THIS REPORT HAS BEEN DELIMITED AND CLEARED FOR PUBLIC REL**EASE** UNDER DOD DIRECTIVE 5200,20 AND NO RESTRICTIONS ARE IMPOSED UPON ITS USE AND DISCLOSURE,

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED,

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.



NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVF FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by DOCUMENT SERVICE CENTER KNOTT BUILDING, DAYTON, 2, OHIO



NRL Report 4409

MARINE BORER CONTROL PART II CREOSOTE FRACTIONATION AND FRACTION EVALUATION

T. R. Sweeney, J. D. Bultman, and A. L. Alexander

Protective Coatings Branch Chemistry Division

September 13, 1954



NAVAL RESEARCH LABORATORY Washington, D.C.

CONTENTS

Abstract Problem Status Authorization	ii 1i 1i
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	3
Fractionation of Creosote Preparation of Panels Panel Evaluation	3 4 4
RESULTS	5
CONCLUSIONS	10
RECOMMENDATIONS	10
REFERENCES	11

ABSTRACT

In this investigation at the Naval Research Laboratory, A.W.P.A. Grade 1 creosote was fractionated by acid, alkali, solvent extraction, and also fractional distillation at reduced pressure. The fractions were then evaluated for their ability to protect wood against marine borer attack by impregnating wooden panels with the fractions (or with whole ereosote fortified with the fractions in the case of those obtained by distillation), subjecting a portion of the impregnated panels to an accelerated leaching test, and finally exposing the panels to borer attack in the sea.

Whole creosote was also chlorinated and the product evaluated in the same manner a the fractions except that the panels were not subjected to accelerated leaching before exposure.

Results of the evaluations indicated that all of the fractions tested as well as the fraction-fortified creosetes conferred resistance to borer attack on the wood; the degree of resistance was a positive function of the concentration of the preservative in the wood. Before leaching it appeared that creosete freed of tar acids, creosote freed of tar bases, creosote freed of both tar acids and bases, and the solvent extraction fraction were all superior to whole creosote, whereas creosote fortified with distillation fractions 2 and 3, respectively, was inferior to whole creosote. After 16 days of accelerated leaching the solvent extraction fraction and the creosote freed of tar acids still appeared superior to whole creosote; creosote fortified with distillation fraction 2 also appeared to be superior to whole creosote after leaching. The other materials tested after leaching seemed to possess about the same degree of resistance to attack as whole creosote. Fortified creosotes prepared with distillation fractions 4, 5, 6, and residue appeared to be about equally effective compared with each other; there were insufficient data to compare them with whole creosote. Chlorinated creosote, insofar as it was tested, appeared no better than whole creosote and possibly slightly inferior.

PROBLEM STATUS

This is an interim report. Further research on the problem, incorporating several modifications indicated by the work thus far, is being conducted.

AUTHORIZATION

NRL Problem C03-04 NR 603-040

Manuscript submitted July 22, 1954

MARINE BORER CONTROL PART II CREOSOTE FRACTIONATION AND FRACTION EVALUATION

INTRODUCTION

Creosote, * as usually used for wood preservation, is the fraction obtained in the range between approximately 200° and 400°C during the distillation of the high-temperature tar produced through the carbonization of bituminous coal. It is a dark, somewhat viscous liquid that has a pungent odor and often contains a considerable quantity of crystalline material at room temperatures. Of an estimated several hundred compounds in creosote, about 90 percent of the material on a weight basis consists of aromatic hydrocarbons. There are also present a few percent each of tar acids and tar bases and, in addition, some neutral oxygen and sulfur compounds.

It is generally agreed that creosote is an excellent wood preservative. For over a century it has been thus employed and indeed has been of interest to the Navy for almost as long. This creditable service record has been accumulated despite an almost completely empirical use of the product and little real knowledge of the properties and constituents which account for its remarkable protective ability. It is logical, therefore, to inquire whether certain of the constituents of creosote make a major contribution to its effectiveness, and it is this problem, i.e., the separation and evaluation of constituents of creosote in relation to its protective action against attacks on timber by marine borers, it was apparent from the outset that an attempt to isolate, identify, and evaluate every constituent of creosote would be a next to impossible task in any finite research program. The logical approach was apparently to first separate creosote into rather broad fractions and then, if any of these proved to be especially effective, to fractionate them much more carefully.

In this study of the chemical nature of creosote, special emphasis has been placed on the protection afforded wood against attacks by marine borers. Methods of assay and techniques reported at this time are those employed prior to July 1953. As experimentation progressed, major changes - resulting from the knowledge gained - were incorporated into the methods and techniques. This report, therefore, summarizes results on work begun prior to July 1953.

The project represents a joint effort by the Naval Research Laboratory and the Marine Laboratory of the University of Miami under Contract No. NOonr-705(00). NRL is engaged in the study of the chemistry and fractionation of creosote and the impregnation of wooden

^{*}Part 1 of this series was published as NRL Report 3940, February 6, 1952

panels with these fractions. The Marine Laboratory has developed procedures(1,2) for testing the fraction-impregnated panels and is conducting the accelerated leaching and panel exposures. In addition, this activity is determining the toxicity of the fractions to Teredo and Limnoria by respirometric techniques of their own development.

A simple pharmacological test for toxicity is not sufficient because the test, in some way, should reflect protection afforded to wood by the material. The most direct way to do this would be simply to impregnate wood panels with the material and expose them to marine borer attack. Such a procedure, however, would yield data much too slowly to be of use in testing a large number of fractions and applying the results as a guide in the fractionation program. Consequently, the accelerated leaching procedure, as described under "Experimental Procedure," was developed.

The presence of several classes of compounds in creosote, e.g., the tar acids, the tar bases, etc., indicated that one approach to its fractionation was to remove systematically these classes of compounds. In the present work creosote was depleted respectively of tar acids, tar bases, and both tar acids and tar bases, and the fractions so obtained assayed for their ability to protect wood against marine borer attack. Because of the complexity of creosote, the quantitative removal of a class of compounds without doing violence to the remaining compounds is an extremely difficult, if not impossible, task. For example, although about twice the quantity of tar acids may be extracted from creosote by means of methanolic alkali rather than by aqueous alkali, there remains after treatment by the former reagent a considerable quantity of hydroxyl in the residual creosote(3).

In addition to the afore-mentioned fractions, seven others were obtained by fractional distillation under reduced pressure. Six of these were assayed for their ability to enhance the protective ability of creosote by fortifying it with these fractions. One additional fraction obtained by solvent extraction, was also tested.

Although the chlorinated phenols are well-known as preservatives of wood against fungi, there seem to be no reports on the use of chlorinated whole creosote either against fungi or marine borers. In general, in the case of fungicides, chlorination of a compound seems to increase such toxicity as the compound already possesses but rarely imparts toxicity to a compound that is not in itself fungicidal to some extent. In considering the possibility that the chlorination of creosote would enhance its effectiveness against marine borers, it was realized that the economics of chlorination would make it feasible on a large scale. It is also possible that, considering the effect of chlorination on compounds of the type that occurs in creosote, e.g., it may have a higher boiling point, lower melting point, and decreased solubility. A possible disadvantage to the chlorinated material is that the chlorinated compounds may slowly hydrolyze in sea water. In view of the possibility of considerably enhancing the ability of creosote to protect wood against marine borers it was deemed justifiable to digress slightly and conduct a short study of chlorinated creosote.

EXPERIMENTAL PROCEDURE

Fractionation of Creosote

<u>Whole Creosote</u> - The creosote used in this investigation was taken from a large stock of A.W.P.A. Grade 1 product which is being reserved as a standard for present and future Navy research. It gave the following analysis* by A.W.P.A. methods:

^{*}Analyses supplied through courtesy of the Barrett Division, Alled Chemical and Dye Corporation

Specific Gravity (38/15.5°C) Water (% vol.)	$1.087 \\ 0.7$
Material Insoluble in Benzol (%)	0.14
Distillation (by wt., dry)	
to 210°C (%)	0.9
235	7.7
270	27.6
315	44.0
355	70.9
Residue	28.7
Coke Residue (%)	1.19
Specific Gravity Distillate (38/15.5°C)	
235-315°C	1.033
315-355°C	1,107
Total Tar Acids:	
A.W.P.A. Method ($\%$)	2.3
Barrett Method (H-11) ($\%$)	2.2
Tar Bases (Barrett H-16) (%)	3.5

<u>Tar-Acid-Free Creosote</u> - This material was prepared by extracting whole creosote with Claisen alkali as described in a previous report(3).

<u>Tar-Base-Free Crossote</u> - A solution of 100 g of creosote in 150 ml of benzene was prepared and extracted successively with four 100-ml portions of 10-percent hydrochloric acid. The residual solution was washed with water until free of acid and the solvent removed by distillation.

<u>Creosote Freed of Tar Acids and Tar Bases</u> - A solution of creosote in benzene in the foregoing ratio was extracted with Claisen alkali(3) and finally washed well with water. The tar-acid-free solution was then extracted with 10-percent hydrochloric acid as described in the section on the preparation of the tar-base-free creosote.

<u>Distillation of Creosote</u> - Creosote was distilled through a saddle-packed heated column (25 cm long and 1.8 cm inside diameter) that used a heated total reflux head and fraction collector. The stillpot was charged with about 1500 g of creosote. Similar fractions from two distillations were combined and the average yield calculated (Table 1).

Solvent Extraction of Creosote - About 160 g of creosote was treated with one third its volume of petroleum ether (b. p. 30° to 60° C) and the proclupitated solid filtered off; the average yield of solid from several runs amounted to 6° C, creent. Additional petroleum ether was added to the filtrate in an amount equal to 25 times the original volume, and the solution was allowed to stand overnight. The clear, light yellow, supernatant liquid was then deconted from the precipitated tar and the solvent removed by distillation. The residual oil (average yield 81.3 percent), which is referred to in this report as the solvent extraction fraction, was the only fraction obtained by this solvent manipulation reported herein. The average yield of tar, calculated by difference, was 12 percent.

Fraction	Temperature (°C)	Pressure (mm Hg)	Yield (%)
1	<200	760	1.5
2	200-235	7 60	18.6
3	235-130	760-15	7.2
4	130-160	15	8.7
5	160-190	15	11.3
6	190-210	15	16.7
Residue	>210	15	33.3

TABLE 1Summary of Creosote Distillation

<u>Chlorinated Creosote</u> - A solution of 570 g of creosote in 3500 ml of carbon tetrachloride was placed in a flask equipped with a reflux condenser and mechanical stirrer. Chlorine was passed through the solution for five hours while it was stirred and heated under reflux. At the end of this period the solution was separated from the tar which had formed during the reaction. The reaction mixture was washed well with sodium bicarbonate solution and finally with water, and the carbon tetrachloride was removed by distillation. The residue, the material tested against marine borers, weighed 500 g and had a chlorine content of 18.4 percent. The tar formed in the reaction weighed 83 g. A small amount of a solid material (7.6 g) was formed in addition to the tar. In a subsequent experiment the same quantity of creosote yielded 494.4 g of product, 90 g of tar, and no solid.

Preparation of Panels

4

Clear, No. 1, white pine panels $(5 \times 1-1/2 \times 1/8 \text{ inches})$ were dried to constant weight (to the nearest 0.1 g) at 105°C. They were then submerged in the whole creosote or fraction to be tested, held at about 75° in an ordinary hydrogenation bomb, and the desired pressure was applied by the admission of nitrogen. The pressure and time of impregnation were varied in order to obtain the desired degree of pickup. After impregnation, the panels were allowed to bleed to constant weight in a desiccator. They were then ready for assay. For this size panel, impregnation in grams multiplied by 3.2 equals impregnation in lb per cu ft.

The tar-acid-free creosote, the tar-base-free creosote, the creosote freed of both tar acids and bases, and the chlorinated creosote were used directly for the impregnations. To test the distillation fractions, panels were impregnated with whole creosote which had been fortified with enough of these fractions so that the total concentration of the fraction in the mixture was twice that in the whole creosote.

Panel Evaluation

The accelerateo beaching of the impregnated panels was carried out in a 25-gallon stainless steel tank which could accommodate about 200 panels. At each end, the tank was equipped with thermoregulators that were capable of maintaining a continuous stream of fresh water at 80° C.

The treated panels were leached for periods of 0, 1, 2, 4, 8, 16, 32, 48, 60, and 72 days. They were then mounted in a rack and exposed in the sea to borer attack. Inspections at 1, 2, 4, 6, and 8 month exposure periods were made by scraping off the fouling and noting the damage done separately by Limnoria and Teredo. Attack was rated

separately (L represents Limnoria, T represents Teredo) from 0 to 5 on an arbitrary scale as follows: 0-no attack, 1-very light attack, 2-light attack, 3-moderate attack, 4-heavy attack, 5-very heavy attack. The numerical rating of damage plotted in the graphs is obtained arbitrarily by adding twice the amount of Teredo attack to the amount of Limnoria attack (L + 2T). This was done to offset the abnormal Limnoria damage due to the very high surface to volume ratio of the panels. In certain cases the Teredo attack at one month was apparently less than for the previous month. This was attributed to Teredo holes being destroyed or covered up by Limnoria attack. In such cases the attack rating for the previous month was retained.

The panels impregnated with chlorinated creosole were not subjected to the accelerated leaching procedure because of the probability of enormously increasing the rate of hydrolysis of the chlorinated compounds by the contact with the hot water.

RESULTS

The extent to which varied impregnations with fractions affect the attack by marine borers is summarized in Tables 2 through 14. These data represent results from panels that have been leached as well as replicates which have not received such accelerated treatment. Whole creosote was used throughout as a standard for comparison. The attack on untreated controls is shown in Tables 2, 6, and 10, which were included for each of the exposure periods. In order to tabulate and condense the data to give an overall view of the results after 6 months of exposure, the treatments in Tables 2 through 14 are recorded as approximate and will not, therefore, coincide exactly with the exact treatments plotted in Figs. 5 and 6 (see page 7) for the zero and 16-day leaching periods. An explanation of the rating system was given under "Experimental Procedure" in this report. It is of particular interest to note from these data that all samples of creosote fortified with fractions obtained as described give a considerable measure of protection. As a result, these samples compared quite favorably with whole creosote and creosote that had been freed of tar acids. This is made clearer, perhaps, in Tables 15 and 16 where the sum of the attacks on the various fractions for several leaching periods is compared to the sum of the attacks on the untreated panels with identical leaching periods, Because essentially all of the control panels for the 6-month period (December 1952-June 1953) were either destroyed or yielded indeterminable Teredo attack because of the heavy Limnoria attack, the ratings listed in Table 16 were derived with data obtained from 4 months' exposure.

As might be anticipated, it was generally true that for whole creosote or any of its fractions and for any given leaching period the extent of attack by marine borers was a positive function of the length of exposure time. This is shown in Fig. 1 for panels treated with whole creosote at various levels with no leaching and in Fig. 2 for panels treated with whole creosote at various levels with 16-day leaching. In general, the resistance to borer attack by panels which had been impregnated with whole creosote or its fractions was a positive function of the concentration of the preservative in the panel; the attack-versus-treatment curves for all leaching periods showed a general but somewhat erratic negative slope. This is illustrated for whole creosote with no leaching in Fig. 3 and for whole creosote fractions with no leaching in Figs. 5a, 5c, and 6a and with 16-day leaching in Figs. 5b, 5d, and 6b.

Figure 7 illustrates the extent of attack made over a period of 8 months on a series of panels which had essentially equal concentrations of creosote but which were leached for different periods of time. For short leaching periods, attack appeared to be erratic although there was a definite trend of increased attack with increased leaching time up to 16 days. For leaching periods greater than 16 days and exposure periods in excess of 4 months, the rate of attack remained essentially constant, and it is for this reason that the 16-day leaching period is emphasized in this report.

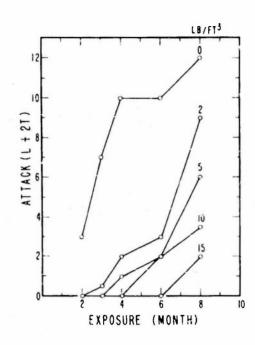


Figure 1 - Relation between attack and exposure for various whole creosote treatments with no leaching

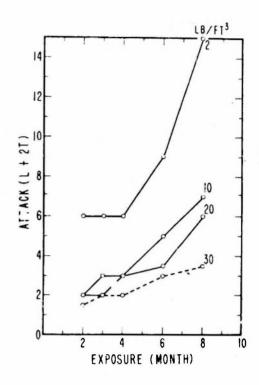


Figure 2 - Relation between attack and exposure for various whole creosote treatments after 16 days of leaching

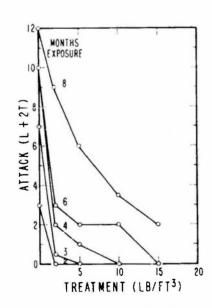


Figure 3 Relation between attack and whole creosote treatment with no leaching for various periods of exposure

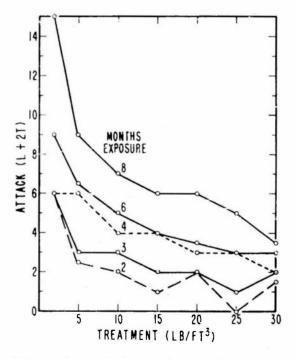


Figure 4 - Relation between attack and whole creosote treatment after 16 days of leaching for various periods of exposure

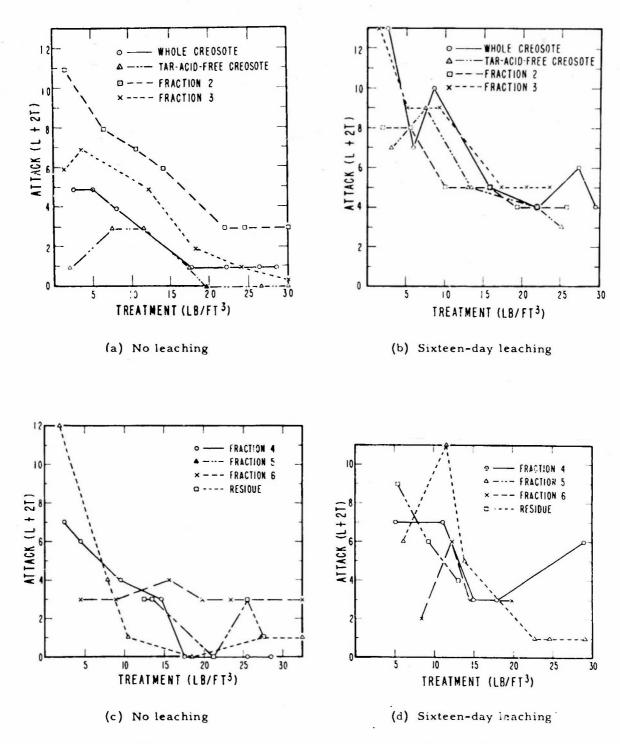
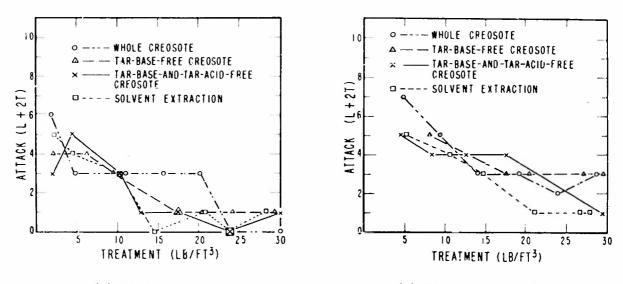


Figure 5 - Relation between attack and treatment with various creosote fractions after 6 months of exposure

1



(a) No leaching

•••••

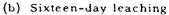


Figure 6 - Relation between attack and exposure for other creosote fractions after 6 months of exposure

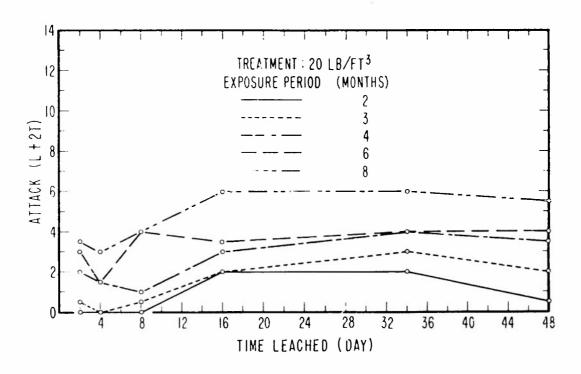


Figure 7 - Relation between attack and leaching time for whole croosote treatments for various exposure periods

A comparison of the attack after 6 months of exposure on panels impregnated respectively with whole creosote, tar acid-free creosote, distillation-fraction-2 fortified creosote, and distillation-fraction-3 fortified creosote is illustrated graphically in Fig. 5a (no leaching) and Fig. 5b (16-day leaching). A similar comparison for whole creosote. tar-base-free creosote, creosote freed of both tar acids and bases, and the solvent extraction fraction is given in Figs. 6a and 6b. In an attempt to compare all of these fractions with each other the graphical data have been calculated as areas under the curves for the treatment range of 5 through 25 pounds per cubic foot, and the results are presented in Table 17. The rating of any fraction based on whole creosote as 100 is obtained by dividing the area under the curve for whole creosote by the area under the fraction curve for the same leaching period and multiplying by 100. Inspection of Table 17 reveals that before leaching the tar-acid-free creosote, the tar-base-free creosote, the creosote freed of both tar acids and bases, and the solvent extraction fraction were all superior to whole creosote. After 16 days' leaching, however, only the solvent extraction fraction remained distinctly superior to whole creosote although the tar-acidfree material still appeared to give slightly better protection than whole creosote. Table 17 also shows that creosote fortified with distillation fraction 2 appeared to be distinctly inferior to whole creosote before leaching but after leaching for 16 days appeared to be surprisingly superior to whole creosote with similar leaching. This result with distillation Iraction 2 is, of course, difficult to explain and theorizing about it does not appear warranted on the basis of the present paucity of data. On the basis of the results presented in Table 17 the materials may be listed in decreasing order of their ability to protect treated wood before leaching as follows:

- 1. Solvent extraction fraction
- 2. Tar-acid-free creosote
- 3. Tar-base-free creosote = tar-acid-and-tar-base-free creosote
- 4. Whole creosote
- 5. Creosote fortified with distillation fraction 3
- 6. Creosote fortified with distillation fraction 2.

After leaching, the order of decreasing effectiveness appears to be

- 1. Solvent extraction fraction
- 2. Creosote fortified with distillation fraction 2
- 3. Tar-acid-free creosote
- 4. Tar-acid-and-tar-base-free creosote
- 5. Whole crecsote = all others.

Marine borer attack as a function of treatment with creosote fortified with fractions 4, 5, 6, and residue respectively is illustrated in Fig. 5c for no-leaching and in Fig. 5d for a 16-day leaching period. Unfortunately, the whole creosote panels for this series were lost so that these fractions can only be compared with each other and not with whole creosote. A number of the fraction panels were lost on test. On some panels the <u>Limnoria</u> attack was so severe that no reading of the <u>Teredo</u> attack could be obtained. In several cases panels which had only a slight <u>Teredo</u> attack after 4 months' exposure were found to be literally riddled after 6 months' exposure. This is reflected in some of the inordinately high values in the curves of Figs. 5c and 5d. No explanation is offered at this time. Creosote fortified with these fractions afforded definite protection to wood, and the fractions appeared to be about equally effective, one with another, when used to fortify creosote. Additional conclusions on these fractions are not warranted because of the paucity and nature of the data.

The results of a 6 months' exposure of panels treated with chlorinated creosote to various retentions as compared with panels treated with whole creosote as controls are shown in Table 14. Unfortunately, many of the significant panels were lost during the exposure. The chlorinated creosote was studied through the use of unleached panels only because it was believed that heating in water to 80°C would tremendously increase the rate of hydrolysis of the chlorinated compounds and therefore give a distorted picture of the preservative characteristics of the material. The data (Table 14) indicate that insofar as it has been tested the chlorinated creosote appears to be an effective preservative although no better than whole creosote and probably slightly inferior. Hence, because of the greater cost of producing chlorinated creosote, it cannot be considered as competitive with whole creosote for marine use.

CONCLUSIONS

Much has been learned from the collaborative work that has been done on this project about the techniques of working with creosote and the scope and limitations of the accelerated leaching test. The latter appears capable of yielding information on the initial and long term effectiveness of experimental preservatives.

All of the fractions studied conferred on wood a marked resistance to borer attack which was, in general, a positive function of the concentration of the preservative in the test panel and a negative function of the period of leaching and time of exposure. After 16 days of leaching and especially after 4 months' exposure, the rate of attack remained fairly constant, that is, the attack appeared to be independent of leaching time.

With no accelerated leaching the solvent extraction fraction, the creosote freed of tar acids, the creosote freed of tar bases, and the creosote freed of both tar acids and bases appeared superior to whole creosote in their ability to protect the test panels against marine borer attack; creosote fortified respectively with distillation fractions 2 and 3 appeared inferior to whole creosote. After 16 days' accelerated leaching the solvent extraction fraction, the creosote freed of tar acids, and the creosote fortified with distillation traction fraction? appeared superior to creosote; the other fractions seemed to be equal to whole creosote in effectiveness.

Creosote fortified with distillation fractions 4, 5, 6, and residue respectively appeared about equally effective one with the other; they could not be compared with whole creosote.

The conclusions drawn in this report are tentative and are based on work which has been of an exploratory nature. They may be invalidated as the result of the more refined measurements now being made in the new series of experiments as outlined under "Recommendations" of the report.

RECOMMENDATIONS

The results presented in this report as well as data now being obtained from panels put on test prior to July 1953 indicate the need for revamping some of the experimental procedures. This was discussed at a conference of representatives from the Noval Research Laboratory and the Marine Laboratory at the University of Miami on 1-3 July, 1953. The following protocol was adopted for future evaluation of creosote fractions:

1. Test panels shall be made of southern pine sapwood that is knot-free, low in resinous materials, and fairly uniform in density; the dimensions shall be $5 \times 1-1/2 \times 1/8$ inches.

2. Test panels with whole creosote shall be impregnated from the level of 5 lb per cu ft to the level of 20 lb per cu ft, and approximately 20 panels shall be prepared over each 5-pound range. An attempt shall be made to spread the impregnated panels evenly over the entire 15-pound range.

3. Test panels prepared with fractions of creosote shall be impregnated from the level of 10 lb per cu ft to the level of 15 lb per cu ft. About 20 panels shall be prepared in this range for each fraction.

4. An attempt shall be made to rate the creosote fractions by plotting attack as a function of treatment. The ratio of creosote treatment to fraction treatment (expressed in terms of its equivalent in whole creosote) permitting equal attack shall be computed at the middle of the fraction curve. This value will then express the protective quality of the fraction relative to whole creosote.

5. Poundage impregnation of a panel with fraction-fortified or fraction-depleted creosote shall be stated in terms of its equivalent in whole creosote.

6. Two sets of panels shall be prepared for each fraction; one shall be exposed without leaching and the other shall be exposed after 16 days of leaching, which will be the only leaching period used. Exposure period shall be set tentatively for 6 months.

7. One set of whole creosote panels shall be prepared for each two fractions tested.

8. Each set of panels to be tested shall be given a number.

9. Panels being exposed shall be inspected and rated bimonthly. They shall be scraped free of fouling biweekly.

10. All creosote fractions which have been evaluated shall be re-evaluated under the revised procedure.

* *

REFERENCES

- (1) "Semi-Annual Progress Report No. 53-5," Marine Laboratory, University of Miami, February 1953
- (2) Smith, F. G. W., "Report of Marine Borer Conference," Marine Laboratory, University of Miami, April 1953
- (3) Sweeney, T. R., and Walter, C. R., "Investigation of the Phenolic Fraction of Creosote," NRL Report 3940, February 6, 1952

TABLE 2

Extent of Attack on Panels Treated with Whole Creosote After Six Months' Exposure (September 8, 1952-March 19, 1953)

						Att	ack	Rat	ing	*							
Time		A	ppr	oxi	mat	te 7	ſrea	tme	ent	(lb	per	cu	ft)				
Leached	Untre	eated	2	2	5	5	1	0	1	5	2	0	2	5	3	0	
(day)						Ту	pe o	of B	ore	r							
	L'	Тŝ	L	Т	L	Т	L	т	L	Т	L	Т	L	Т	L	Т	
0	5	2	3	1	3	1	2	1	1	0	1	0	1	0	1	0	
1			1	1	4	1	2	1			1	1					
2	ŧ						4	1			2	1					
4	5	3	3	3	4	2	3	1	3	1	3	1				5.00	1.12
8	{						3	2			3	2			2	1	1
16	5	1	5	4	5	1	4	3	3	1	2	1	2	2	2	1	
32	5	3					4	1	4	1	4	1			1	1	
48							4	1	4	2	3	1	3	2	3	1	
60	5	2					3	1	4	1	3	1	3	1	2	1	
72	5	5					5	2	2	2	4	2	3	1	3	1	

*1 = Very light attack
2 = Light attack

IL = <u>Limnoria</u> IT = <u>Teredo</u>

3 = Moderate attack
4 = Heavy attack
5 = Very heavy attack

TABLE 3 Extent of Attack on Panels Treated with Tar-Acid-Free Creosote after Six Months' Exposure (September 8, 1952-March 19, 1953)

					1	Atta	.ck	Rat	ing	ŧ				
Time		A	ppr	oxi	mat	еT	rea	tme	ent ([]b]	pe r	cu	ft)	
Time Leached	2	2	ŧ	5	1	0	1	5	2	0	2	25	3	0
(day)						Тур	e o	f B	ore	r	.			
	L†	Т\$	L	Τ	L	Т	L	Т	L	Т	L	Т	L	Т
0	1	0	1	1	1	1	1	0	Ú	0	0	0	0	0
1	5	2	3	1	1	1			3	1	1	2		
2							2	3			1	1		
4	5	2	5	1					3	1	2	1		
8	3	3	3	2	3	1	2	1	2	1	2	1		
16	3	2	3	2	3	1	2	1	2	1	1	1		
32					4	1	3	2	3	2	3	1	3	1
48			5	1	5	2	5	1	2	1	3	1	2	1
60							4	3	4	2	3	2	4	1
72							4	1	3	1	4	1	3	1

*l = Very light attack
2 = Light attack

3 = Moderate attack

4 = Heavy attack 5 = Very heavy attack

+L = <u>Limnoria</u> \$T = <u>Teredo</u>

13

TABLE 4

Extent of Attack on Panels Treated with Creosote Fortified with Distillation Fraction No. 2 after Six Months' Exposure (September 8, 1952-March 19, 1953)

				-	ł	Atta	ck l	Rat	ing,	*			_		
Time		A	ppr	oxii	nati	e T	reat	me	nt (lp f)er	cu	ſt)		
Time Leached		2	5	5	1	0	1	5	2	0	2	5	3	0	
(day)						Тур	e o	f Bo	orei	•					
	L†	T ^{\$} L T L T L T L T L T L T													
0	5	3	4	2	3	2	4	1	1	1	1	1	1	1	
1	4	2	3	1	3	1									
4	5	2	3	1	3	1	3	1							
16	4	2	4	2	3	1	3	1	2	1	2	1			
48							4	1	4	2	3	1	2	1	
72									4	1	4	3			

*1 = Very light attack 2 = Light attack

tL = <u>Limnoria</u> \$T = <u>Teredo</u>

ļ

3 = Moderate attack

4 = Heavy attack 5 = Very heavy attack

-

15

_

TABLE 5

Extent of Attack on Panels Treated with Creosote Fortified with Distillation Fraction No. 3 after Six Months' Exposure (September 8, 1952-March 19, 1953)

					A	ita	ck I	Rati	ng*						
		Aŗ	pro	oxin	nate	e Ti	reat	me	nt (lb p	er	cu f	t)		
Time Leached	2		5	5	1	0	1	5	2	0	2	5	3	0	
(day)					1	Гур	e of	Bo	orer	•					
	L†	╶╞╶╫╍╞╼╫╶┊╶╢╶┊╌╢╶┊╸╟													
0	4	1	5	1	3	1	1	0	1	1	1	0	0	0	
1	4	2	5	2	4	1			4	1					
4	3	2	4	2	3	1	3	1	2	1					
8	4	2	3	1					2	1	1	1			
16	5	4	5	2	5	2	3	1	3	1	3	1			
32							4	1	3	1	2	1			
48							4	1	4	1	4	2	3	1	
60							4	1	3	1	4	1			
72									2	2	3	3	1		

***1** = Very light attack

2 = Light attack 3 = Moderate attack

4 = Heavy attack

5 = Very heavy attack

tL = <u>Limnoria</u> \$T = Teredo

TABLE 6

Extent of Attack on Panels Treated with Creosote Fortified with Distillation Fraction No. 4 after Six Months' Exposure (December 12, 1952-June 12, 1953)

						Att	ack	Ra	ting	*						
Time		A	ppr	oxi	mai	te I	rea	atm	ent	(1b	per	cu	ſt)			
Leached	Untre	eated	2	2	Ę	5	1	0	1	5	2	20	2	5	3	0
(day)						Ту	pe o	of B	lore	r						
	Lţ	ТŚ	L	Т	L	Т	L	Т	L	'n	L	Т	L	Т	L	Т
0	5	?	5	?	4	1	2	1	1	1	0	0	0	0	0	0
1	5	?	3	2	3	2	1	1					1	1		
2	5	?														
4	Dest	royed	4	1	3	2	2	1	2	1	2	0			1	0
8	5	?	5	?	5	?	2	5			Lo	l ost			1	1
16	Dest	royed			5	?	5	?	1	1	1	1			2	2
32	5	?			4	1	5	?	2	1	Lo	bst			1	1
48	4	2							3	0	3	2	1	1	3	2
60	Dest.	royed							2	1	2	1	3	2	L	bst
72	Dest	royed									Lo	l ost	3	1	3	2

*1 = Very light attack
2 = Light attack

3 = Moderate attack

4 = Heavy attack

5 = Very heavy attack

? = Indeterminable attack

'L = <u>Limnoria</u> T = <u>Teredo</u>

,

TABLE 7

Extent of Attack on Panels Treated with Creosote Fortified with Distillation Fraction No. 5 after Six Months' Exposure (December 12, 1952-June 12, 1953)

					ł	Atta	ck	Rat	ing	•				
Time		A	ppro	oxir	nati	e T	reat	me	nt (lp b	ber	cu	ft)	
Leached (day)	2	2	5	5	1	0	1	5	2	0	2	5	3	0
(uay)					,	Тур	e o	f Bo	orei	•				
	\mathbf{L}^{\dagger}	Т\$	L	Т	L	Т	L	т	L	Т	L	т	L	т
0	2	5	2	1	1	0	1	0	0	0	1	0	1	0
1			4	?	1	2			1	0				
2			-						Lo	st				
4			1	1	1	1			1	0				
8	2	2	2	2	Lo	ost			2	0	2	2		
16			4	1	1	5	3	1	1	0	1	0	1	0
32			4	2	4	1			1	1	1	1	Lo	st
48					4	?	3	0	Lo	st	1	1	3	1
60									3	3	3	2	La	st
72									3	1	2	1	Lo	st

*1 = Very light attack
2 = Light attack

+L = <u>Limneria</u> \$T = Teredo

3 = Moderate attack 4 = Heavy attack

5 = Very heavy attack ? = Indeterminable attack

TABLE 8

Extent of Attack on Panels Treated with Creosote Fortified with Distillation Fraction No. 6 after Six Months' Exposure (December 12, 1952-June 12, 1953)

					ł	Atta	ck l	Rat	ing	k				
T i		A	ppr	oxii	nate	e T	reat	me	nt (lb p	oe r	cu i	īt)	
Time Leached	2	2	5	5	1	0	1	5	2	0	2	5	3	0
(day)					,	Тур	e of	í Bo	orei	•				
	Ľ.	Т\$	L	Т	L	Т	L	Т	L	Т	L	Т	L	Т
0	Lo	pst	1	1	1	1	2	1	1	1	1	0	1	0
1	4	5	Lo	ost					1	1				
2			4	?					1	2				
4	2	1	1	1	Lo) st			Lo	st				
8	Lo	ost	5	?					2	1				
16			2	0	2	2	1	1	1	1				
32			Lo	bst	3	1	5	?	1	1	3	1	Lo	st
48					Lo	i ost	4	1	5	?	2	1	3	2
60							5	?	5	?	2	1	2	1
72									3	1	5	?	3	1

*1 = Very light attack
2 = Light attack

L = LimnoriaT = Teredo

3 = Moderate attack

4 = Heavy attack
5 = Very heavy attack
? = Indeterminable attack

TABLE 9

Extent of Attack on Panels Treated with Creosote Fortified with Distillation Residue after Six Months' Exposure (December 12, 1952-June 12, 1953)

					A	tta	ck l	Rati	ing*					
Time		Ap	pro	oxin	nato	Tr	eat	me	nt (lb p	er	cu f	t)	
Leached	2	2	5	5	1	0	1	5	2	0	2	5	3	0
(day)					2	Гуре	e of	Bc	orer	•				
	Ľ'	T٩	L	Т	L	Т	L	T	L	Т	L	Т	L	Т
0	Lo	ost			1	1	1	1	0	0	1	1	1	0
1	5	?			1	1	1	0						
2			1	1	3	1	3	1	1	2				
4	Lo	ost	Lo	l ost	2	1	2	1	2	1				
- 8	4	2			1	1	2	1	Lo	 				
16			3	3	4	1	2	1	Lu	ost				
32					2	1	2	1	4	?			1	1
48					4	2			1	1	2	1	3	1
60			107		Lo	ost			3	1	4	2	Lo	ost
72					4	3			5	?	5	?	3	1

*1 = Very light attack
2 = Light attack

3 = Moderate attack

4 = Heavy attack

5 = Very heavy attack

? = Indeterminable attack

tL = LimnoriaT = Teredo

TABLE 10 Extent of Attack on Panels Treated with Whole Creosote after Six Months' Exposure (August 28, 1953-March 1, 1954)

						Att	ack	Rat	ting	*						
Time		A	ppi	roxi	ma	te I	rea	tm	ent	(1b	per	cu	ft)			
Time Leached	Untr	eated	2	2	:	ō	1	0	1	5	2	0	2	5	3	0
(day)	1					Тy	pe c	of B	ore	r						
	L†	T۶	L	Т	L	Т	L	Т	L	Т	L	т	L	т	L	Т
0	3	4	2	2	1	1	1	1	1	1	1	1	0	0	0	0
2	3	4	3	2												
4	2	3	3	2	2	3	1	1								
8	3	3	3	2	2	1	1	1	1	1	1	1			1	0
16	4	5			3	2	1	2	1	1	1	1	0	1	1	1
32	5	5					2	1	2	1	1	1	1	1	1	0
48													1	1	1	0
60	4	?											1	0	1	1
72	4	5											1	1		

*1 = Very light attack 2 = Light attack 3 = Moderate attack

†L = <u>Limnoria</u> \$T = <u>Teredo</u>

4 = Heavy attack

5 = Very heavy attack ? = Indeterminable attack

TABLE 11

Extent of Attack on Panels Treated with Creosote Freed of Tar Bases after Six Months' Exposure (August 28, 1953-March 1, 1954)

	Attack Rating*													
TT: man	Approximate Treatment (lb per cu ft)													
Time Leached	2	2	5	5	10		1	15 2		20		5	3	0
(day)					,	Тур	e of	f Bo	orei	•				
	L†	Тş	L	Т	L	Т	L	т	L	т	L	Т	L	Т
0	2	1	2	1	1	1	1	0	1	0	1	0	1	0
2	3	2	2	2					1	1				
4	2	2	3	2			2	1	1	1				
8	2	4	2	2			1	1	1	1				
16			2	2	2	1	1	1	1	1	1	1	1	1
32					2	1	2	1	2	1	1	1	1	0
48							2	1	2	1	2	1	1	0
60							3	1	1	1	3	1	2	1
72							2	2	2	1	2	1	2	0

*1 = Very light attack 2 = Light attack

a replace another an ar warder

3 = Moderate attack 4 = Heavy attack

5 = Very heavy attack

+L = <u>Limnoria</u> sT = <u>Teredo</u>

TABLE 12

Extent of Attack on Panels Treated with Creosote Freed of Tar Acids and Tar Bases after Six Months' Exposure (August 28, 1953-March 1, 1954)

					1	Atta	ck	Rat	ing	k.				
-	Approximate Treatment (lb per cu ft)													
Time Leached	2	2	5	5		10		15		20		5	5 3	
(day)						Тур	e o	f Bo	orei	r		-		
	Lt	Т۶	L	T	L	т	L	Т	Ĺ	Т	L	Т	L	Т
0	1	1	3	1	1	1	1	0	1	0	0	0	0	0
2	3	2							1	0				
4	3	3	2	2	2	1	2	1	1	0				
8	4	2	3	2	2	1	1	υ	1	0			1	0
16			3	1	2	1	2	1	2	1			1	0
32					4	1	2	1	2	1	1	0	2	1
48					3	2	3	1	2	0	2	1	1	0
60					3	1	3	1	3	1	1	Ú	2	1
72					2	2	2	1	2	1	2	1	1	1

- *1 = Very light attack
 2 = Light attack
- $\frac{1}{T} = \frac{\text{Limnoria}}{\text{T} = \frac{\text{Teredo}}{\text{T}}}$

- 3 = Moderate attack
- 4 = Heavy attack 5 = Very heavy attack

TABLE 13

Extent of Attack on Panels Treated with Solvent Extraction Fraction after Six Months' Exposure (August 28, 1953-March 1, 1954)

.....

	Attack Rating*													
This is a	Approximate Treatment (lb per cu ft)													
Time Leached	2	2		5		10		15 2		0	2	5	3	0
(day)						Тур	e o	f Bo	orei	r				
	L†	Т۶	L	Т	L	Т	L	Т	L	Т	L	Т	L	T
0	3	1	2	1	1	1	0	0	1	0	0	0	1	0
2	1	2					2	2						
4	3	2	2	2	2	1	1	1						
8	3	3	2	2	1	1	1	1	1	1				
16			3	1	2	1	1	1	1	0	1	0	1	0
32					2	1	1	1	1	1	1	1		
48											1	0		

*1 = Very light attack
2 = Light attack
3 = Moderate attack

+ L - <u>Limnoria</u> \$ T = <u>Teredo</u>

4 = Heavy attack 5 = Very heavy attack

TABLE 14

Extent of Attack on Panels Treated with Chlorinated Creosote after Six Months' Exposure (Jan. 28, 1953-July 28, 1953) with no Prior Leaching

	Attack Rating*												
	Approximate Treatment (lb per cu ft)												
2 5 10 15 20 25 30									0				
	Type of Borer												
Lt	Т¢	L	т	L	т	L	Т	L	Т	L	Т	L	т
			Cł	lor	ina	ted	Cre	eose	ote				
3	1	1	1	1	1	L	ost	Lc	st	0	0	0	0
2	1	1	1	1	1	0	1	0	0	0	0	0	0
3	1	1	1	Lo) st	0	0	Lo	ost	0	0	0	0
2	2	1	1	0	0	1	0	0	0	0	0	0	0
		1	1	0	0	0	0	0	0	0	0	0	0
		0	1	Lo	st	L	ost	0	0	0	0		
		1	1			L	ost			0	0		
						0	0						
						0	0						
						1	0						
		- 1	Who	oie	Cre	osc	ote (Con	trol	s	e.		
1	1	Lo	ost	L	ost	0	0	0	0	0	0	0	0
Lo	ost	Lo	 ost	L	 ost	1	0	0	1	0	0	0	0
1	1	1	1	L	ost	L	 ost	0	1	0	0	0	0
				L	l ost			0	0	0	0		
										0	0		

*1 = Very light attack
2 = Light attack
3 = Moderate attack
4 = Heavy attack
5 = Very heavy attack

L = LimnoriaT = Teredo

24

TABLE 15

Comparison of Treated and Untreated Panels After Six Months' Exposure

		Sum of Attack*							
Exposure Date	Fraction	Approximat⊕ Treatment (lb per cu ft)							
		0	2	<u>ۇ</u> .	10	15			
8 September 1952	Untreated	27							
	Tar-Acid-Free Creosote		17	129					
	Distillation-Fraction 2 Fortified		28	21	17	1 6			
	Distillation-Fraction 3 Fortified		2 6	2-4	19	11			
	Whole Creosote		27	210	19	11			
28 August 1953	Untreated	32							
15	Solvent Extract			155	11	6			
	Tar-Base-Free Creosote			166		8			
-	Tar-Acid-and-Tar-Base-Free Creosote			166	11	9			
	Whole Creosote			18	11				

*This sum was computed from the appropriate tables by adding the Limnoria attack rating to twice the <u>Teredo</u> attack rating (L + 2T) for panells leached 0, 4, and 16 days.

R.

いいたい 二日 二日の ちのちまっ

TABLE 16

Comparison of Treated and Untreated Panels After Four Months' Exposure

		Sum of Attack* Approximate Treatment (1b per cu ft)						
Exposure Date	Fraction							
		0	2	5	10			
12 December 1952	Untreated	20						
	Distillation-Fraction 4 Fortified		19	7				
	Distillation-Fraction 5 Fortified			11	4			
	Distillation-Fraction 6 Fortified		12	8	-			
	Residue		12		6			

*This sum was computed from the appropriate tables by adding the Limnoria attack rating to twice the Teredo attack rating (L + 2T) for panel's leached 0, 1, 4, and 8 days.

TABLE 17

Comparison Beiween Attack on Creosote-Treated Panels and Attack on Fraction-Treated Panels after Six Months' Exposure over the Range of 5 to 25 Pounds per Cubic Foot

Exposure Date	Time Leached (day)	Fraction	Area	Rating
8 September 1952	0	Whole Creosote	49.7	100
		Tar-Acid-Free Creosote	31.2	159
		Distillation-Fraction 2 Fortified	110,4	45
		Distillation-Fraction 3 Fortified	73.0	68
	16	Whole Creosote	125.3	100
		Tar-Acid-Free Creosote	109.6	114
		Distillation-Fraction 2 Fortified	100,3	125
		Distillation-Fraction 3 Fortified	133.2	94
28 August 1953	0	Whole Creosote	51.3	100
		Tar-Base-Free Creosote	39.8	129
		Tar-Base-and-Tar-Acid-Free Creosote	39.8	129
		Solvent Extract	29.5	174
	16	Whole Creosote	74.9	100
		Tar-Base-Free Creosote	75.6	99
		Tar-Base-and-Tar-Acid-Free Creosote	70.6	106
		Solvent Extract	56.2	133

* *

NAVY OPPO PRNS. WAS

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.



NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SI ECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE RECARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR COF PORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by DOCUMENT SERVICE CENTER KNOTTBUILDING, DAYTON, 2, OHIO