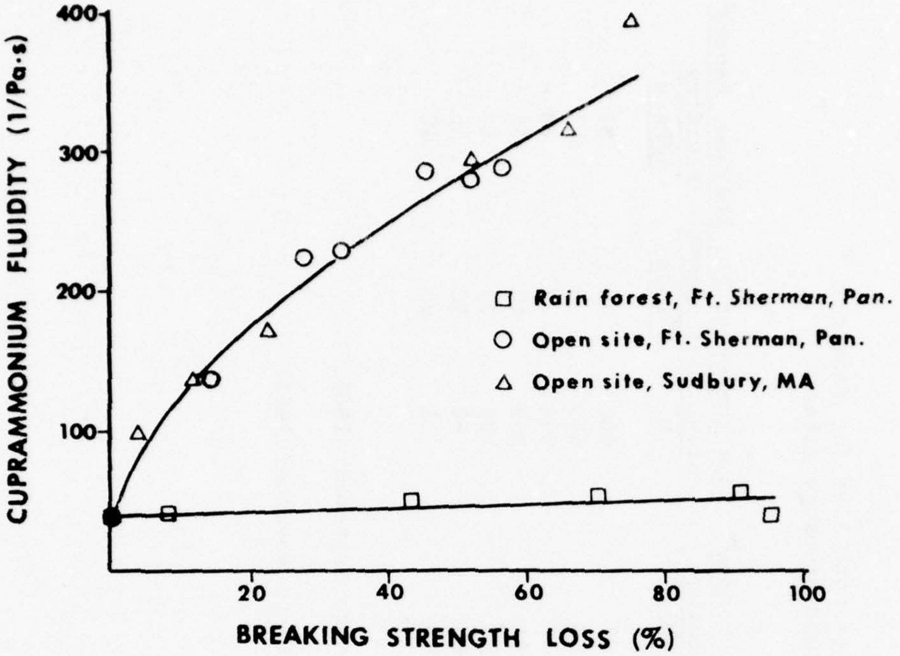

Figure 1 The relationship of cuprammonium fluidity to breaking strength loss for fabric 7 (untreated greige duck) exposed at three outdoor sites for a 12 month exposure period.

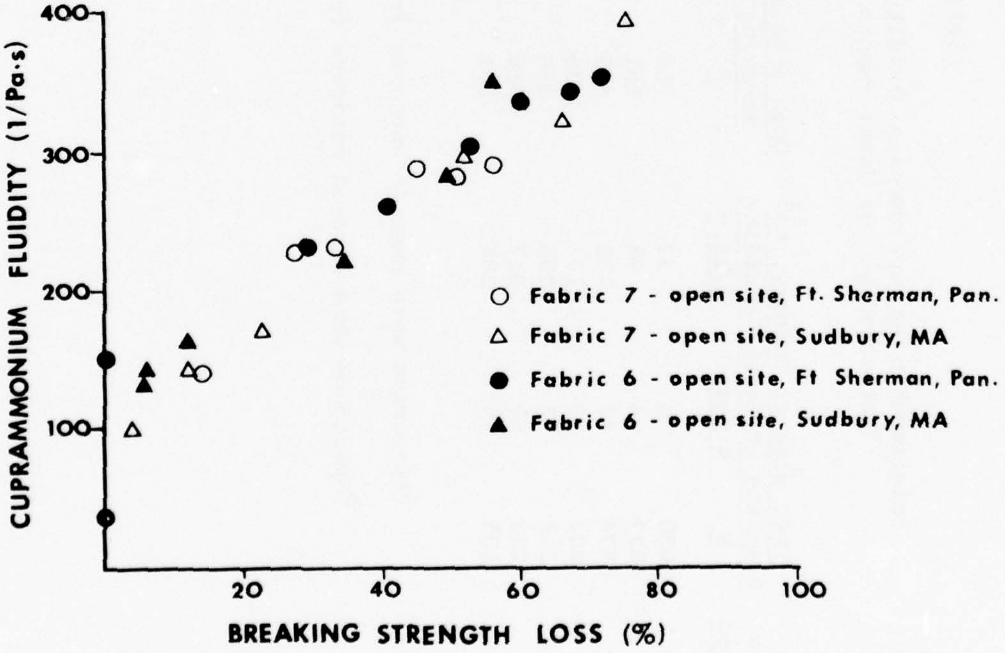

Figure 2 The relationship of cuprammonium fluidity to breaking strength loss for fabric 6 (Cu-Zr treated greige duck) and fabric 7 (untreated greige duck) exposed at two outdoor sites for a 12 month exposure period.

significantly different from the scatter of the values as a group. The largest discrepancy was the difference of 114 l/Pa·s at 0 breaking strength loss which resulted from application of the treatment. Prior to treatment the fluidity of the base fabric was 37 l/Pa·s Following treatment the observed value was 151 l/Pa·s If the 114 l/Pa·s fluidity increase was due to chemical degradation caused by the treatment, a substantial, easily measurable breaking strength loss would have occurred. Since fabric 6 had not lost any breaking strength as a result of treatment, the 114 l/Pa·s increase was primarily due to lack of sample weight correction rather than degradation of the base fabric by the treatment. The lack of such a large discrepancy at other breaking strength loss levels is at least partially due to removal of the add-on during weathering. In fact, the best agreement between both sets of data occurs graphically at the higher breaking strength loss levels. Hence, observed fluidity measurements corresponding to breaking strength losses in excess of approximately 30% are likely to be more accurate than observed fluidity measurements corresponding to smaller breaking strength losses.

In Table 6 the breaking strength and cuprammonium fluidity data from treated fabric 6 are related to months of outdoor exposure at the three sites. Exposure of the fabric to the rain forest environment had little effect on the breaking strength of the test specimens as was anticipated from the laboratory soil burial experiment, and there was no evidence of surface growth. Likewise there was no significant change in the fluidity values of samples exposed at this site. At the Sudbury open site the fluidity and breaking strength values were relatively stable during the first six months, which included the winter season, and relatively volatile during the latter six months that included summer. Degradation at the Panama open site proceeded more regularly between bimonthly harvests.

Influence of Treatment on Weather-Resistance of Base Fabric

Table 7 contains data describing the effect of open site exposure on the breaking strength and cuprammonium fluidity of fabrics 1, 2, 6 and 7. The breaking strength data indicated that copper borate-zirconyl ammonium carbonate treated fabric 6 had been degraded more severely than its control during the first two months of exposure at Panama. Their respective breaking strength retentions after two months of exposure were 71 and 86%. The immediate deterioration of treated fabric 6, at the maximum treatment level, was confirmed by the increase in cuprammonium fluidity. The 79 l/Pa·s increase from 151 to 230 l/Pa·s following two months of exposure at Panama would be a minimum rather than a close estimate of the increase in cuprammonium fluidity. If no treatment was removed during weathering, the observed 79 l/Pa·s increase could be compared directly with the 101 l/Pa·s increase measured in the control. However, 37%, a substantial portion of the treatment, was removed during two months of weathering (Table 8). Therefore, there was a larger cotton fraction in the sample weight of weathered fabric 6 than

TABLE 6

Relationship of cuprammonium fluidity to breaking strength loss for fabric 6 (Cu-Zr treated greige duck) exposed at three outdoor exposure sites

Months Exposed	Open Site at Sudbury, MA[a]			Open Site at Ft. Sherman, Panama[b]			Rain forest at Ft. Sherman, Panama[b]		
	Breaking Strength		Fluidity	Breaking Strength		Fluidity	Breaking strength		Fluidity
	N	% Loss	1/Pa.s	N	% Loss	1/Pa.s	N	% Loss	1/Pa.s
0	659	0	151	659	0	151	659	0	151
2	623	5	133	467	29	230	654	1	113
4	619	6	141	387	41	261	654	1	121
6	583	12	163	307	53	303	623	5	139
8	432	34	219	263	60	335	601	9	151
10	338	49	282	214	68	342	525	20	169
12	294	55	350	187	72	352	525	20	143

[a] Specimens were exposed outdoors from October 1964 to September 1965.

[b] Specimens were exposed outdoors from December 1964 to November 1965.

TABLE 7

Effect of open-site weathering on the breaking strength and cuprammonium fluidity of fabrics 1, 2, 6 and 7

		Open-site at Ft. Sherman, Panama[c]			Open-site at Sudbury, MA[d]		
		Breaking str.		Fluidity	Breaking str.		Fluidity
Fabric	Month exp.	N	% Ret.	1/Pa·s	N	% Ret.	1/Pa·s
	0	650	100	37	650	100	37
	2	561	86	138	627	96	98
Fabric 7[a]	4	472	73	224	574	88	138
untreated	6	436	67	231	503	77	171
greige duck	8	356	55	287	312	48	295
	10	316	49	283	222	34	317
	12	285	44	290	165	25	395
	0	659	100	151	659	100	151
	2	467	71	230	623	95	133
Fabric 6	4	387	59	261	619	94	141
Cu-Zr	6	307	47	303	583	88	163
treated	8	263	40	335	432	66	219
greige duck	10	214	32	342	338	51	282
	12	187	28	352	294	45	350
	0				596	100	
Fabric 2[b]	2				574	96	
untreated	4				454	76	
greige duck	6				316	53	
	8				187	31	
	0				592	100	
Fabric 1	2				619	105	
untreated	4				516	87	
greige duck	6				347	59	
	8				240	41	

[a] Fabric 7, control for fabric 6.

[b] Fabric 2, control for fabric 1.

[c] Specimens were exposed from December 1964 to November 1965.

[d] Fabrics 6 and 7 were exposed outdoors from October 1964 to September 1965 and fabrics 1 and 2 from January 1965 to August 1965.

TABLE 8

Effect of weathering on the Cu and Cu-8 contents of fabrics 6 and 1, respectively

	Fabric 6 Cu-Zr treated greige duck						Fabric 1 Cu-8 treated greige duck	
	Rain forest site at Ft. Sherman Panama[a]		Open site at Ft. Sherman Panama[a]		Open site at Sudbury, MA[b]		Open site at Sudbury, MA[c]	
Months exposed	% Cu	% Ret.	% Cu	% Ret.	% Cu	% Ret.	% Cu-8	% Ret.
0	0.522	100	0.522	100	0.522	100	1.03	100
2	0.461	88	0.331	63	0.422	81	0.87	84
4	0.435	83	0.302	58	0.235	45	0.82	80
6	0.421	81	0.126	24	0.031	6	0.25	24
8	0.402	77	0.048	9	0.014	3	0.02	2
10	0.356	68	0.012	2	0.007	1		
12	0.317	61	0.009	2	0.007	1		

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[a] Specimens were exposed outdoors from December 1964 to November 1965.

[b] Specimens were exposed outdoors from October 1964 to September 1965.

[c] Specimens were exposed outdoors from January 1965 to August 1965.

in nonweathered fabric 6. The net effect would be to lower the fluidity of the weathered fabric relative to the nonweathered fabric and thus to reduce the extent of fluidity increase. Since treated fabric 6 had apparently not been degraded on application of the treatment, it can be reasoned that its true fluidity in the absence of all treatment should be approximately 37 1/Pa·s the fluidity of the base fabric. Therefore, if treated fabric 6 had immediately lost all treatment on weathering, its fluidity could be calculated directly by basing the data from treated weathered samples on the untreated nonweathered control. But since the sample actually retained 63% of its copper content after 2 months of Panama open site exposure, 230 minus 37 or 193 1/Pa·s must be a maximum estimate of the fluidity increase. The best estimate, of course, lies between the extreme values of 79 and 193 1/Pa·s corresponding to 100 and 0% treatment retention, respectively, of treated fabric 6 after two months of Panama open site exposure. When the Panama exposure was terminated at 12 months, there was only 2% of the original copper content remaining in the fabric. Therefore, if the 12 months weathered sample and its control can both be based as a reasonable approximation on the untreated nonweathered control, the treated fabric had been more severely degraded than its control because the terminal values were 352 and 290 1/Pa·s respectively. The breaking strength data also indicated more degradation in the treated fabric since the treated fabric retained only 28% of its strength relative to the 44% retention measured in the control. The Panama exposure data, in effect, substantiated the accelerated Weather-Ometer degradation of the treated fabric previously discussed.

Table 7 also contains the data obtained from exposure at the Sudbury site. The breaking strength and fluidity data indicated that the copper borate-zirconyl ammonium carbonate treatment had protected the base fabric from actinic degradation. There was less breaking strength loss in the treated fabric than in the control throughout the 12 months exposure. The cuprammonium fluidity data supported the breaking strength data, in general. Lack of significant change in the fluidity data of the treated fabric for the first six months of exposure was probably due to some degree of protection afforded by the treatment coupled with reduced seasonal radiation at Sudbury (Appendix). Apparently two opposing effects were in approximate balance; i.e., fluidity decrease due to removal of the treatment and fluidity increase due to actinic degradation. After six months the copper content of the treated fabric was reduced from 0.522% to 0.031%. As the loss of treatment stabilized and the seasonal radiation increased, the fluidity values began to increase. When the exposure was terminated at 12 months, the treated fabric was less degraded than the control. Consequently, there was no evidence in the Sudbury exposure data to confirm the accelerated rate of deterioration experienced by the base fabric during Weather-Ometer exposure or during Panama open site exposure. The results from copper 8-quinolinolate treated fabric 1 indicated that it lost less breaking strength, in general, than its control during exposure at the Sudbury site. Hence, the breaking strength data were in agreement with Weather-Ometer findings which also indicated less breaking strength loss in the copper 8-quinolinolate treated fabric than in the untreated control.

Although the copper borate-zirconyl ammonium carbonate treatment in fabric 6 imparted protection during the outdoor exposure at Sudbury, the Panama open site exposure was the more valid test of the performance of this treatment during severe actinic irradiation. The copper content of treated fabric 6 was reduced from 0.522% to 0.031% between October 1964 and April 1965 at Sudbury (Table 8). Consequently, the treatment was essentially removed prior to the more rigorous test of spring and summer conditions. The climatological data for Sudbury, MA, which are tabulated in the Appendix, indicate spring and summer to be the seasons of the greatest total solar radiation, since the months from April to August were the only months to supply monthly total radiation in the 5×10^8 to 7×10^8 joules per metre^2 range. Spring and summer are also the seasons of severe actinic degradation. The data from the fabrics exposed at the Sudbury site indicate they were more severely degraded during these seasons. Unfortunately there were no Panama open site data available for copper 8-quinolinolate treated fabric 1. However, chemical data obtained from fabric 1 following weathering at Sudbury indicated that 80% of the fungicide content was present at the beginning of the four month interval from May to August 1965. Hence, fabric 1 did not lose much of its copper 8-quinolinolate content until the months of increased seasonal radiation.

Durability of Treatment and Stability of Biological Activity

Table 8 depicts the effect of weathering on the copper and copper 8-quinolinolate content of fabrics 6 and 1, treated with copper borate-zirconyl ammonium carbonate and copper 8-quinolinolate, respectively. The persistence of copper 8-quinolinolate during weathering was determined by a chemical method which assayed the entire molecule (reference 7), and the persistence of treatment in fabric 6 was gauged from the copper content of the fabric (reference 6). The presence of copper borate-zirconyl ammonium carbonate treatment could also be verified visually by the bluish tint of the treated fabric. The tint was easily discernible at levels greater than 0.1% copper. The slow loss of this treatment during exposure at the rain forest location supported the data in Table 3 which had been obtained from soil burial of the leached specimens. These data had indicated the leached specimens to be nearly as rot-resistant as the **nonleached** specimens. However, exposure at either open site accelerated the rate of copper loss from fabric 6 which had been treated with copper borate-zirconyl ammonium carbonate. Furthermore, it appears that the less severe climatological conditions at Sudbury during the fall and winter seasons were also sufficient to cause a severe loss of treatment.

Although the outdoor exposure of fabrics 1 and 6 which were begun January 1965 and October 1964, respectively, were parts of separate studies, it was of interest to compare the persistence of the two treatments in relation to the differences in climatological conditions.

During the first four months of weathering, the loss of copper 8-quinolinolate from fabric 1 was gradual; the severest loss occurred during the next four months interval which included the months from May to August 1965. The severest loss of copper from fabric 6, which had been treated with copper borate-zirconyl ammonium carbonate, occurred during the six month interval from October 1964 to March 1965. It is evident from the data contained in Table 8 that a larger percentage of the copper 8-quinolinolate treatment persisted during 8 months of outdoor exposure at Sudbury.

Table 9 lists the precipitation and total solar radiation received by fabrics 1 and 6 during eight months of outdoor exposure at Sudbury. The total precipitation received by the two fabrics was relatively comparable. However, fabric 1 received the greater total radiation 39% more joules per metre^2 than fabric 6. It was also noted that fabric 6 lost most of its copper content during the months of lesser total radiation from October to March. In contrast, fabric 1 did not lose much copper 8-quinolinolate until the months of severe total radiation from May to August, which are also months of severe actinic degradation. Although there was no facility available for direct measurement of the actinic portion of the total radiation, the months both fabrics were exposed outdoors can be compared. Months common to both fabrics included the interval from January 1965 to May 1965. In addition, fabric 1 was exposed June, July, and August 1965. By contrast, fabric 6 was exposed October, November, and December 1964. Hence, it is likely that fabric 1 was also exposed to a larger dosage of actinic radiation. In summary, the available data indicate that not only was copper 8-quinolinolate more durable than the copper borate-zirconyl ammonium carbonate treatment to weathering but more durable despite exposure of the copper 8-quinolinolate treated fabric to a larger dose of total and quite likely actinic radiation as well.

Table 10 contains data describing the rot-resistance of fabrics 1 and 6 before and after exposure at the two open sites. Soil burial data from Table 3 were included to demonstrate the rot-resistance prior to weathering. Fabric 1, which originally contained 1.03% copper 8-quinolinolate, did not become susceptible to microorganisms until it was reduced to 0.02% after eight months of weathering. In contrast, fabric 6 retained little microbiological resistance after four months of weathering at Sudbury, although the copper content of the fabric had only been reduced from 0.522% to 0.235%. The rapid loss of biocidal action and copper content during open site exposure but not rain forest exposure indicated that the treatment in fabric 6 was presumably unstable to actinic irradiation. However, the rot-resistance of fabric 6 after Panama open site exposure was significantly better than the microbiological resistance remaining after Sudbury exposure. In fact, fabric 6 contained only 0.048% to 0.012% copper when it became susceptible to microorganisms after eight to ten months of exposure at this site. But the better soil burial performance following exposure at this site might not have been strictly due to the treatment, because the treatment rapidly lost biocidal

TABLE 9

Comparison of the precipitation and total solar radiation received by fabrics 1 and 6 during 8 months of outdoor exposure at Sudbury, MA

	Fabric 1 Cu-8 treated greige duck			Fabric 6 Cu-Zr treated greige duck	
Month & year	Precipitation cm	Total radiation* J/m^2	Month & year	Precipitation cm	Total radiation* J/m^2
Jan 65	7	2.0×10^8	Oct 64	5	3.4×10^8
Feb 65	9	2.8×10^8	Nov 64	8	2.2×10^8
Mar 65	6	3.8×10^8	Dec 64	11	1.4×10^8
Apr 65	7	5.1×10^8	Jan 65	7	2.0×10^8
May 65	8	6.8×10^8	Feb 65	9	2.8×10^8
June 65	7	6.6×10^8	Mar 65	6	3.8×10^8
Jul 65	2	6.7×10^8	Apr 65	7	5.1×10^8
Aug 65	7	5.5×10^8	May 65	8	6.8×10^8
	53	3.9×10^9		61	2.8×10^9

*Short wave vertical Eppley (2 metre).

TABLE 10

Breaking strength (N) of fabrics 6 and 1 following soil burial of open-site weathered specimens

Fabric 6 Cu-Zr treated greige duck Months exposed Ft. Sherman, Panama[a]	Followed by soil burial months 0	1	2	3	Months exposed Sudbury, MA[b]	Followed by soil burial months 0	1	2	3	Fabric 1 Cu-8 treated greige duck Months exposed Sudbury, MA[c]	Followed by soil burial months 0	1	2	3
0	699	681	659	623	0	699	681	659	623	0	592	592	490	352
2	467	467	418	414	2	623	507	191		2	619	507	619	423
4	387	392	369		4	619	93			4	516	441	312	71
6	307		187							6	347	271		
8	263	156								8	240	80		
10	214	67												

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[a] Specimens exposed outdoors from December 1964 to November 1965.

[b] Specimens exposed outdoors from October 1964 to September 1965.

[c] Specimens exposed outdoors from January 1965 to August 1965.

action following milder conditions at Sudbury. The difference in microbiological resistance following exposure at the two sites cannot be resolved on the basis of the available data. Complex interactions between treatment, fabric and environment are probably responsible for this difference between sites. Clearly, an analytical method specific for the entire molecule would have provided more information regarding the stability of the treatment than the chemical test employed. Hence, in the absence of a specific chemical test, the biological test provided essential data not obtainable by chemical means.

Zirchrome

Rot-Resistance

Table 11 contains the results obtained from laboratory tests performed on osnaburg fabrics treated by the Zirchrome Process. Cuprammonium treated osnaburg fabric 18 is included as a basis for evaluating the data obtained from the Zirchrome treated fabrics. At the time when these tests were performed, the cuprammonium salts treatment was extensively used for the protection of cotton osnaburg sandbags. The data for cuprammonium treated fabric 18 and Zirchrome treated fabric 19 each represent the average of two sets of independent data obtained under comparable conditions. The other four fabrics are a separate group previously tested and only one set of results was obtained from each of these fabrics. The soil burial data from the cuprammonium treated fabric indicated that it lost 11% breaking strength after three weeks of soil burial. In contrast, copper 8-quinolinolate treated fabric 1 (Table 3) did not lose any strength during the first 30 days of soil burial. As the cuprammonium treated fabric rotted, discolored areas retaining little to no strength developed. This was evident after only three weeks of soil burial. All other treated fabrics discussed in this report were more uniform in this respect. The visual appearance of the fabric after soil burial and the initial breaking strength loss of 11% together suggested that the treatment on the fabric was spotty or uneven. After three months of soil burial, the breaking strength losses in copper 8-quinolinolate treated fabric 1 and cuprammonium treated fabric 18 were the same.

Greige fabric 12 and scoured fabric 15 were prepared by one set of experimental conditions and greige fabric 13 and scoured fabric 16 by another. The results indicate that the scoured fabric for each set of experimental conditions was more rot-resistant than its greige counterpart. This was anticipated. Following soil burial, the breaking strength losses of scoured fabrics 15 and 16 were comparable to the losses measured in the cuprammonium treated fabric. Scoured fabric 19, which was evaluated in the same study as the cuprammonium treated fabric, did not perform as well. However, the cuprammonium treated fabric was really no better, functionally speaking, because the discolored, rotted-out areas could prematurely leak sandbag filling material.

TABLE 11

Breaking strength of treated osnaburg fabrics after soil burial of original, leached and Weather-Ometer exposed specimens[a]

Durability tests performed	Fabric 12[b] Zirchrome treated greige osnaburg		Fabric 13[b] Zirchrome treated greige osnaburg		Fabric 15[b] Zirchrome treated scoured osnaburg		Fabric 16[b] Zirchrome treated scoured osnaburg		Fabric 18 cuprammonium treated osnaburg		Fabric 19 Zirchrome treated scoured osnaburg	
	N	% Ret.	N	% Ret.	N	% Ret.	N	% Ret.	N	% Ret.	N	% Ret.
Original + 0 wk. s.b.	383	100	476	100	338	100	405	100	392	100	343	100
Original + 3 wk. s.b.	294	77	352	74	316	93	352	87	347	89	298	87
Original + 6 wk. s.b.	267	70	191	40	285	84	276	68	338	86	218	64
Original + 9 wk. s.b.	22	6	13	3	27	8	18	4	258	66	165	48
Original + 12 wk. s.b.	-	-	-	-	-	-	-	-	231	59	40	12
Leached + 0 wk. s.b.	356	93	418	88	320	95	360	89	427	109	329	96
Leached + 3 wk. s.b.	222	62	276	66	303	95	214	59	343	80	227	69
Leached + 6 wk. s.b.	49	14	80	19	116	36	138	38	267	63	165	50
Leached + 9 wk. s.b.	9	3	40	10	18	6	18	5	191	45	165	50
Leached + 12 wk. s.b.	-	-	-	-	-	-	-	-	147	34	22	7
Weath-Om + 0 wk. s.b.	312	81	383	80	289	86	352	87	360	92	329	96
Weath-Om + 3 wk. s.b.	222	71	303	79	276	96	249	71	294	82	249	76
Weath-Om + 6 wk. s.b.	44	14	129	34	249	86	178	51	263	73	160	49
Weath-Om + 9 wk. s.b.	9	3	31	8	18	6	22	6	254	71	160	49
Weath-Om + 12 wk. s.b.	-	-	-	-	-	-	-	-	174	48	76	23

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[a] The percent retention values after leaching + 0 days soil burial and Weather-Ometer exposure + 0 days soil burial are based on the original fabric as received.

[b] Soil burial harvests of fabrics 12, 13, 15, and 16 were performed on a monthly basis. The data shown on the 3, 6 and 9 week lines actually represent 1, 2, and 4 months of soil burial, respectively. Soil burial was terminated at 4 months.

Fabrics treated by the Zirchrome Process were not as rot-resistant as the copper borate-zirconyl ammonium carbonate treated fabrics previously discussed. In addition, the Zirchrome treated fabrics generally lost some microbiological resistance after leaching unlike the copper borate-zirconyl ammonium carbonate treated fabrics. Fabric scouring apparently did not reduce the loss of microbiological resistance due to leaching because scoured fabrics 15 and 16 were not consistently better than greige counterparts 12 and 13. In general, Weather-Ometer exposure caused a smaller loss of rot-resistance than did leaching. Again, there was no substantial difference between scoured and greige fabrics. Cuprammonium treated fabric 18 also lost some microbiological resistance as a result of leaching and Weather-Ometer exposure.

Weather-Ometer Exposure

Table 12 demonstrates the effect of Weather-Ometer exposure on the breaking strength of fabrics treated by the Zirchrome Process. Cuprammonium treated fabric 18 was also included although there was no control available for it. It lost only 8% breaking strength as a result of 100 hours of Weather-Ometer exposure. The Zirchrome treated fabrics unlike the copper borate-zirconyl ammonium carbonate treated fabrics listed in Table 4 did not consistently have a greater breaking strength than their respective controls. Hence, all calculations of breaking strength loss were based on the original treated fabric rather than on the untreated fabrics. The percentages as calculated indicated that the breaking strength losses following 100 hours of Weather-Ometer exposure were approximately the same for the greige fabrics whether Zirchrome treated or not. However, Zirchrome treated scoured fabrics 15 and 16 lost less breaking strength due to Weather-Ometer exposure than scoured control 17. The same was true for Zirchrome treated scoured fabric 19 relative to scoured control 20.

Hence, the results from the scoured fabrics supported the contention that the Zirchrome finish improved the weather-resistance of cotton fabric. In no instance was there any evidence of accelerated Weather-Ometer degradation of the base fabric in the presence of the Zirchrome treatment.

Outdoor Exposure

Table 13 contains the results obtained from fabrics weathered at the Sudbury open site. This is the only case in which data from cuprammonium treated fabric 18 and Zirchrome treated fabric 19 plus its control represent one set of results rather than two averaged together. These results indicated that cuprammonium treated fabric 18 and Zirchrome treated fabric 19 retained 41% and 58% of their breaking strength, respectively, following 10 months of outdoor exposure. After the same exposure conditions the control for Zirchrome treated fabric 19 retained only 16% of its breaking strength. Hence, the outdoor exposure data indicated

TABLE 12

Effect of Weather-Ometer exposure on the breaking strength of osnaburg fabric before and after treatment with Zirchrome or cuprammonium

Fabric no.	Fabric description	Breaking strength before 100 hours of Weather-Ometer exposure	Breaking strength after 100 hours of Weather-Ometer exposure	
		N	N	% Loss
12	Zirchrome treated greige osnaburg	383	312	19
13	Zirchrome treated greige osnaburg	476	383	20
14	Untreated greige osnaburg (control for fabrics 12 & 13)	409	338	17
15	Zirchrome treated scoured osnaburg	338	289	14
16	Zirchrome treated scoured osnaburg	405	352	13
17	Untreated scoured osnaburg (control for fabrics 15 & 16)	347	271	22
18	Cuprammonium treated osnaburg	392	360	8
19	Zirchrome treated treated scoured osnaburg	343	329	4
20	Untreated scoured osnaburg (control for fabric 19)	338	312	8

TABLE 13

Effect of open-site weathering at Sudbury, MA on the breaking strength of fabrics 18, 19, and 20*

Months exposed	Fabric 18 Cuprammonium treated osnaburg		Fabric 19 Zirchrome treated scoured osnaburg		Fabric 20 Untreated scoured osnaburg (control for Fabric 19)	
	N	% Ret.	N	% Ret.	N	% Ret.
0	378	100	338	100	338	100
2	298	79	276	82	245	72
4	227	60	240	71	138	41
6	191	51	218	64	89	26
8	156	41	187	55	67	20
10	156	41	196	58	53	16

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*Specimens were exposed outdoors from April 1968 to January 1969.

that the Zirchrome finish protected the base fabric from actinic degradation and thus supported comparable Weather-Ometer findings obtained from scoured osnaburg. However, the results obtained from copper borate-zirconyl ammonium carbonate treated fabric 6 previously discussed demonstrated that tropical exposure should be the ultimate test for a treatment destined to be used in that environment. Hence, a final judgement on the merits of the Zirchrome finish would have to depend on the outcome of such tests although there were no indications from the available data that the treatment would perform other than satisfactorily in a tropical environment.

CONCLUSIONS

The copper borate-zirconyl ammonium carbonate treatment provides good rot-resistance relative to copper 8-quinolinolate. In the fabrics tested the microbiological protection was at least equal to but generally superior to the protection afforded by the copper 8-quinolinolate treated reference fabric. In general, the microbiological resistance of fabrics treated with copper borate-zirconyl ammonium carbonate was not significantly affected by either leaching or Weather-Ometer exposure. However, several exceptions existed, and an attempt to reconcile the accelerated degradation of fabric and loss of biocidal action during Weather-Ometer exposure with treatment composition was not successful.

One of the erratic fabrics was the 119-metre test run prepared for full field evaluation in both tropical and temperate climates. The tropical exposure data substantiated the accelerated fabric degradation which had occurred during Weather-Ometer exposure, but the temperate exposure data did not. Nevertheless, the fabric specimens exposed in the temperate environment did lose substantial biological activity in support of similar findings following Weather-Ometer exposure, although the results of chemical analysis indicated that a considerable portion of the copper content had not been removed. In contrast, the available data indicated that copper 8-quinolinolate was more durable to outdoor exposure at this site and provided microbiological protection until the treatment was essentially removed. Inexplicably the copper borate-zirconyl ammonium carbonate treated fabric retained better biolgical activity following exposure to the harsher tropical environment.

The microbiological protection afforded by the Zirchrome Process was inferior to the protection provided by the copper borate-zirconyl ammonium carbonate treatment. Also the protection was not as durable to the effects of Weather-Ometer exposure and particularly leaching. Weather-Ometer and outdoor exposure data from the temperate site indicated that the Zirchrome finish improved the weather-resistance of scoured osnaburg, and there was no evidence of accelerated degradation in the presence of the finish. However, Zirchrome treated greige fabrics did not perform as well as Zirchrome treated scoured fabrics either in soil burial or Weather-Ometer tests.

With one exception, the Zirchrome treatment rendered scoured osnaburg as rot-resistant as the fabric treated with cuprammonium salts. However, the protection provided by the cuprammonium treatment was also not durable to the effects of Weather-Ometer exposure and leaching. The cuprammonium treatment was judged more uneven that the other treatments in the fabrics tested because of the early breaking strength loss during soil burial and rotted-out, discolored areas which could prematurely leak filling material. On the other hand, the Zirchrome treatment could not be considered a suitable substitute because of the large tearing strength loss resulting from treatment.

In view of the above deficiencies and/or inconsistencies in behavior to environmental stress, neither zirconium-containing finish can be presently recommended as preferable to military fungicides in current use for the preservation of cotton fabric.

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APPENDIX

Climatological data from Shelter Point, Fort Sherman, Panama

		Average ambient temperature °C			Average relative humidity %			Total solar radiation[a] J/m^2	Wind[b]		
	Precip.	Daily			Daily					Average	Maximum
Mo. & yr.	cm	max.	min.	monthly	max.	min.	monthly	monthly	Prev. dir.	hrly. speed m/s	hrly. speed m/s
Dec 64	13	29	24	26	99	78	91	6.2×10^8	NE	4	10
Jan 65	13	28	24	26	94	72	83	5.9×10^8	NE	6	10
Feb 65	3	29	25	26	97	73	87	6.0×10^8	NNE	5	10
Mar 65	0	30	25	27	96	66	85	7.3×10^8	NE	5	8[c]
Apr 65	5	31	25	28	89	66	80	7.3×10^8	NE	5	8
May 65	28	31	24	28	99	75	89	5.6×10^8	NE	3	8[c]
Jun 65	21	31	25	27	99	76	90	4.3×10^8	ENE	3	8
Jul 65	28	31	26	28	96	75	88	5.8×10^8	ENE	4	7
Aug 65	50	31	24	27	99	77	93	4.4×10^8	WNW	3	5
Sep 65	33	31	24	27	100	73	91	4.9×10^8	SSW	2	8
Oct 65	49	31	25	28	100	74	92	4.8×10^8	SSW	3	9[c]
Nov 65	68	30	25	27	100	83	95	3.8×10^8	WNW	3	8[c]

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[a] Short wave vertical Eppley (2 metre).

[b] Wind speed at height of 4 metre above ground.

[c] Occurred more than once during month.

Climatological data from Sudbury, MA

		Average ambient temperature °C			Average relative humidity %			Total solar radiation (J/m^2)[b]	Wind[c]		
		Daily			Daily					Average	Maximum
Mo. & yr.	Precip. cm	max.	min.	Monthly	max.	min.	monthly	monthly	Prev. dir.	hrly. speed m/s	hrly. speed m/s
Oct 64	5	19	1	10	97	38	68	3.4×10^8	NW	1	5
Nov 64	8	13	-3	5	95	43	70	2.2×10^8	NW	1	6[d]
Dec 64	11	4	-7	-1	94	65	80	1.4×10^8	N	2	8
Jan 65	7	36	-11	-5	87	44	65	2.0×10^8	N	2	7
Feb 65	9	5	-10	-2	87	41	58	2.8×10^8	W	2	6
Mar 65	6	8	-4	2	92	42	67	3.8×10^8	NW	2	7
Apr 65	7	14	-1	6	92	38	65	5.1×10^8	N	2	6
May 65	8	26	7	18	94	36	65	6.8×10^8	NW	2	5
Jun 65	7	28	9	19	96	41	70	6.6×10^8	NW	1	5
Jul 65	2	30	11	21	100	48	71	6.7×10^8	SSW	1	3[d]
Aug 65	7	30	12	21	100	48	74	5.5×10^8	SSW	1	3[d]
Sep 65	6	26	8	17	100	57	75	4.1×10^8	N	1	3

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[a] Includes snow converted to cm of rainfall.

[b] Short wave vertical Eppley (2 metre).

[c] Wind speed at height of 2 metre above ground.

[d] Occurred more than once during month.

Climatological data from Skunk Hollow, Fort Sherman, Panama

Mo. & yr.	Open rainfall at clearing cm	Rainfall under canopy cm	Average ambient temperature °C Daily max.	Average ambient temperature °C Daily min.	Average ambient temperature °C monthly	Average relative humidity % Daily max.	Average relative humidity % Daily min.	Average relative humidity % monthly
Dec 64	13	13	26	23	24	*	*	*
Jan 65	15	15	26	23	24	100	83	94
Feb 65	4	4	26	23	25	100	82	93
Mar 65	0	0	28	24	26	92	72	83
Apr 65	6	5	28	23	26	92	67	80
May 65	28	24	28	24	26	100	84	94
Jun 65	18	11	28	24	26	100	93	98
Jul 65	23	19	28	25	27	99	87	95
Aug 65	49	51	26	21	23	100	91	96
Sep 65	33	31	27	24	26	100	90	97
Oct 65	55	54	27	24	25	100	91	98
Nov 65	70	68	26	23	25	100	96	99

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*Less than 75% of data available.