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TECHNICAL REPORT

70-62-PR

BIODEGRADATION OF SHOEBOARD AND LEATHERBOARD FOOTWEAR COUNTER MATERIALS

by

Marvin Greenberger, Theodore M. Wendt and Arthur M. Kaplan

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FOREWORD

This report is an evaluation of the microbiological resistance of shoeboard and leatherboard footwear counter materials, treated and untreated. The study was conducted to determine the rot-resistance of counters fabricated from either leatherboard or shoeboard stock and the effectiveness of treatment with certain fungicides.

We acknowledge the efforts of Dr. Ludwig Seligsberger and Mr. Richard F. Lacerte of the NLABS Leather Technology Group for supplying some of the test data. Thanks are also due to Mr. John A. Ursillo for performing some of the tests and for compilation of the data.

The work was accomplished under project number 1J062110A031.

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ABSTRACT

Fungicide-treated shoeboard and leatherboard footwear counter materials with suitable controls were evaluated for rot-resistance in the soil burial test. Copper 8-quinolinolate, sodium pentachlorophenate and zinc dimethyldithiocarbamate were the fungicides evaluated for use in shoeboard. Paranitrophenol was evaluated for use in leatherboard. Copper 8-quinolinolate (0.5 to 1.0 percent) and sodium pentachlorophenate (1 to 2 percent) effectively inhibited microbiological degradation of shoeboard which is basically a susceptible composite material. However, the effectiveness of sodium pentachlorophenate is not relevant because of toxicity considerations and because it was incompatible with the shoeboard matrix, showing a tendency to tender the cellulosic portion of the shoeboard and migrate to the surface. Leatherboard, because of its inherent resistance to microbiological deterioration, is a more desirable counter material from the biological point of view than fungicide-treated shoeboard which will eventually deteriorate after a suitable induction period.

BIODEGRADATION OF SHOEBOARD AND LEATHERBOARD
FOOTWEAR COUNTER MATERIALS

1. Introduction

The military specification for footwear counters, (MIL-C-41814B), contains the minimum performance standards to which all counters for military footwear must comply. Footwear manufacturers can select counters fabricated from either leather, leatherboard or shoeboard stock providing the counters meet minimum performance requirements.

Prior to the availability of suitable alternative materials, military footwear counters were made solely from leather stock. Advances in the technology of polymeric binders made possible the fabrication of lower cost counter material from reclaimed cellulosic or leather fibers termed shoeboard and leatherboard, respectively. Although many mechanical properties of these lower cost materials are known to be superior to those of natural leather, there was no information available regarding their rot-resistance. Therefore, the suitability of these composite-board materials for use in footwear intended for tropical service was unknown.

A preliminary 8-week soil burial screening program was undertaken to evaluate the microbiological resistance of representative shoeboard samples from several manufacturers. The preliminary soil burial data indicated that shoeboard was susceptible to significant microbiological deterioration during the first 2 weeks of exposure. Apparently, the susceptible cellulosic fibers in the shoeboard matrix were not protected by the polymeric styrene-butadiene binder in which they were imbedded.

As a result, the current study was undertaken to evaluate the effectiveness and compatability of several fungicides in a shoeboard matrix comprised of cellulosic fibers and a styrene-butadiene binder. Because leather is basically a much more biologically resistant material than cellulose, fungicide-treated and untreated samples composed of leather fibers in a natural rubber binder were included for purposes of comparison.

This report contains comparative soil burial data, before and after leaching, from treated and untreated shoeboard and leatherboard specimens. The first section of the results includes breaking strength data from the soil buried strips demonstrating the relative effectiveness of certain fungicides. The second section contains single hole stitch tear strength data demonstrating the effectiveness of the fungicides in the finished counter. Finally, the last section contains the data from accelerated heat-storage tests indicative of potential degradative interaction between the treatment and the shoeboard matrix.

The preliminary screening program and the current study were cooperative efforts of the National Shoeboard Conference, the NLABS Leather Technology Group, and the NLABS Applied Microbiology Group. Fungicide-treated and untreated shoeboard samples were provided by members of the National Shoeboard Conference. The Applied Microbiology Group conducted soil burial exposure of shoeboard and leatherboard samples, heat-ageing tests of treated and untreated samples, physical testing of shoeboard and leatherboard strip and counter specimens, chemical analyses to determine level of fungicide treatment in treated samples and compiled and analyzed the data. The Leather Technology Group performed some physical testing of shoeboard strip specimens and all physical testing of shoeboard counters which had been exposed to soil burial. Leatherboard samples used in the study were provided by Ferrersflex Corp. of America.

2. Materials and Methods

a. Materials

Colonial Board Sample No. NP-550 was one of the untreated shoeboard samples screened in the preliminary study. Since it was typical of the preliminary samples evaluated, it was selected as a standard material for treatment with several cellulosic preservatives to assess the relative value of each biocide treatment.

The Applied Microbiology Group recommended use of copper 8-quinolinolate in 2 concentrations, 0.25 percent and 0.50 percent, and secondarily suggested a trial using lauryl pentachlorophenate. Copper 8-quinolinolate was recommended because of its effectiveness at low concentrations, relative non-toxicity to humans, and resistance to leaching. Lauryl pentachlorophenate was suggested for trial because of possible cost advantages over copper 8-quinolinolate and, because of the nature of the shoeboard composite, there was a possibility that it would be suitable for this use even though it has not been recommended for other military applications.

After treatment, some of the 3/32 inch thick boards were cut into 1/2 inch x 6 inch strips so that the directional fibers characteristic of shoeboard were parallel to the long dimension. The rest were fabricated into experimental counters to simulate the finished product. The leatherboard data were obtained from untreated and p-nitrophenol-treated Ferrersflex FC-130 leatherboard which has nondirectional fibers in the matrix.

The p-nitrophenol treatment applied to the leatherboard was not recommended by the Applied Microbiology Group because leatherboard should be considered a material distinctly different from leather, which is commonly treated with p-nitrophenol. Chemical and physical characteristics of leather which make it suitable for treatment with p-nitrophenol are lacking or vastly altered in the leatherboard. The p-nitrophenol treatment given the leatherboard was applied on the recommendation of others concerned, because of the presence of leather fiber in the leatherboard composite. The leatherboard data were obtained only from 1/2 inch x 6 inch cut strips. None of the leatherboard was fabricated into counters or tested in the form of counters.

Table I lists the fungicides evaluated in this study. Sodium pentachlorophenate was evaluated rather than lauryl pentachlorophenate recommended by the Applied Microbiology Group, and zinc dimethyldithiocarbamate was included at the request of shoeboard industry representatives. Since analytical data were available for all the treated samples, the treatment levels listed in Table I were expressed as analytical concentrations rather than less precise nominal concentrations. These concentrations should not be interpreted as recommended treatment levels. Normally higher concentrations than those listed in Table I are required at application to achieve these add-on levels. The only outright application failure occurred during the preparation of NP-550 shoeboard to contain 1 percent of a fungicide preparation composed of at least 90 percent zinc dimethyldithiocarbamate. Chemical analysis for zinc concentration indicated that the shoeboard contained 0.5 percent of the zinc dimethyldithiocarbamate preparation after treatment.

b. Methods

The fungicide concentrations listed in Table I were determined by spectrophotometric methods for the quantitative analysis of copper 8-quinolinolate, sodium pentachlorophenate and zinc dimethyldithiocarbamate. Copper 8-quinolinolate and zinc dimethyldithiocarbamate concentrations were determined by wet digestion of samples using a 50:50 mixture of concentrated nitric and sulfuric acids followed by atomic absorption analysis for copper and zinc concentrations, respectively. The concentration of each fungicide was then calculated from the percent of the metal in the respective fungicides. The copper 8-quinolinolate concentrations were confirmed by subsequent colorimetric analysis for the 8-quinolinol moiety using the ferric ion method (Haskins and Luttermoser, 1951). Sodium pentachlorophenate concentrations in shoeboard samples were colorimetrically determined by reacting pentachlorophenol with 4-aminoantipyrine and potassium ferricyanide according to Gottlieb and Marsh (1946).

Leaching and soil burial testing were conducted in accordance with textile Methods 5830 and 5762, respectively, of Federal Test Method Standard No. 191. Cut strips were buried horizontally, and counters were buried resting on their bases.

Accelerated heat-storage tests were performed in a dry oven at either 130°F or 212°F. The breaking strengths of cut strips were measured on an

TABLE I

Concentrations of Industrial Fungicides Evaluated

No.	Material	Fungicide	Concentration*
1.	Shoeboard NP-550-MD	ZnD** (zinc dimethyldithiocarbamate)	0.5%
2.	"	NaP (sodium pentachlorophenate)	0.7%
3.	"	NaP (sodium pentachlorophenate)	2.4%
4.	"	Cu-8 (copper 8-quinolinolate)	0.31%
5.	"	Cu-8 (copper 8-quinolinolate)	0.71%
6.	Leatherboard FC-130	PNP (paranitrophenol)	0.38%

* - weight % by analysis.

** - This fungicide is a preparation reported to be 90.0% plus zinc dimethyldithiocarbamate and 7.8% zinc 2-mercaptobenzothiazole. The concentration of this fungicide preparation was calculated as weight percent zinc dimethyldithiocarbamate, the predominant chemical in the mixture.

Instron tensile tester. Since the breaking strength data from replicate measurements were sufficiently reproducible for comparing the relative effectiveness of the fungicides, no attempt was made to refine the data by conversion to pounds/square inch cross-sectional area. The single hole stitch tear strength and crush resistance of counter specimens were conducted in accordance with Methods 2141 and 2051, respectively, of Federal Test Method Standard No. 311 as modified to comply with Military Specification MIL-C-41814B, except that specimens were not immersed in distilled water for the single hole stitch tear strength test.

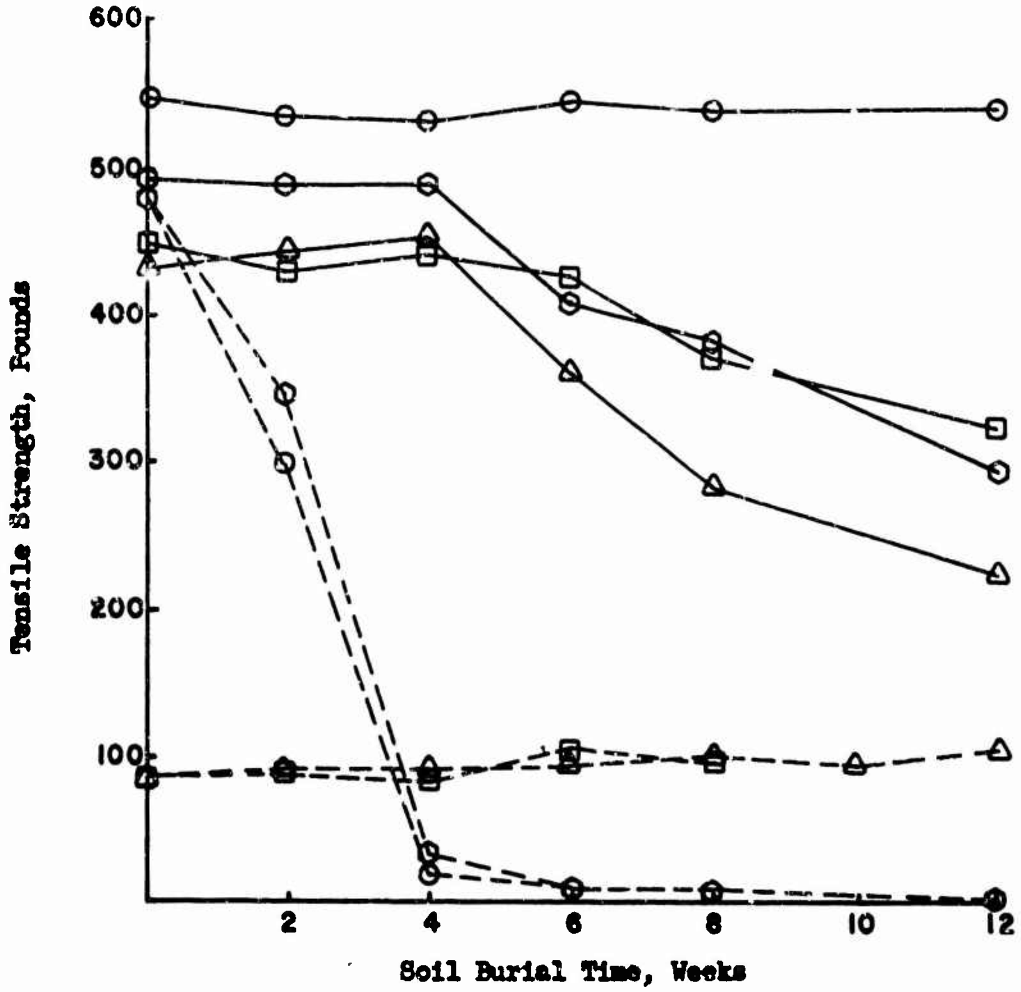
3. Results and Discussion

The preliminary screening of shoeboard samples indicated that counters for tropical footwear would require fungicidal treatment. Since tropical footwear must tolerate not only moisture but actual submersion, the fungicidal treatment selected should be resistant to leaching. As a result, the leaching test was included to determine the permanence of the treatment. Exposure of the leather-encapsulated counter to light was not considered likely. Therefore, stability of the treatment to light exposure was not considered essential, and no weathering of samples was performed.

a. Soil Burial Data From Strips

Figures 1 and 2 present the breaking strength data as average strength in pounds obtained from soil burial of the treated and untreated shoeboard and leatherboard strips. The 1/2 inch x 6 inch strip configuration was chosen, as for the earlier work, because it was suitable for breaking strength measurements. Since the breaking strength of a material is a useful gauge of the extent of microbiological deterioration, this measurement was selected as the primary means for comparing the relative effectiveness of the fungicides and for judging the usefulness of the single hole stitch tear strength test as a tool for gauging the extent of biodeterioration of the counters recovered from soil burial.

In Figures 3 and 4 the breaking strength data from the treated and untreated shoeboard and leatherboard strips are expressed as average percent strength retention to facilitate comparisons between shoeboard and leatherboard materials having different initial breaking strengths. The data from the control shoeboard strips demonstrate the basic susceptibility of shoeboard stock to microbiological deterioration. The shoeboard control retained only 62 percent of its breaking strength following 2 weeks of soil burial and only 4 percent following 4 weeks. In contrast, the untreated control leatherboard strips proved to be resistant to microbiological degradation during the 12-week soil burial test program and during soil burial extended for an additional 12 weeks. Therefore, there was no need for inclusion of a fungicide to protect the leatherboard matrix from tensile strength loss due to biodeterioration in soil burial. The soil burial data

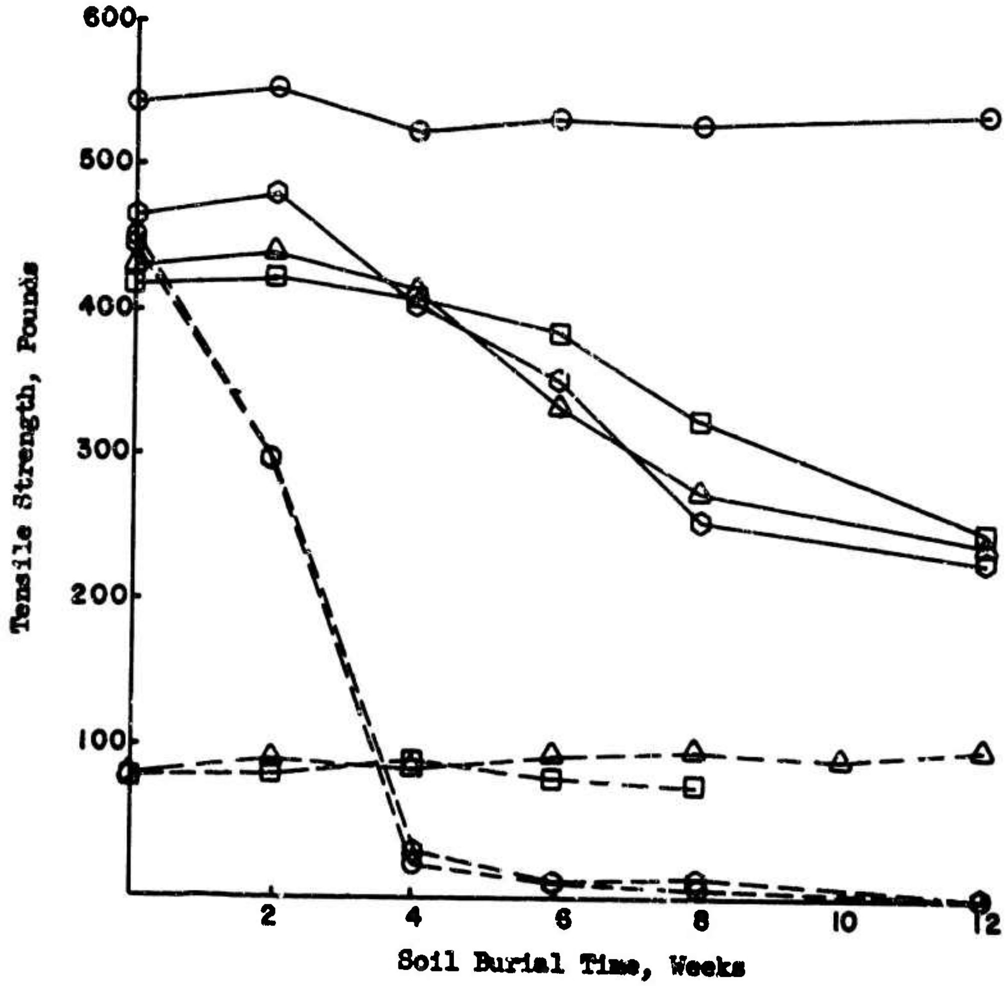


K E Y

Each point represents the mean of 5 replicates.

Shoeboard:	Control		O- - -O
	ZnD	0.5%	O- - -O
	Cu-8	0.31%	△——△
	Cu-8	0.71%	□——□
	NaP	0.7%	O——O
	NaP	2.4%	O——O
Leatherboard:	Control		□- - -□
	PNP	0.38%	△- - -△

Figure 1. Tensile Strength as a Function of Soil Burial Time for Unleached Shoeboard and Leatherboard, Treated and Control.

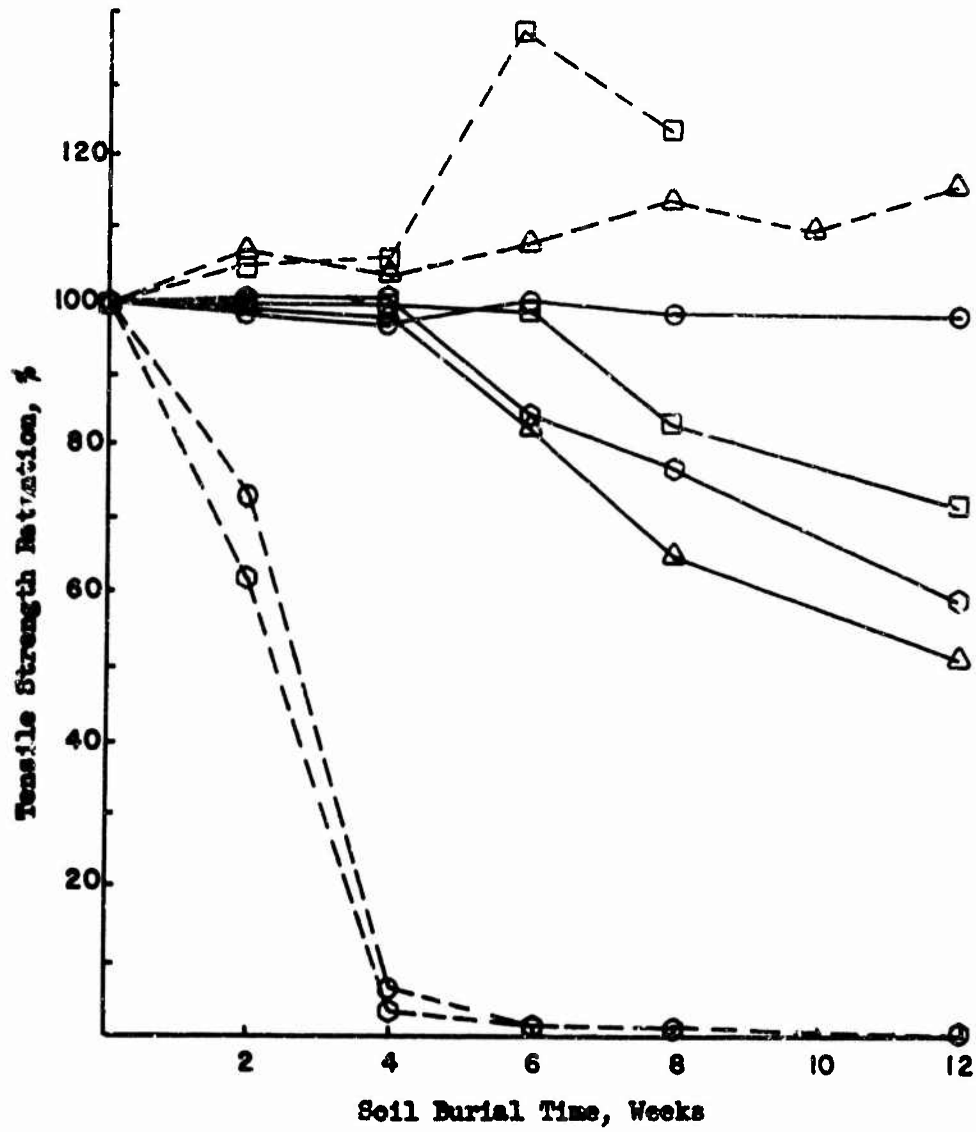


K E Y

Each point represents the mean of 5 replicates.

Shoeboard:	Control		⊖- - - -⊖
	ZnD	0.5%	⊖- ··· - -⊖
	Cu-8	0.31%	△———△
	Cu-8	0.71%	⊟———⊟
	NaP	0.7%	⊖———⊖
	NaP	2.4%	⊖———⊖
Leatherboard:	Control		⊟- - - -⊟
	PNP	0.38%	△- - - -△

Figure 2. Tensile Strength as a Function of Soil Burial Time for Leached Shoeboard and Leatherboard, Treated and Control.

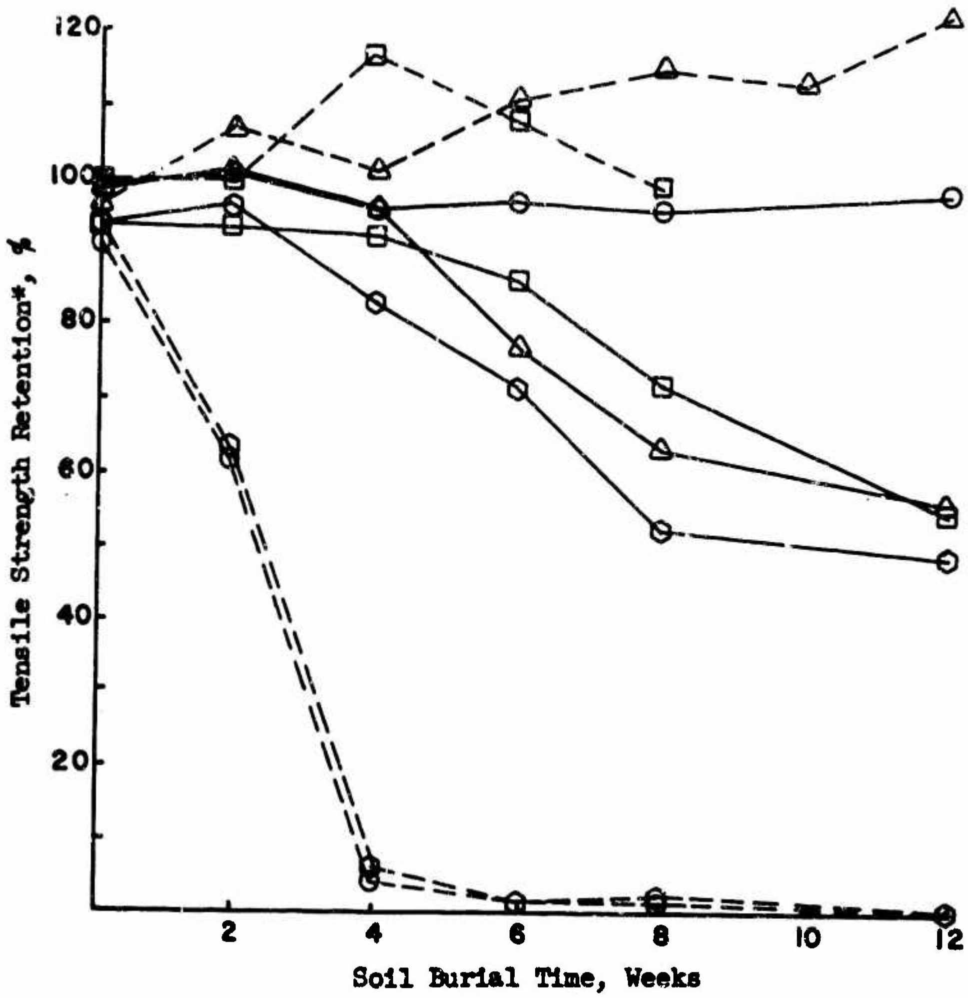


K E Y

Each point represents the mean of 5 replicates.

Shoeboard:	Control		⊖- - - -⊖
	ZnD	0.5%	⊖- - - -⊖
	Cu-8	0.31%	△———△
	Cu-8	0.71%	⊟———⊟
	NaP	0.7%	⊖———⊖
	NaP	2.4%	⊖———⊖
Leatherboard:	Control		⊟- - - -⊟
	PMP	0.38%	△- - - -△

Figure 3. Percent Tensile Strength Retention as a Function of Soil Burial Time for Unleached Shoeboard and Leatherboard, Treated and Control.



K E Y

Each point represents the mean of 5 replicates.

Shoeboard:	Control		○- - - -○
	ZnD	0.5%	○- - - -○
	Cu-8	0.31%	△——△
	Cu-8	0.71%	□——□
	NaP	0.7%	○——○
	NaP	2.4%	○——○
Leatherboard:	Control		□- - - -□
	PNP	0.38%	△- - - -△

Figure 4. Percent Tensile Strength Retention as a Function of Soil Burial Time for Leached Shoeboard and Leatherboard, Treated and Control.

*% Strength Retention Based on Tensile Strength of Original, Unleached Material.

indicate that the untreated leatherboard increased 16 percent in breaking strength after the 12-week test period and as much as 81 percent after 24 weeks' total soil burial. The p-nitrophenol-treated leatherboard increased 23 percent in tensile strength after only 8 weeks. This phenomenon has been attributed to strengthening of the polymeric matrix by additional polymerization reactions - a form of delayed curing dependent on the exact composition of the proprietary board materials. It was impossible to detect any comparable strengthening of the control shoeboard matrix because of its rapid deterioration in soil. Of the treated shoeboard samples, only the 2.4 percent sodium pentachlorophenate-treated shoeboard showed increased tensile strength in soil burial. This increase of as much as 17 percent occurred only after 24 weeks of soil burial. Only untreated leatherboard and 2.4 percent sodium pentachlorophenate-treated shoeboard were subjected to the additional 12 weeks' soil burial for a total of 24 weeks' exposure in soil. None of the shoeboard samples treated with the other fungicides showed any increase in tensile strength after soil burial.

Both unleached and leached shoeboard strips treated with 0.5 percent zinc dimethyldithiocarbamate preparation, deteriorated as rapidly as their respective controls during soil burial. This was to be anticipated since the analytical concentration indicated that the original shoeboard contained only 1/2 of the desired 1 percent nominal concentration. Analysis of the shoeboard for zinc cations by atomic absorption revealed that the zinc content was equivalent to approximately 0.5 percent by weight of zinc dimethyldithiocarbamate. Furthermore, it was reported that the zinc remaining in the shoeboard was probably present as zinc oxide.[1] Apparently, the fungicide was sensitive to the conditions of manufacture of the shoeboard and decomposed during production of the shoeboard stock. Copper 8-quinolinolate in adequate concentration provided good protection against microbiological degradation and prolonged the life of the shoeboard matrix. The unleached shoeboard containing 0.31 percent copper 8-quinolinolate retained 100 percent of its original breaking strength during 4 weeks of soil burial but lost 17 percent after 6 weeks of burial. In contrast, the unleached shoeboard containing 0.71 percent copper 8-quinolinolate retained 95 percent of its original breaking strength during 6 weeks of soil burial but lost 17 percent after 8 weeks. After 12 weeks of soil burial, unleached shoeboard treated with 0.31 percent and 0.71 percent copper 8-quinolinolate retained 51 and 72 percent, respectively, of their initial breaking strength. These data indicate that although both treatment levels protected the unleached shoeboard from microbiological degradation, the higher treatment level inhibited the initiation of biodeterioration more effectively. Therefore, the 0.71 percent treated shoeboard was able to retain a greater percentage of its strength than the 0.31 percent treated shoeboard at equivalent soil burial periods subsequent to the initiation of deterioration in both samples.

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[1] Personal communications with R. T. Vanderbilt Co., New York, New York

Figures 2 and 4 contain the tensile strength and percent strength retention data, respectively, from soil buried shoeboard strips which had been leached. The soil burial data obtained from the leached shoeboard samples containing copper 8-quinolinolate indicate that the performance of the treatment was not significantly affected by leaching. The soil burial results from leached shoeboard strips treated with 0.31 percent copper 8-quinolinolate were comparable overall to those obtained from unleached shoeboard strips. Leached shoeboard strips treated with 0.71 percent copper 8-quinolinolate also resisted microbiological deterioration quite well. The differences between the percent retention data from leached and unleached shoeboard strips treated with 0.71 percent copper 8-quinolinolate ranged from 6 to 11 percent during 8 weeks of soil burial and were unimportant. However, there may have been a slight loss of protection after 12 weeks in soil burial because unleached shoeboard strips retained 72 percent of their initial breaking strength and leached strips only 54 percent.

Sodium pentachlorophenate also provided good microbiological protection extending the lifetime of the shoeboard matrix. The unleached shoeboard containing 0.7 percent sodium pentachlorophenate retained 100 percent of its original breaking strength during 4 weeks of soil burial but lost 16 percent after 6 weeks of burial and 41 percent after 12 weeks. In contrast, the unleached shoeboard containing 2.4 percent sodium pentachlorophenate retained 98 percent of its original breaking strength during 12 weeks of soil burial and showed a 9 percent tensile strength gain after 24 weeks of soil burial. The higher treatment level, in this case, effectively inhibited the initiation of any measurable degradation during test exposure.

The soil burial data obtained from the leached shoeboard samples containing sodium pentachlorophenate indicate that the performance of this treatment was also not severely affected by leaching. The differences between the percent retention data from unleached and leached strips treated with 0.7 percent sodium pentachlorophenate were 17, 13, 25 and 11 percent after 4, 6, 8 and 12 weeks, respectively, of soil burial. Although these differences were larger than the differences observed in the data from either set of copper 8-quinolinolate treated strips, there was no progressive sequence in these values. Hence, part of the 17 percent difference and, more particularly, the 25 percent difference is probably due to random fluctuations in the data. After 24 weeks of soil burial leached strips treated with 2.4 percent sodium pentachlorophenate showed a 17 percent gain in tensile strength. No important differences could be detected between the rot resistance of leached and unleached shoeboard treated with 2.4 percent sodium pentachlorophenate after any soil burial period.

The higher concentration of sodium pentachlorophenate, however, was not entirely retained by the shoeboard. Sodium pentachlorophenate crystallized on the surface of the strips treated with the higher concentration during soil burial (Figures 5 and 6). The shoeboard with the lower (0.7 percent) sodium pentachlorophenate treatment may have also had some surface crystallization, but the lesser concentration would have rendered the crystals less apparent in cursory visual examination.

A request for approval by the Surgeon General's Office to use sodium pentachlorophenate has been denied because of its tendency to crystallize on the surface of treated shoeboard and its irritating effects on skin.

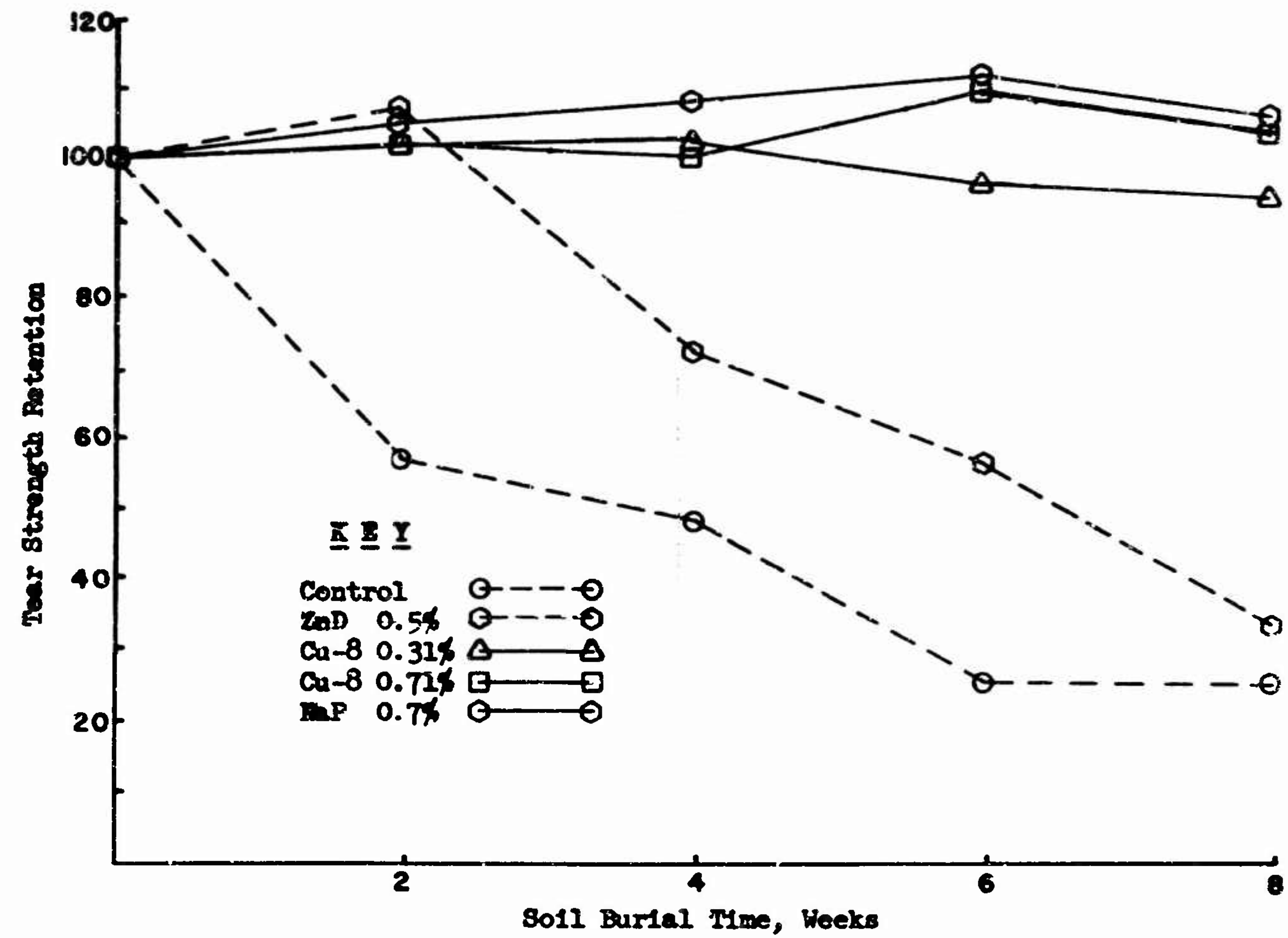
b. Soil Burial Data From Counters

Figures 7, 8, 9 and 10 contain the single hole stitch tear strength data from the experimental counters. These counters were fabricated from the same treated and untreated shoeboard as the strips discussed in the previous section. The data were obtained from dry half-counters tested either perpendicular or parallel to the base of the counter. In general, the data indicate that the directionality of the test had no significant bearing on the outcome, although the results from parallel tests performed on the control counters and the 0.5 percent zinc dimethyldithiocarbamate-treated counters appeared to be slightly lower, overall, than results from perpendicular tests. After 2 to 6 weeks of soil burial exposure, the average tear strengths of the untreated counters were below the MIL-C-41814B requirement of 60 pounds minimum strength. The average tear strengths of leached and unleached counters treated with 0.5 percent zinc dimethyldithiocarbamate were close to or below this limit after 6 to 8 weeks of soil burial exposure. It is important to note that the specification requires 60 pounds minimum wet strength. If the counters had been tested wet, the data generated after each soil burial interval would have probably been even lower because the test would have been more rigorous. Therefore, failure would probably have occurred after a shorter period of soil burial exposure.

There was no significant loss of tear strength in the sodium pentachlorophenate and the copper 8-quinolinolate-treated counters at any of the concentration levels tested through 8 weeks of soil burial. Also no differentiation could be made between the tear strength data from leached and unleached counters. Since no significant deterioration was observed in these counters, it is likely that treatment with 0.7 percent of either fungicide would probably meet the 60 pound minimum wet tear strength requirement after 8 weeks of soil burial exposure. This presumption requires testing by the performance of the standard wet tear strength test on counters so treated. If there is any latent deterioration in dry counters, it is possible that they could fail to meet the 60 pound limit if they were tested wet.

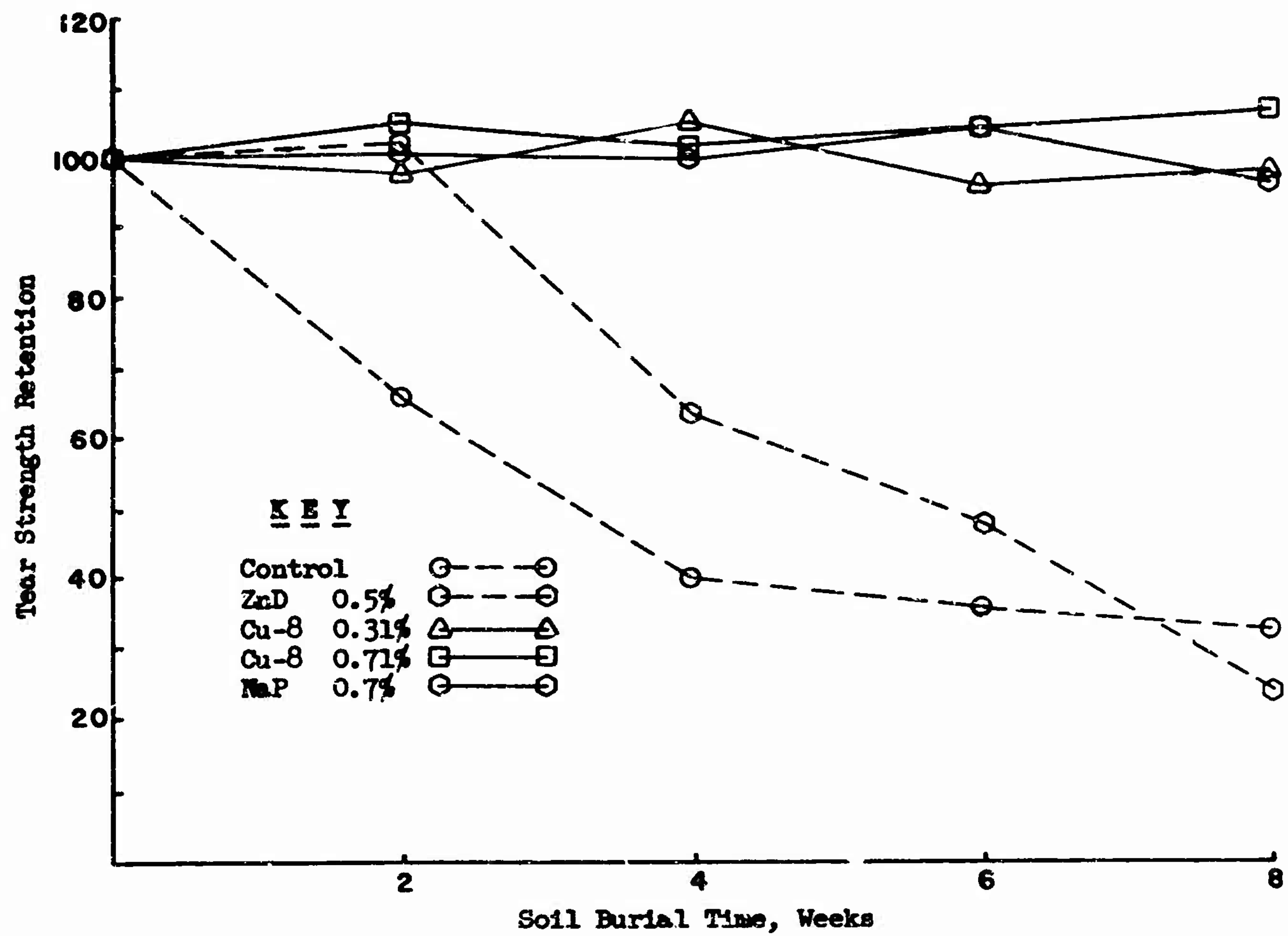
Figure 5. 2.4% Sodium Pentachlorophenate-Treated Shoeboard Unburied (20X).

Figure 6. 2.4% Sodium Pentachlorophenate-Treated Shoeboard After 4 Weeks Soil Burial (20X).



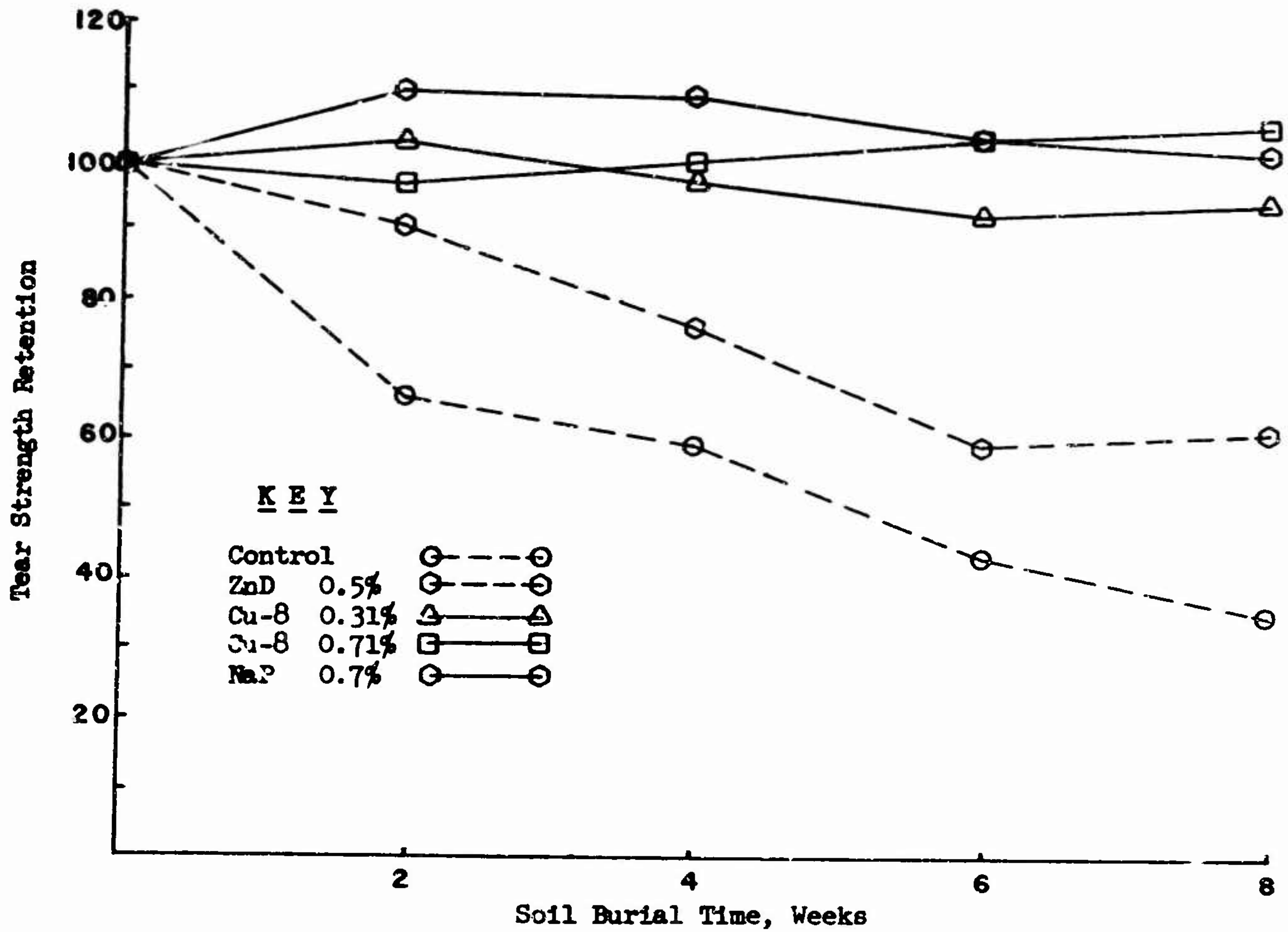
Each point represents the mean of 5 replicates.

Figure 7. Percent Tear Strength Retention, Parallel Test, as a Function of Soil Burial Time for Unleached Counters, Treated and Control.



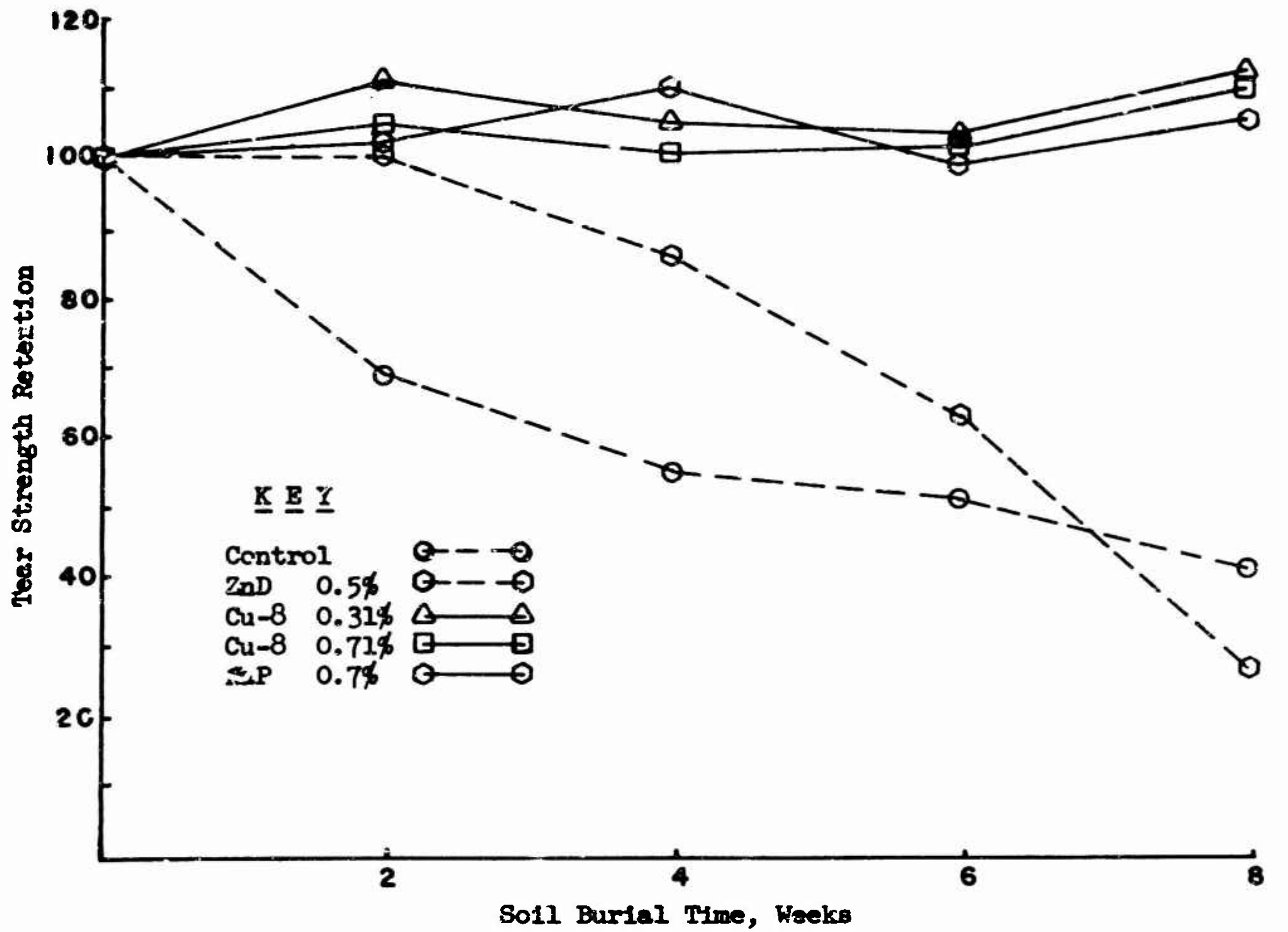
Each point represents the mean of 5 replicates.

Figure 8. Percent Tear Strength Retention, Parallel Test, as a Function of Soil Burial Time for Leached Counters, Treated and Control.



Each point represents the mean of 5 replicates.

Figure 9. Percent Tear Strength Retention, Perpendicular Test, as a Function of Soil Burial Time for Unleached Counters, Treated and Control.



Each point represents the mean of 5 replicates.

Figure 10. Percent Tear Strength Retention, Perpendicular Test, as a Function of Soil Burial Time for Leached Counters, Treated and Control.

On the basis of the more definitive shoeboard strip deterioration data, the recommended final analytical concentrations of copper 8-quinolinolate and sodium pentachlorophenate would be on the order of 0.5 to 1.0 percent and 1.5 to 2.0 percent, respectively.

Although the counters susceptible to rapid biodeterioration could be differentiated from those not readily susceptible, the tear strength data from counters were less informative than the tensile strength data from strips. For a given treatment and soil burial interval, the tear strength retentions of counters decreased more slowly than the tensile strength retentions of strips. This could be the result of either a less sensitive test and/or less deterioration to be measured. Undoubtedly, there was a difference in sensitivity between physical tests because different mechanical properties were being measured. At least several factors could have contributed to differences in the extent of deterioration. First, there was a difference in chemical composition since the counters were treated with unknown finishing compounds while the strips had no finishing treatment. Therefore, the counters could be either more or less susceptible to biodeterioration depending on the chemical nature of the finishing compounds and the uniformity of their application. Also because of their configuration, the counters were buried vertically. This is a less severe test than the horizontal test to which the strips were subjected because there is less soil contact. Since longer periods of time in soil burial are required for the characterization of treatments by dry stitch tear strength measurements than by tensile strength measurements, from a practical standpoint, quicker screening results are to be obtained from tensile strength measurements performed on strips.

c. Heat-Storage Tests

Since sodium pentachlorophenate is known to tenderize cellulose, it was suspected that some degradation might occur during the long-term storage of shoeboard treated with this compound. As a result, strips treated with 2.4 percent sodium pentachlorophenate were subjected to heat-storage tests at 130°F and 212°F.

Table II contains the tensile strength data obtained before and after accelerated heat-storage for 3 days at 212°F. The control strips lost 30 percent of their original strength as a result of 3 days of heat-ageing at 212°F. The strips treated with 2.4 percent sodium pentachlorophenate lost 60 percent of their strength after exposure to the same conditions. These results indicate that sodium pentachlorophenate degraded some component of the shoeboard, probably the cellulose fiber. Since these data were obtained from an admittedly severe test which damaged the control itself, other strips were exposed for more extended periods at 130°F - a more realistic temperature relative to actual storage conditions in a tropical climate.

TABLE II

Tensile Test Results on Heat-Aged (72 hours at 212°F)
Shoeboard Strips Containing Sodium Pentachlorophenate (2.4%)

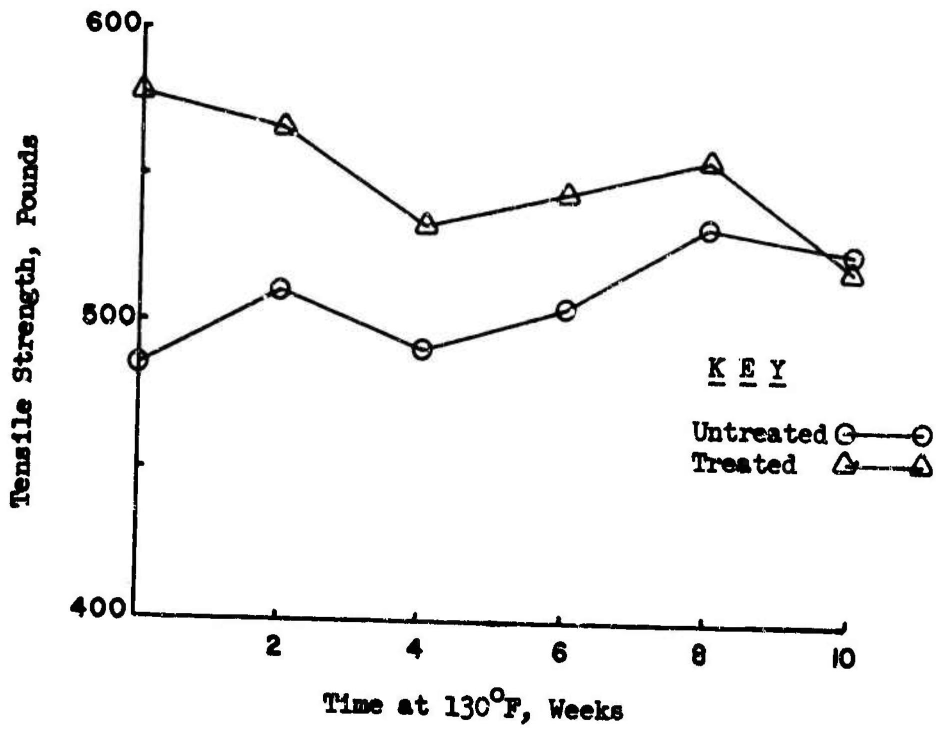
Treatment	Tensile Strength, Original, Pounds	Tensile Strength after 72 Hours at 212°F	% Loss
Control, NP-550	485	341	30
2.4% sodium pentachlorophenate treated NP-550	547	221	6C

Each figure is the mean of 5 replicates

Figures 11 and 12 contain the tensile strength data obtained before and after heat-storage at 130°F. The strength of the control strips increased 8 percent after 10 weeks of heat-ageing. During the same test interval, the strips treated with 2.4 percent sodium pentachlorophenate lost 10 percent of their strength. This loss is not particularly significant if considered alone. However, if the observed increase in the strength of the control strips was due to strengthening of the matrix by delayed curing and if the same delayed curing occurred in the treated material, then the true loss in the sodium pentachlorophenate-treated strips would be closer to 20 percent.

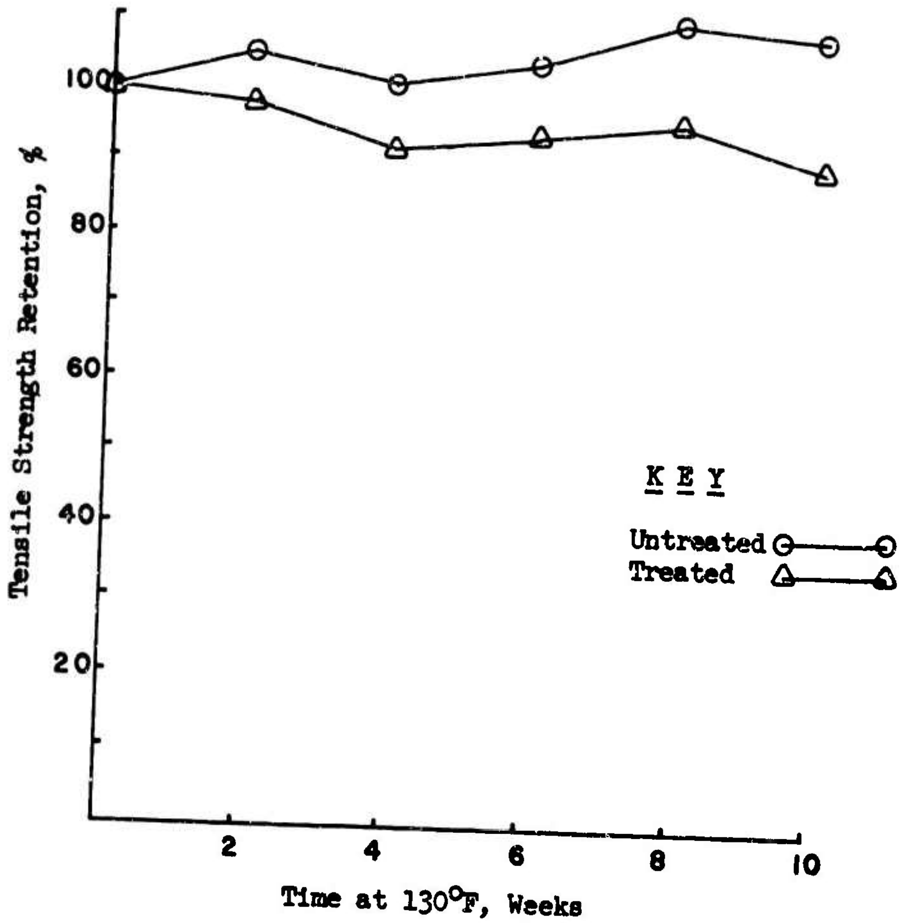
Although copper 8-quinolinolate does not degrade cellulose and a report by Mitton and Gatza (1965) indicates that it also does not detrimentally interact with styrene-butadiene, it was nevertheless essential to perform further tests prior to any recommendation for its inclusion in shoeboard counters. It was considered important to check for potential degradative interaction of copper 8-quinolinolate with the end-item itself and, in particular, for any negative effect on crush resistance and single hole stitch tear strength which are important mechanical properties of the counter.

Table III contains the crush resistance data obtained from the accelerated heat-ageing of counters treated with 0.71 percent copper 8-quinolinolate. There was no substantial difference between the results obtained before and after 6 days of accelerated heat-ageing at 212°F. Also, there was no significant difference between the data obtained from untreated counters and counters treated with 0.71 percent copper 8-quinolinolate. The control counters were crushed 10.7 percent of their initial height af-



Each point represents the mean of 5 replicates.

Figure 11. Tensile Strength of Control and 2.4% Sodium Pentachlorophenate-Treated Shoeboard Strips vs. Heat Ageing Time at 130°F.



Each point represents the mean of 5 replicates.

Figure 12. Percent Tensile Strength Retention of Control and 2.4% Sodium Pentachlorophenate-Treated Shoeboard Strips vs. Heat Ageing Time at 130°F.

ter 6 days of heat-ageing at 212°F. The counters treated with 0.71 percent copper 8-quinolinolate were crushed 11.6 percent of their initial height after exposure to the same conditions. Since neither counter was crushed more than 30 percent of its initial height, both the treated and untreated counters satisfied the crush resistance requirement of MIL-C-41814B after 6 days of accelerated heat ageing.

TABLE III

Crush Test Results on Heat-Aged
(6 days at 212°F) Shoeboard Counters
Containing Copper 8-quinolinolate (0.71%)

Time at 212°F Days	% Heat Reduction by Crush Test	
	Untreated	Treated
0	11.4	16.0
3	11.4	8.7
6	10.7	11.6

Figures 13 and 14 contain the single hole stitch tear strength data obtained before and after accelerated heat-storage at 212°F. Both untreated counters and counters treated with 0.71 percent copper 8-quinolinolate tended to increase substantially in tear strength after 3 days of accelerated heat-ageing probably due to delayed curing of the polymer. Subsequent heat-ageing for an additional 3 days tended to result in a small reduction of this large tear strength increase. This reduction in tear strength is probably related to the degradation which occurred in the control shoeboard strips discussed above and consequently would be a manifestation of the severity of heat-ageing at 212°F.

The results from parallel and perpendicular tests indicate that there was no significant difference between treated and untreated counters after 6 days of accelerated heat-ageing at 212°F. Although these counters were tested dry, there was no reason to doubt that any of them would fail to meet the 60 pound minimum wet tear strength requirements of MIL-C-41814B.

4. Conclusions

The rot-resistance data indicate that shoeboard is basically susceptible to microbiological degradation. The deterioration of shoeboard, however,

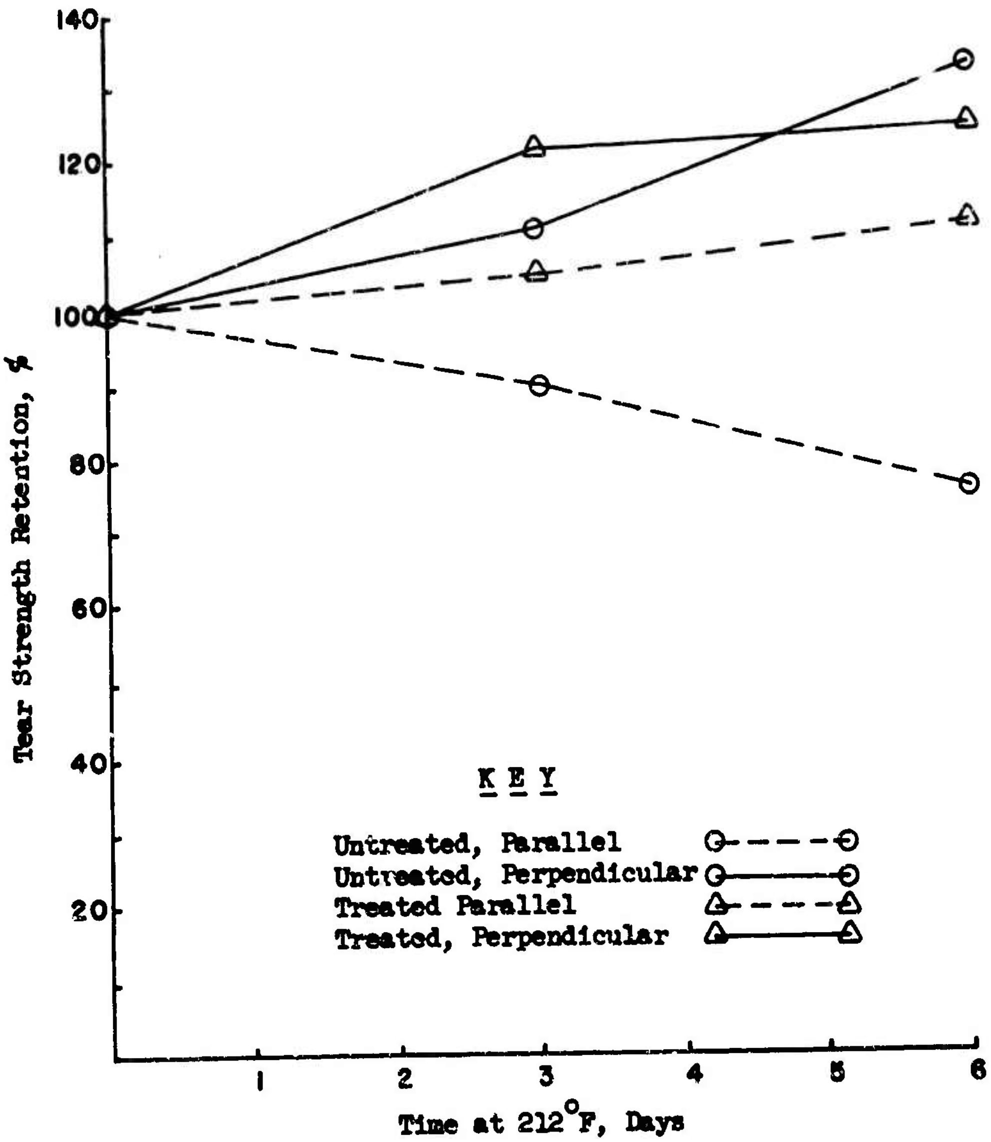


Figure 13. Percent Tear Strength Retention vs. Heat Ageing Time at 212°F for Control and 0.71% Copper 8-Quinolinolate-Treated Half Counter; Parallel & Perpendicular Tests Not on Same Specimen.

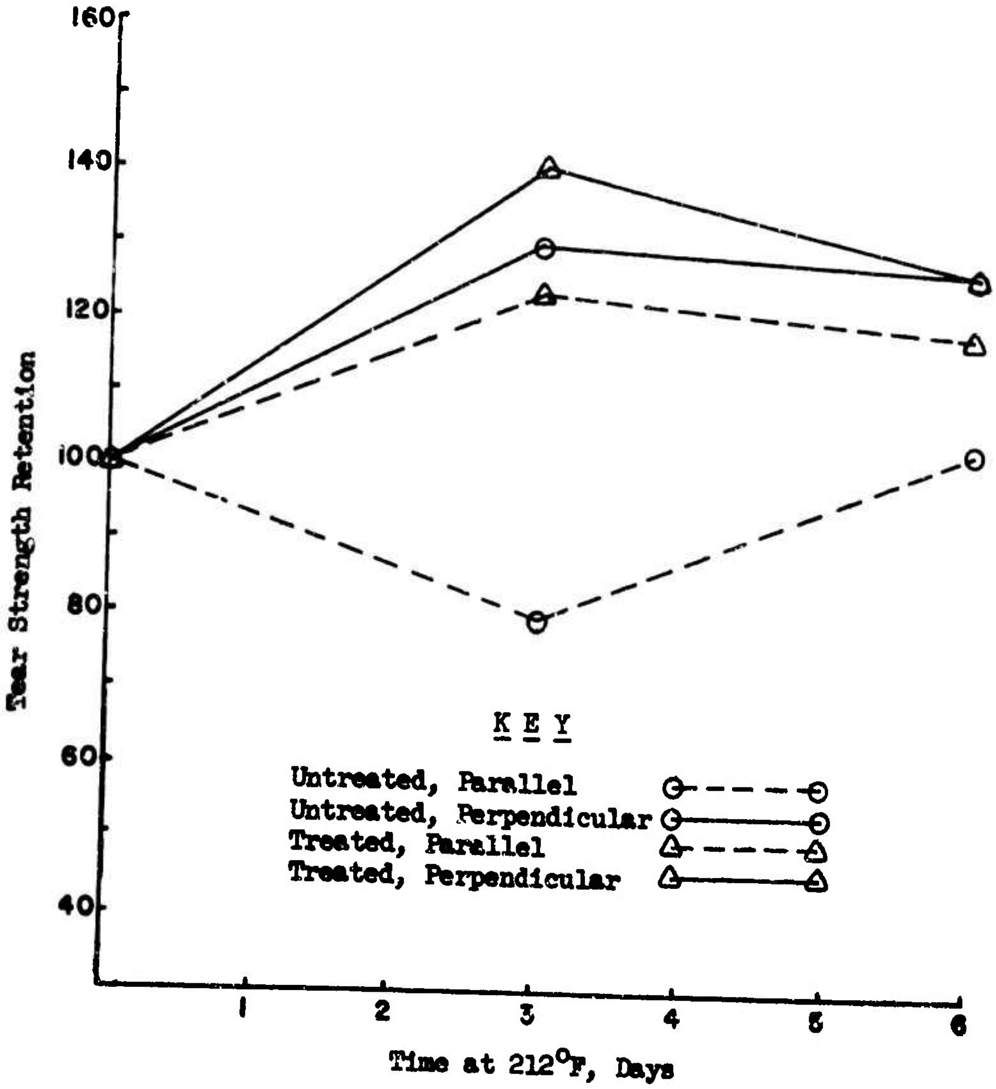


Figure 14. Percent Tear Strength Retention vs. Heat Ageing Time at 212°F for Control and 0.71% Copper 8-Quinolinolate-Treated Half Counter; Parallel & Perpendicular Tests On Same Specimen.

can be effectively postponed by the inclusion of 0.5 to 1.0 percent copper 8-quinolinolate. Although 1 percent sodium pentachlorophenate would also be effective, it would be regarded less desirable because it tends to migrate from the shoeboard matrix and is prone to tender the cellulosic portion of the shoeboard. Moreover, the effectiveness of sodium pentachlorophenate in protecting treated shoeboard is not relevant since the request for its use in this material has been denied by the Office of the Surgeon General.

Although the deterioration of shoeboard can be effectively postponed by inclusion of 0.5 to 1 percent copper 8-quinolinolate, it cannot be eliminated. After a suitable length of time, cellulosic shoeboard will deteriorate. A more desirable alternative would be to select a counter material which is inherently resistant to microbiological deterioration. Such a material is available. The data indicate that untreated leatherboard is resistant to biodeterioration for as long as 24 weeks in soil burial and, therefore, requires no fungicide to protect its structural stability. Plate tests performed on leatherboard treated with 0.38 percent p-nitrophenol indicate that the fungicide did not prevent superficial surface growth at this concentration. If superficial surface growth is regarded as undesirable for health reasons, some other treatment will be necessary to suppress such growth.

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13. ABSTRACT

Fungicide-treated shoeboard and leatherboard footwear counter materials with suitable controls were evaluated for rot-resistance in the soil burial test. Copper 8-quinolinolate, sodium pentachlorophenate and zinc dimethyldithiocarbamate were the fungicides evaluated for use in shoeboard. Paranitrophenol was evaluated for use in leatherboard. Copper 8-quinolinolate (0.5 to 1.0 percent) and sodium pentachlorophenate (1 to 2 percent) effectively inhibited microbiological degradation of shoeboard which is basically a susceptible composite material. However, the effectiveness of sodium pentachlorophenate is not relevant because of toxicity considerations and because it was incompatible with the shoeboard matrix, showing a tendency to tender the cellulosic portion of the shoeboard and migrate to the surface. Leatherboard, because of its inherent resistance to microbiological deterioration, is a more desirable counter material from the biological point of view than fungicide-treated shoeboard which will eventually deteriorate after a suitable induction period.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Resistance						
Paranitrophenol						
Copper 8-quinolinolate						
Zinc dimethyldithiocarbamate						
Sodium pentachlorophenate						
Tests						
Rotting						
Biodeterioration						
Shoeboard						
Leatherboard						
Footwear						
Counters						
Fungicides						

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