Resistance of Organic Materials and Cable Structures to Marine Biological Attack

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The increasing use of submarine telephone cable has resulted in the need for information on the performance of organic materials and cable structures under marine conditions. Recently, Bell Telephone Laboratories initiated a program to acquire fundamental data on the resistance of a wide range of organic materials, as well as immediately applicable engineering information. The present progress report describes the program which includes accelerated, laboratory-microbiological tests, as well as the acquisition of data from actual marine exposures. In biochemical oxygen demand-type tests conducted to date polyethylene was not utilized as a carbon source by marine bacteria. Polyvinyl chloride plastics served as a source of energy for the organisms depending on the way in which the materials were plasticized. Five elastomers were utilized by the bacteria. There has been a steady rise in capacitance values for GRS-insulated conductors exposed in sea water and sediment under laboratory conditions for thirteen months. These increases appear due to biological activity on the insulation. The general performance of materials undergoing marine exposure is reported including reference to penetration of a few synthetic materials by marine borers. Brief mention is made of the examination of submarine cable samples from service.

I. INTRODUCTION

As a result of the increasing use of submarine telephone cable, there is a growing demand for information on the performance of organic materials and cable structures under marine conditions. Particularly important is the need for data on the resistance of materials to attack by marine organisms. Although considerable published information exists on the behavior of natural organic materials such as wood, jute, hemp and the like, there is virtually no data on plastics, elastomers, casting resins or similar materials.

About three and a half years ago, the Laboratories initiated a program to determine the resistance to marine biological attack of materials which might find application in submarine cable. The program has two primary objectives: (1) acquisition of fundamental information regarding the biological resistance of a wide range of selected organic materials, and (2) accumulation of immediately applicable engineering information on materials.

II. OUTLINE OF PROGRAM

It seemed evident that marine borers or microorganisms, particularly bacteria, might be expected to be the major agents of deterioration.

Marine borers are mollusks or crustaceans which bore into a material for food or shelter depending on the particular organism involved. Of the crustaceans, the gribble, *Limnoria*, is the most outstanding. Cellulose material such as wood and cordage form its food supply and natural habitat. There are a few references which suggest that members of the genus *Limnoria* have bored into gutta percha. One by Chilton¹ refers to the activity of *Limnoria* in the splice of a submarine cable in about 60 fathoms off New Zealand. Preece² identifies *Limnoria* as the organism responsible for failure of the Holyhead-Dublin cable in 1875. Jona³ states that he frequently found *Limnoria* in cables in the Adriatic Sea. Menzies⁴ points out that no American species is known to occur in depths exceeding 50 feet; however, one species is known to occur off Japan at a depth of 163 fathoms. He suggests that the absence of wood probably limits the distribution of the animals in deep water.

In the bibliography by Clapp and Kenk,⁵ there are ten, separate citations to the attack of submarine cables by molluscan borers belonging to the family *Teredinidae*. In most cases, attack was confined to cellulose constituents such as jute and hemp, although in a few instances mention is made of attack on gutta percha insulation. Although the teredine borers, along with *Limnoria*, are considered to be relatively shallow water organisms, Roch,⁶ in his paper on Mediterranean teredos, refers to *Teredo utriculus* being obtained from depths as great as 3500 meters. There is one reference⁷ to teredo attack of lead-covered submarine cable.

The other important family of boring mollusks is the *Pholadidae*. Members of this family are sometimes referred to as the "burrowing clams" and include rock, shell and wood borers. Some genera, such as *Xylophaga*, are found in water up to 1,000 fathoms or more deep.⁴ Bartsch and Rehder⁸ report the penetration of the lead sheath of a submarine cable by one of the *Martesia*, another genus of the family *Pholidi*-

dae. Members of the same family were reported by Snoke and Richards⁹ to have bored through the lead sheath of a submarine telephone cable.

The bacteria generally are single-celled organisms, a large number of which are heterotrophic, that attack organic matter and use it as a source of carbon or energy. The bacteria play an important part in the biology of the sea, their most important function being to decompose organic material into carbon dioxide, water, ammonia and minerals. The characteristics, distribution and function of the marine bacteria have been described in great detail by ZoBell.¹⁰ Bacteria are found in sea water and sediment from shallow depths to the deepest portions of the sea. During the Danish Galathea Deep-Sea Expedition from 1950 to 1952, bacteria were found in depths as great as 10,280 meters.¹¹ Many of these bacteria have been found to be barophilic²¹, growing exclusively or preferentially at pressures approximating 15,000 psi. ZoBell and Morita¹² have reported experiments performed with these bacteria to determine the effects of high pressure on such factors as viability and enzyme production. Marine bacteria have been found capable of oxidizing rubber products,13 as well as a wide variety of gaseous, liquid and solid hydrocarbons. 14 Although evidence to date indicates that among the microorganisms, the bacteria are particularly likely agents of deterioration in the ocean, it is possible that the fungi may also be contributors. Barghoorn and Linder¹⁵ report the physiological behavior and growth on various media of seven species of marine fungi isolated from wood continuously submerged in the sea. Deschamps²⁰ has discussed the role of fungi and bacteria in aiding the attack of wood by marine borers. Also, the occurrence of marine fungi in wood test panels, driftwood and piling in Biscayne Bay has been reported by Myers.¹⁶

A program designed to provide fundamental and engineering data on the susceptibility of organic materials to marine borers and microorganisms in an environment that covers about 70 per cent of the earth's surface could be almost unlimited. The practical parameters which finally were established were based on a number of considerations. Fundamental data on the basic inertness or relative rates of attack by microorganisms could best be determined under controlled laboratory conditions; however, more than one procedure would be needed to determine performance in the environments of water and sediment. Because of the relatively rapid activity of marine borers under natural conditions, and their critical requirements as far as laboratory culture is concerned, it was decided that any borer tests would be conducted in the field. This meant that the natural exposure tests would serve as correlative tests

for the laboratory microbiological portion of the program, as well as a means of evaluating the relative performance of materials in the physical and chemical conditions of the ocean.

The integrated program, shown in Fig. 1, involves a series of three laboratory tests on the one hand, and actual marine exposure on the other. Eventually, more than fifty different materials including plastics, elastomers, natural and synthetic fibers, as well as sections of cable will be tested. The present paper is in the nature of a progress report in which only a portion of the data to be acquired are presented. The results of the program to date will be examined beginning with the laboratory experiments.

III. LABORATORY TESTS

3.1 Biochemical Oxygen Demand Type Test

The BOD (biochemical oxygen demand) type of test as applied in this study is really composed of two separate bioassay procedures. In one case, the oxygen consumed by aerobic bacteria is determined, and in the other a metabolic by-product resulting from anaerobic activity is measured. With a few changes, both methods follow those which have been employed by ZoBell¹³ in tests of elastomers and various natural organic materials.

There is one point which should be emphasized regarding both the aerobic and anaerobic procedures used in this accelerated sea water test. It is considered primarily a screening test which provides basic data on

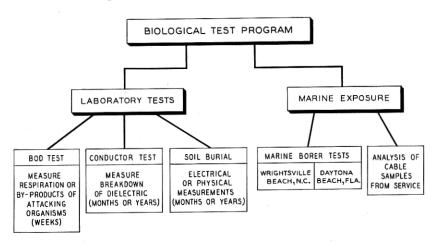


Fig. 1 — Outline of marine biological test program.

the ability of marine bacteria to utilize a compound as a carbon source at the time of test. It will not reflect changes brought about in the material due to prolonged exposure in sea water, or ecological relationships which might make the material more or less susceptible to attack by certain bacteria. The other laboratory tests and natural exposure test will help furnish data on questions involving changes in materials due to long-term marine exposure.

TABLE I — MATERIALS TESTED AGAINST AEROBIC AND ANAEROBIC MARINE BACTERIA

Designation	Туре
Polyethylene ¹ 2.0 melt index ² 0.2 melt index (Source A) 0.2 melt index (Source B) 0.2 melt index + 5% butyl rubber + antioxidant 0.2 melt index + antioxidant 0.7 melt index (high density) nat. + antioxidant 0.7 melt index (high density) + carbon black and antioxidant Belief and Charita's	P5310466 P5304156 P5312587 P5308396 P5308390 P5503135 P5503133
Poly(Vinyl Chloride) ³ Plasticizer Polyester A Di-2-ethylhexyl phthalate (DOP) Shore A 88 Tricresyl phosphate (TCP) None (rigid) None ⁴ None ⁴ Tri-2-ethylhexyl phosphate Nitrile rubber/polyester C Di-2-ethylhexyl phthalate (DOP) Shore A 62 Nitrile rubber Polyester E/DOP (BTL 46-55) None (PVC resin) Casting Resins Epoxide (cast), unfilled straight epoxy resin cured with	BTL 24-54 BTL 23-54 BTL 529-53 P5503087 P5502078 P5502077 P5502081 P5502074 P5502082 P5502076 P5503115 P5510645
amine hardener Styrene polyester, silica-filled Elastomers ⁵ GR-S jacket GR-A jacket Butyl jacket Natural rubber jacket Neoprene jacket Jute	BTL 54-14 BTL 54-18 BTL 54-19 BTL 54-23 BTL 54-164

¹ Except where noted polymers are low density grades manufactured by the high pressure process.

² ASTM D1238
³ With the exception of P5510645 all PVC compositions contained typical organo-metallic type stabilizers (such as Ba, Cd, and Pb), fatty acid lubricants in low concentrations, and in some cases small quantities of inorganic fillers.
⁴ Semi-flexible PVC copolymer.

⁵ These compounds all contain, in addition to the basic elastomers, sulfur, accelerators, waxes, processing oils, and reinforcing quantities of carbon black. (54-164 also contains clay.)



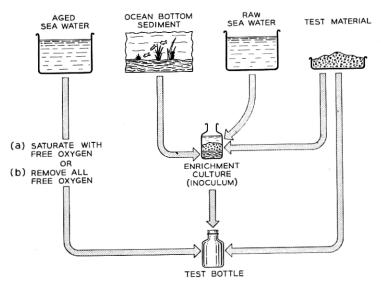


Fig. 2 — Flow chart of biochemical oxygen demand (BOD) type test.

The materials which have been tested thus far by the BOD type procedure include polyethylene, polyvinyl chloride plastics, casting resins, elastomers and jute. The individual materials are listed in Table I. Other plastics and elastomers are still to be tested.

The general features of both the aerobic and anaerobic parts of the test procedure are shown in the flow chart in Fig. 2. Certain features of the test are common to both parts. These features will be described first. The four primary constituents of the test are aged sea water, test material, ocean bottom sediment, and raw (unaltered) sea water. Aged sea water is raw sea water which has been filtered through Millipore filters of 0.5 micron pore size, and then aged in the dark until the biochemical oxygen demand (BOD) is quite low; i.e., until the water contains about 1 ppm of organic matter. This usually requires about eight weeks of aging. In the first tests which were run, materials were finely ground so as to expose a large surface area, and so accelerate attack. However, it soon became apparent in efforts to relate the rate of oxidation to surface area exposed that only crude estimates could be made of the irregular surface areas. Consequently, after the first few tests, thin sheets of material were employed wherever possible so that a measured amount of surface area could be exposed in each case.

The inoculum for the test comes from specially prepared enrichment cultures. Approximately 90 cc of marine sediment is placed in a 250 ml

prescription bottle. About 1 gram of a finely divided test material is also placed in the bottle which is then filled about three-quarters full of raw sea water. To include as heterogeneous a population of marine bacteria as possible, another inoculum is prepared for addition to the enrichment culture. The additional inoculum is made by placing in a vial a small particle of each of seven different sediments furnished by Dr. ZoBell of the Scripps Institute of Oceanography. These sediments are identified in Table II. Following this, one or two drops of liquid are added to the same vial from each of twenty-nine different enrichment cultures which also were provided by Dr. ZoBell. These cultures are identified in Table III. Transfers from eight different cultures of marine sulfate-reducing bacteria are included, and the vial shaken thoroughly. About five drops of pooled inoculum are added to the enrichment culture prepared for each test material. The completed enrichment cultures are incubated at 25° C for a minimum of six weeks prior to use. During the incubation period those bacteria in the culture which are capable of utilizing the test material tend to develop preferentially.

The same enrichment culture is used whether the test procedure is aerobic or anaerobic since both conditions prevail in this type of enrichment culture — aerobic in the water and upper sediment, and anaerobic in the deeper, compacted sediment. From this point on, in describing the method used in the material tests, it is necessary to describe the aerobic and anaerobic procedures separately.

In the aerobic tests, 0.01 per cent ammonium phosphate is added to sufficient sea water (usually about 7 liters) for a given test run. Oxygen is bubbled through the sea water in a carboy for a minimum of sixteen hours at which time the oxygen content of the sea water is about 25 ppm. Since as many as four or more test materials may be included in a test run, the inoculum is prepared by combining in one vial a small amount of liquid from the enrichment culture for each material to be

Table II — Sources of Sediments* used in Preparing Enrichment Cultures

Ref. No.	Source
XG 17-4 (surface). 5403-1 (surface). XS-384 (surface). 5402-7 (0-5 cm). 56:180 (4520 fathoms). 56:184 (2650 fathoms). 56:177 (4550 fathoms).	Gulf of Mex., Miss. Delta Gulf of Mex., Rockport, Texas Gulf of Mex., Miss. Delta Pacific, 7° 22.2'N, 127° 17'W Pacific, 19° 02'N, 174° 58'W

^{*} Obtained from Dr. C. ZoBell, Scripps Institute of Oceanography.

included in the run. Once in the vial, the inoculum is shaken and added to the aged sea water at the rate of 1 ml per 10 liters of medium. This amount of inoculum was calculated to give the maximum number of bacteria, consistent with a minimum addition of organic matter. The carboy is then placed under slight, positive oxygen pressure.

The test is run in 60 ml glass-stoppered bottles. A small amount of test material is placed in each bottle. At the outset of the experiments, when ground material was used, this amounted to 0.05 gram, or a surface area of 4 to 45 sq cm, depending on the material. Later, when thin sheets of about 4 mils thickness were used, the samples were cut to a size of 2.54 cm square. The samples are placed in the bottles the night before, and enough aged sea water added to permit surface wetting. With many materials this seems to result in less accumulation of air bubbles on the surfaces of the materials during subsequent filling with the medium.

Table III — Enrichment Cultures* Used as Supplementary Sources of Inoculum in Preparation of Enrichment Cultures for Current Program

Ref. No.	Description
34-134	rubber in distilled water
34 - 134	anthracene in sea water
34-134	sewage outfall, rubber in sea water
34-134	mixed hydrocarbons in sea water
34 - 134	garden soil, rubber in sea water
34-132	Athabaska tar sand, hydrocarbon-oxidizing bacteria and
01 102	sulfate-reducers in sea water
34-134	tricresol in sea water
34-134	mixed hydrocarbons in sea water
25-143	0.10% phenol in sea water
34-134	0.25% phenol in sea water
34-134	cork in sea water
34-134	Shell oil No. 10 in sea water
25-141	lignin in sea water
34-134	sewage outfall, rubber in sea water
34-134	sawdust and mud in sea water
34-134	garden soil, rubber in sea water
34-134	rubber in tap water
34-134	mixed crude oil in sea water
34-134	kerosene in sea water
34–134	paraffin in sea water
34-134	rubber in tap water
	Athabaska tar sand, mixed crude oil in sea water
_	thiokol in sea water
_	neoprene in sea water
	cellulose acetate in sea water
_	butadiene (Buna A) in sea water
_	pooled aerobic hydrocarbon-oxidizing bacteria in sea water
_	crude coal tar in sea water
	shellac in sea water

^{*} Obtained from Dr. C. ZoBell, Scripps Institute of Oceanography.

Of course, air bubbles would be a source of error in later oxygen determinations.

Usually, sufficient test bottles are made up to provide duplicates for analysis after each period of incubation. Oxygen pressure, maintained on the sea water in the carboy, assures no loss of oxygen from the medium and forces it through tubing into the test bottles. Since incubation periods of 0, 1, 2, 4 and 8 weeks are used as a general guide, and two test bottles must be sacrificed for analysis after each interval, ten test bottles are used for each material. One set of ten control bottles containing only inoculated, aged sea water suffices for a test run, as long as the bottles for materials and controls are made up from the same batch of sea water and incubated at the same time. Incubation is carried out in the dark in a constant temperature water bath maintained at 20° ± 0.5°C. Incubation in the water bath minimizes the fluctuation in oxygen content of the sea water which might be encountered as the result of "breathing" of the bottles in atmospheric incubation. After the various incubation periods, the free oxygen content of the sea water in the bottles is determined by a modified Winkler procedure.

In the anaerobic portion of the test, the procedure is essentially the same as for the aerobic part, the only differences being in the preparation and handling of the sea water medium, the incubation times, and the analytical method. Of course, with the anaerobic bacteria it is necessary to remove all free oxygen from the sea water medium if the organisms are to function. Consequently, instead of bubbling oxygen through the medium, the sea water is boiled for ten minutes and placed hot in a

Table IV — Oxygen Consumption by Marine Bacteria in BOD Test with Polyethylene as the Only Source of Organic Carbon

Test Material ²	O ₂ Consum	ption Afte	r Weeks of 1	Incubation
rest materiai-	1	2	4	8
2.0 melt index³	2.2 0.8 1.4 0.9 0.2 0.9	3.7 1.6 3.4 3.0 3.8 4.3 5.3	6.0 2.4 5.2 6.2 5.8 7.4 8.3	ppm 10.2 10.9 10.8 8.5 —1 9.3 11.2

¹ Samples accidentally destroyed.

² Except where noted polymers are low density grades manufactured by the high pressure process.

³ ASTM D1238

Table V — Oxygen Consumption by Marine Bacteria in BOD Test WITH POLY(VINYL CHLORIDE) PLASTICS, EPOXIDE CASTING RESIN OR JUTE AS ONLY SOURCES OF ORGANIC CARBON

Test Material	O2 Consumption After Weeks of Incubati			
Test Material	1	2	4	8
	ppm	рþт	ррт	ÞÞт
PVC — no plasticizer (rigid)	11.1	12.9	11.6	18.7
PVC — tricresyl phosphate (TCP)	9.5	13.2	21.6	22.2
Shore A 88	9.1	13.4	19.7	20.7
PVC — polyester A	19.3	22.2	*	*
Epoxide casting resin		4.1	5.1	4.2
Jute	10.0	15.0	16.5	*
Controls (inoculated sea water)	6.8	6.8	7.7	7.7

^{*} All free O2 in sea water consumed.

carboy containing 0.01 per cent ammonium phosphate. Nitrogen is introduced into the carboy immediately. When the sea water is cool, inoculum, which is prepared as described for the aerobic procedure, is added and additional nitrogen pressure placed on the carboy for filling the test bottles. Since anaerobic activity is usually slower than aerobic, the time in test is increased. Analysis for hydrogen sulfide in the sea water is carried out at 0, 4, 8, 12 and 16 weeks. Since the sulfate-reducing bacteria are ubiquitous anaerobic marine species, the hydrogen sulfide produced by them in the course of breaking down organic material is used as an indicator of their activity. The sulfide in the sea water is determined volumetrically according to the method described in the Official

Table VI — Oxygen Consumption by Marine Bacteria in BOD Test with Poly(Vinyl Chloride) Plastics AS THE ONLY SOURCE OF ORGANIC CARBON

Plasticizer -	O2 Consu	O2 Consumption After Weeks of Incubation			
r asticizet	1	2 4	4	8	
	ррт	рþт	ppm	рþт	
Nitrile rubber/polyester C	10.3	12.9	21.4	*	
Nitrile rubber	9.2	12.3	18.7	*	
None ¹	3.7	4.2	6.5	10.5	
None ¹	4.0	5.5	8.4	11.0	
Tri-2-ethylhexyl phosphate	11.7	14.4	23.1	*	
Di-2-ethylhexyl phthalate (DOP) Shore A 62.	6.4^{-1}	8.4	11.5	*	
Polyester E/DOP (BTL 46-55)	*				
Controls (inoculated sea water)	3.5	4.5	7.1	9.7	

^{*} All free O₂ in sea water consumed.

1 Semi-flexible PVC copolymer.

Table VII — Oxygen Consumption by Marine Bacteria in BOD Test with Polyethylene, Polyester Casting Resin or Poly-(Vinyl Chloride) Resin as Only Source of Organic Carbon

Test Material	O ₂ Consum	Consumption After Weeks of Incubatio			
Test Material	1	2	4	8	
	ppni	ррт	ррт	р́рт	
Polyethylene 0.7 melt index (High Dens.) Nat. + antioxidant	3.1	3.3	6.1	6.5	
Polyethylene 0.7 melt index (High Dens.) Blk Styrene polyester, silica-filled Poly (Vinyl Chloride) resin Controls (inoculated sea water)	$2.9 \\ 5.5 \\ 4.2 \\ 2.5$	4.1 7.0 4.1 3.8	$7.1 \\ 9.3 \\ 7.3 \\ 6.7$	7.0 12.1 7.2 6.7	

and Tentative Methods of Analysis of the Association of Agricultural Chemists.

The results of the aerobic test procedure are presented in Tables IV to VIII inclusive. In these tables the oxygen consumption values obtained with materials which went through the same test run are included in the same table. The materials included in Tables IV and V, with the exception of jute, were exposed in finely ground or shaved form. Since it was not possible to obtain reliable estimates of the surface areas exposed to attack in this case, the oxygen consumption values in these tables are not directly comparable with respect to rate. The data serve the important basic purpose of indicating whether these materials can serve as a source of energy for the bacteria. However, data in Tables VI to VIII inclusive are based on the use of equally thin sheets of material with about 12.9 sq cm of surface area exposed to attack. Two exceptions

Table VIII — Oxygen Consumption by Marine Bacteria in BOD
Test with Elastomers as the Only Source
Of Organic Carbon

		sumption After Days of Incubation		
Elastomer	3	7	14	28
	ppm	ррт	ppm	ppm
GR-S jacket (54-14)	$\frac{15.8}{6.1}$	10.9	23.5	*
Butyl jacket (54-19)	13.9	*	20.0	
Natural rubber jacket (54-23)	$\begin{array}{c} 14.1 \\ 1.9 \end{array}$	4.1	10.3	*
Neoprene jacket (54-164)	0.0	-0.4	0.0	

^{*} All free O2 in sea water consumed.

to this are the polyvinyl chloride resin and styrene polyester in Table VII which could not be prepared in sheet form.

Results for polyethylene are described in Tables IV and VII. The oxygen consumption values in these tables are almost identical to the control values obtained using only inoculated sea water. There is no evidence in any of these tests of polyethylene being utilized as a source of carbon by the bacteria. In fact, in Table IV, all of the eight week values for polyethylene are slightly below those for inoculated sea water alone.

The results with the polyvinyl chloride plastics vary according to the manner in which the compounds are plasticized. The data are contained in Tables V, VI and VII. First, as may be noted in Table VII, there is no attack on the polyvinyl chloride resin. This indicates that the susceptibility of these plastics can be attributed to materials added in compounding. Every polyvinyl chloride plastic tested shows some evidence of attack; (distinct oxygen consumption above the control rate), except the semi-flexible copolymers which contain no added external plasticizer. In these compounds, acrylates are employed as copolymers. The most severe attack occurred on the plastic in Table VI which con-

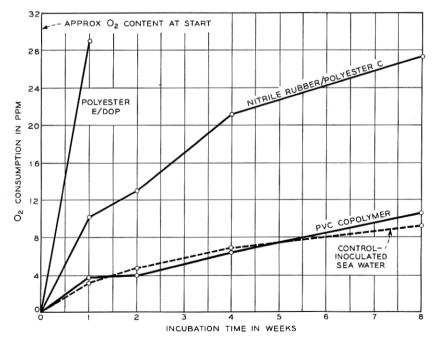


Fig. 3 — Examples of O₂ consumption by marine bacteria in BOD test with Poly (Vinyl Chloride) plastics as carbon source.

tains a combination of polyester E and di-2-ethylhexyl phthalate (DOP), and one in Table V plasticized with polyester A. These polyesters are fatty acid-type compounds. Typical oxygen consumption values for three different polyvinyl chloride plastics, representing different rates of utilization by the bacteria, are plotted in Fig. 3. As noted in Table I, very low concentrations of organo-metallic stabilizers and fatty acid lubricants were in all the compounds tested except the resin alone. However, of the three materials which contained no added external plasticizer only the rigid plastic is utilized. This material contained about 8 to 10 times as much fatty acid lubricant as the other two compounds.

Two casting resins were tested, one an epoxide (Table V), and the other a silica-filled styrene polyester (Table VII). Under the conditions of this test, the epoxide resin is not utilized by the organisms. In the case of the styrene polyester, results are less conclusive. After eight weeks, an oxygen consumption value 5.4 ppm higher than that for the controls suggests the possibility of attack. Additional tests are planned with this material to obtain more data on which to base a final decision.

As might be expected, the jute fibers are quite susceptible to attack; all oxygen was consumed from the test medium between the fourth and eighth week (Table V). The fact that results in the same test run with the polyvinyl chloride compound plasticized with polyester A show that all oxygen was consumed from the test medium in 17 days does not mean that this latter compound is more susceptible to attack than jute. In the jute, bacterial attack is necessarily restricted to a progressive surface attack, but with the polyvinyl chloride compound, leaching of the sus-

Table IX — Hydrogen Sulfide Production by Marine Bacteria in Anaerobic Sea Water Test with Polyethylene as the Only Source of Organic Carbon

	H ₂ S Prod	oduction After Weeks of Incubatio			
Test Material ¹	4 8 12 ppm ppm ppm 0.22 0.32 0.22	12	16		
2.0 melt index ²	$\begin{array}{c} 0.22 \\ 0.22 \\ 0.22 \\ 0.22 \\ 0.22 \\ 0.22 \\ 0.22 \end{array}$	1		ppm 3 3 0.38 0.58 0.24 0.45 0.58	

¹ Except where noted polymers are low density grades manufactured by the high pressure process.

² ASTM D1238 ³ Insufficient samples

ceptible plasticizer into the sea water medium might greatly accelerate utilization of that material and be reflected in rapid oxygen consumption.

Five different elastomers have been evaluated by the BOD test to date. The results with aerobic bacteria are presented in Table VIII. First, it is apparent that all of the elastomers tested can serve as a source of carbon for the bacteria. As may be noted in the table, GR-S jacket (54–14), butyl jacket (54–19) and natural rubber (54–23) are oxidized at about the same rate—all oxygen being consumed from the test medium between the third and seventh day analyses. GR-A (54–18) and neoprene jacket (53–164) are more resistant than the other three elastomers in the test. During the fourteen-day test period, approximately twice as much oxygen was consumed in the case of the GR-A as with the neoprene.

The results of anaerobic bacterial activity, as reflected by analyses for hydrogen sulfide in the sea water medium, are contained in Tables IX to XII, inclusive. As with the results of the aerobic test, materials in a given test run are included in the same table. No polyethylene is utilized as a source of carbon by the sulfate-reducing bacteria. In no case is the production of hydrogen sulfide, with different polyethylenes

TABLE X — HYDROGEN SULFIDE PRODUCTION BY MARINE BACTERIA
IN ANAEROBIC SEA WATER TEST WITH POLY(VINYL CHLORIDE)
PLASTICS, EPOXIDE CASTING RESIN, OR JUTE
AS ONLY SOURCES OF ORGANIC CARBON

	H ₂ S Prod	I ₂ S Production After Weeks of Incubation			
Test Material	4	8	12	16	
	ррт	ppm.	ррт	ppm	
Poly(Vinyl Chloride) Plastics No plasticizer (rigid) Tricresyl phosphate (TCP) Di-2-ethylhexyl phthalate (DOP) Shore	$\frac{1.90}{0.22}$	3.50 0.22	4.20 0.64	5.60 0.38	
A 88	$0.26 \\ 2.60 \\ 1.50$	$0.26 \\ 38.40 \\ 7.00$	0.26 38.40	0.61 47.70	
Nitrile rubber/polyester C	$\begin{array}{c} 1.50 \\ 4.10 \\ 0.22 \end{array}$	$9.60 \\ 0.22$	$ \begin{array}{c c} 19.98 \\ 12.40 \\ 0.90 \end{array} $	18.60 11.50 0.51	
No plasticizer¹ Tri-2-ethylhexyl phosphate	$0.32 \\ 0.26$	$0.64 \\ 0.96$	1.89	1.02 0.99	
Di-2-ethylhexyl phthalate (DOP) Shore A 62. Polyester E/DOP (BTL 46-55)	$0.22 \\ 12.20$	0.22	1.09 94.10	0.58 82.90	
Epoxide casting resin	$\frac{0.16}{1.90}$	$0.64 \\ 13.40$	0.86 38.60	$0.48 \\ 52.20$	
Controls (inoculated sea water)	0.10	0.64	0.70	0.58	

¹ Semi-flexible PVC copolymer

Table XI — Hydrogen Sulfide Production by Marine Bacteria in Anaerobic Sea Water Test with Polyethylene, Polyester Casting Resin or Poly(Vinyl Chloride)
Resin as Only Sources of Carbon

Test Material		S Production After Weeks of Incubation			
1est Material	4	8	12	16	
	ррт	ффт	ppm	þþт	
Polyethylene — 0.7 melt index (High Dens.) Nat. + antioxidant	0.35	0.58	0.90	1.12	
Blk. + antioxidant Silica-filled styrene polyester	$0.26 \\ 0.83$	$0.48 \\ 0.83$	$0.38 \\ 1.02$	$0.74 \\ 1.02$	
Poly(Vinyl Chloride) resin	0.48	0.58 0.86	0.58 0.91	0.58 0.91	

as the test material (Tables IX and XI), significantly greater than in the control bottles. In fact, in most cases it is actually less than that for the controls.

Four polyvinyl chloride plastics appear to have served as a source of carbon for the anaerobic organisms. In order of decreasing susceptibility they are the compounds plasticized with (1) polyester E/DOP, (2) polyester A, (3) nitrile rubber/polyester C, and (4) no plasticizer (rigid). Just as in the case of the aerobic procedure, the plastic plasticized with polyester E/DOP is used much more rapidly than any of the other polyvinyl chloride compounds. There is no evidence of attack on polyvinyl chloride resin, again indicating that the attack is on the plasticizers, not the polyvinyl chloride itself. In this regard, it should be pointed out again that although the polyvinyl chloride compound listed as "no plasticizer (rigid)" in the tables and text does not contain an external plasticizer (rigid)" in the tables and text does not contain an external plas-

Table XII — Hydrogen Sulfide Production by Marine Bacteria in Anaerobic Sea Water Test with Elastomers as the Only Sources of Organic Carbon

Elastomer	H ₂ S Prod	duction after Weeks of Incubatio			
Elastomer	4	8	12	16	
GR-S jacket (54-14) GR-A jacket (54-18)	ppm 0.66 0.96	ppm 0.77 0.95	ppm 0.56 0.72	ppm 0.75 0.87	
Butyl jacket (54-19)	$\substack{1.52\\1.62}$	6.64 2.48	8.03 3.58	$9.65 \\ 3.74$	
Neoprene jacket (54-164)	$\substack{1.06\\0.37}$	1.20 0.43	$0.99 \\ 0.43$	$0.96 \\ 0.42$	

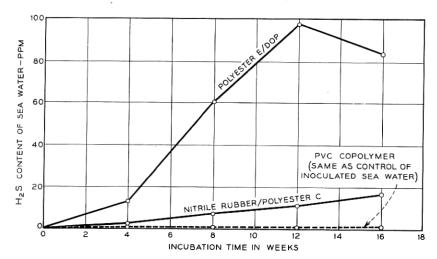


Fig. 4 — Examples of H₂S production by marine bacteria in anaerobic sea water test with Poly (Vinyl Chloride) plastics as carbon source.

ticizer, fatty acid lubricant probably serves as a source of nutrient. For comparative purposes, the examples of hydrogen sulfide production plotted in Fig. 4 are for the same plastics included in Fig. 3 which relates to the data from the aerobic procedure.

Jute is attacked by the anaerobic bacteria just as it is utilized by the aerobic organisms. However, neither the epoxide casting resin (Table X) or the polyester casting resin (Table XI) seem to serve as a source of carbon.

The results of the anaerobic test with the elastomers are presented in Table XII. It is interesting to note that early attack occurs on the natural and butyl rubber jackets, but that none of the other elastomers is utilized by the organism. It is somewhat surprising that attack on GR-S did not progress at about the same rate as on natural and butyl rubber.

The data which have been obtained in the aerobic and anaerobic parts of the BOD-type test are summarized in Table XIII. There is one outstanding fact about the data — no material was utilized by the anaerobic bacteria which was not utilized also by the aerobic organisms. Under the conditions of the test, however, materials did serve as a carbon source for aerobic bacteria and not for the anaerobes.

3.2 Conductor Test

It is apparent that the BOD test provides considerable fundamental information on the ability of halophilic bacteria to utilize organic ma-

terials as a carbon source in sea water. There is little or no opportunity for ecological factors to come into play, however, particularly with regard to marine sediment. In the conductor test, sea water and marine sediment form a part of the test environment, and the test is run over a much longer period of time, thus encouraging more natural and dynamic organism associations. Likewise, the natural relationship between material and environment is simulated more closely than it is in the more accelerated test. In these respects, the conductor test is intermediate to the BOD-type test and natural marine exposure.

The material to be tested is coated on a conductor to provide about 10 mils of insulation. A standard coil of this insulated conductor is then exposed in a 16-ounce bottle so that half of the coil is in marine sediment, and half is in sea water. The ends of the coil are brought through holes in the bottle cap and attached to terminals in the cap. The general features of the test setup are shown in Fig. 5. The bottle is incubated at 20°C. Capacitance and conductance measurements, taken monthly, indicate any change in the insulation. Some conductors are placed in sterile sea water and sediment to serve as controls. This type of test can be continued for months or years if necessary.

Most of the conductor tests are now being initiated. Two materials, however, GR-S and a rigid polyvinyl chloride, have been under study

TABLE XIII—SUMMARY OF MATERIALS UTILIZED AS SOURCE OF CARBON BY AEROBIC OR ANAEROBIC MARINE BACTERIA IN BOD-Type Test

Utilized as Source of Carbon by				
Anaerobic Bacteria				
PVC — no plasticizer (rigid)				
PVC — polyester A				
PVC — nitrile rubber/polyester C				
PVC — nitrile rubber				
PVC — polyester E/DOP (BTL 46-55)				
rvc — polyester E/DOI (BIL 40-55)				
Butyl jacket (54-19)				
Natural rubber jacket (54-23)				
Jute				

for several months in a "dry" run to establish the biological procedure, as well as the techniques of measurement which are to be employed. The capacitance and conductance data which have been obtained on these two materials to date are presented in Figs. 6 and 7, respectively. In the case of the test samples, each point represents the average value for four test coils, but for the controls each point represents only one coil.

With the GR-S test samples, there is a sharp rise in the capacitance values between the second and third month, amounting to about 110 $\mu\mu$ f. Thereafter, the rise in the curve continues, the slope decreasing somewhat at about the eighth-month point. Over the entire test period, the capacitance ranged from 632 $\mu\mu$ f at the start to 850 $\mu\mu$ f after 13 months



Fig. 5 — General setup of conductor test showing a coil half in sediment and half in sea water.

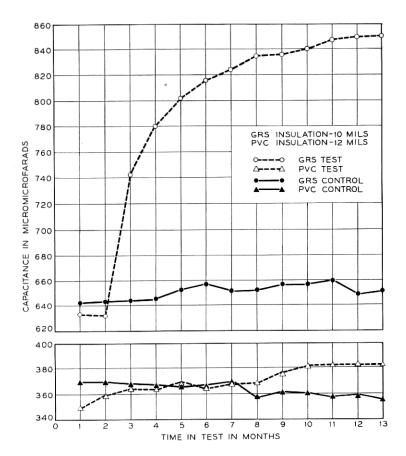


Fig. 6 — Capacitance changes resulting from exposure of GR-S (51-92) and Poly (Vinyl Chloride) (BTL 172-54) insulated conductors in sea water and sediment.

exposure — a total change of 218 $\mu\mu$ f. If it is assumed that the insulating materials were removed equally along the length of the coil, it can be computed that this change in capacitance represents a loss of 8.1 mils of insulation. The following formula is used to arrive at this figure:

$$D = d \left(\frac{D_0}{d} \right)^{C_0/C}$$

where D =present diameter in mils,

 D_0 = original diameter in mils,

d = diameter of wire in mils,

 C_0 = original capacitance in $\mu\mu$ f (start of test),

 $C = \text{present capacitance in } \mu \mu f.$

In contrast, capacitance values for the controls have remained essentially unchanged.

There has been no substantial increase in the capacitance of the polyvinyl chloride-insulated conductors although there is some evidence of an upward trend in the data for the coils in the biologically active environment. There was a rise in capacitance of about 15 $\mu\mu$ f between the one and three month period, and a similar rise between the eighth and tenth month. Future measurements should indicate whether any biological attack is occurring.

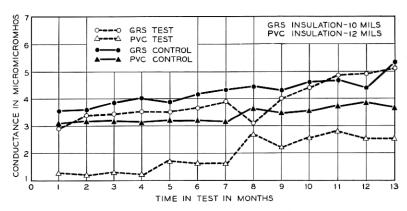


Fig. 7 — Conductance changes resulting from exposure of GR-S (51-92) and Poly (Vinyl Chloride) insulated conductors in sea water and sediment.

As may be noted from the conductance data for both materials in Fig. 7, the patterns of the curves for the test and control samples are essentially the same. In all cases there has been a slight increase in conductance over the 13 month test period. For GR-S it has increased from about 1.5 to 2.0 $\mu\mu$ mhos and for the polyvinyl chloride from about 0.75 to 1.5 $\mu\mu$ mhos.

In a test of this kind the rise in capacitance, such as that which occurs with the GR-S, without any marked corresponding increase in conductance suggests that the insulation is being modified by the attack, rather than actually removed as assumed previously. It also suggests that the action is most likely due to bacteria rather than fungi which might be expected to penetrate the insulation directly to the conductor and so have a more pronounced effect on conductance. When the test is terminated, it is hoped that these insulated conductors can be run through a capacitance and conductance monitor to locate the specific points of deterioration, and to determine the extent and type of attack.

IV. SOIL BURIAL

Since this phase of the test program is yet to be started no extended coverage is possible in this paper, except to point out the reason for its inclusion. There is some evidence in the results of the marine exposure tests at the Laboratories that the general order of susceptibility of materials to marine microorganisms is the same as it is to terrestrial microorganisms. This observation has also been supported in discussions with some other investigators. The current program at the Laboratories offers an excellent opportunity to compare the performance of a wide range of materials in the two environments. If a correlation pattern can be established, considerably more data in the literature can be brought to bear on the problem. Perhaps at a later date it will be possible to present data comparing material performance in the laboratory soil-burial test and marine-type tests.

V. MARINE EXPOSURE

5.1 Marine Borer Tests

The Laboratories, in cooperation with the William F. Clapp Laboratories, Inc., Duxbury, Massachusetts, is conducting the marine borer tests. This phase of the program was initiated in 1954 and involves the natural exposure of specimens at two locations — Wrightsville Beach, North Carolina, and Daytona Beach, Florida. These tests are aimed primarily at obtaining information on marine borer attack; however, the samples are exposed in such a way that information is obtained on microbiological activity as well. In addition, valuable data is obtained on the purely physical and chemical effects of the environment on the materials.

Wrightsville Beach and Daytona Beach were selected as test sites because of the severe and diversified borer activity present in the two areas. At present, more than fifty different materials are exposed at the two locations. Represented are plastics, elastomers and natural organic materials. All of the materials which have been put through the BOD-type test, or are still to be included, are represented in the marine borer portion of the test program. Where possible, test specimens are made in solid rod or tube form about one inch in diameter and three feet long to simulate cable shape. In the case of fibers and tapes, samples are wrapped on \(^3_4\)-inch diameter Lucite rods 3 feet long. These rods are assembled in racks of about 26 rods each. An untreated, southern pine two by four, susceptible to borer attack, is fitted around the samples at midpoint, where it functions as a bait piece to lead the organisms into direct contact with each test rod. Of course, where there is no bait piece



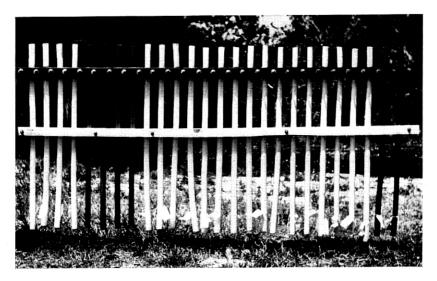


Fig. 8 — A test rack used in marine borer test prior to exposure. Note bait piece of untreated wood fastened across middle of test rods.

it is possible to determine whether the organisms can attack the samples directly from the water. Fig. 8 is a photograph of one of the racks prior to exposure in the sea. The lower 10 inches of the rods are embedded in the bottom sediment where bacterial action is relatively high. Thus, each sample is subjected to water exposure and possible borer attack through the transition zone from water to sediment and into the generally anaerobic conditions of the sediment.

Due to the short time that these tests have been in progress, it is impossible to draw extensive conclusions, particularly with regard to microbiological activity. Long exposure times may bring about physical or chemical changes in a material which may render it more, or less, susceptible to attack. However, until more detailed data are available, some interesting preliminary examples of biological activity can be cited which may be of some interest and serve to illustrate the kind of information which is steadily being acquired.

With but two exceptions, there has been no direct penetration by borers, or microbiological deterioration, of any of the plastics. Polymonochlor-trifluoroethylene in the form of a 0.0035 inch-thick tape wrapped on a 3-inch diameter Lucite rod for exposure, was penetrated at one point by a pholad. This attack occurred after three years of exposure at Daytona Beach. Apparently the mollusk bored through an accumulation of calcareous fouling and then progressed through the plastic into the Lucite rod. In another instance, after $2\frac{1}{2}$ years of exposure at Wrights-ville Beach, there was penetration of a silicone rubber test rod at a single point by a pholad. In this case, the test sample was a solid rod of the elastomer one inch in diameter. Attack occurred on the cross-sectional face of the mud end of the rod. Penetration was to a depth of about 4 mm, and the dimensions of the hole at the point of entry were 1.5 by 2.0 mm. Although these examples serve to demonstrate the ability of pholads to bore into these materials, it should be emphasized again that attack has been confined to single points and is not general on these materials.

The physical relationship of one material to another can be very important as far as borer attack is concerned. A piece of one of the Lucite rods on which jute roving was wrapped for exposure is shown in Fig. 9. The holes in the rod resulting from penetration by pholads are readily apparent. One of the organisms may be seen protruding from the left-

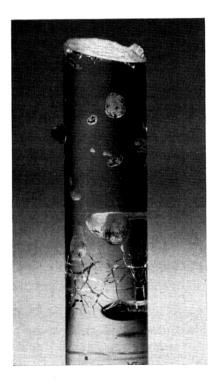


Fig. 9 — Section of Lucite rod showing penetration by pholads. One of the mollusks can be seen protruding from the left-hand side of the rod. Original magnification 2X.

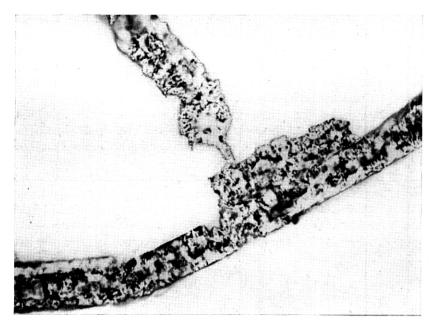


Fig. 10 — Cellulose acetate fiber showing extensive surface erosion after one year of marine exposure. Original magnification 1000X. Photo by F. G. Foster.

hand side of the rod. In this case, the pholads obtained their start in the jute wrapping and then were able to progress into the Lucite. There was no attack evident on portions of the rod which were not wrapped with jute. Also, it is interesting to note that the jute in this particular case was treated with an impregnant consisting of 50 parts asphalt, 50 parts paraffin and 2 parts zinc naphthenate. Although this mixture was not highly effective as a preservative, it did serve to hold the jute in position long enough to enable the borers to become established. There has been no evidence of penetration of Lucite rods on which untreated jute was wrapped. Here, apparently, the jute was destroyed by microbiological attack or other borers such as limnoria before the pholads could become well established.

In this progress report no detailed comparison of the performance of natural fibers, such as jute treated with various preservatives, will be attempted. Results in many cases are still inconclusive. As might be anticipated, however, the jute specimens as a group have suffered much heavier deterioration by borers and microorganisms than the plastics, elastomers and casting resins. Particularly noteworthy is the fact that although there is considerable evidence of bacterial attack upon micro-

scopic examination, there is also much degradation evident by the fungi. Pin holes in the cell walls with associated fungal hyphae are extensive.

Secondary cellulose acetate has been quite susceptible to microbiological deterioration. Yarn has been destroyed in just six months of marine exposure, not by borers, but predominantly by bacteria. Upon microscopic examination, the fibers show severe surface erosion due apparently to bacterial attack. In the marine samples which have been stained and examined, hyphae have been evident in only one isolated instance. The extent of the pitting and surface erosion in one of the marine samples after one year in test can be seen in Fig. 10. This characteristic pattern of erosion is also evident in samples of cellulose acetate yarn from soil burial. Such a sample after 60 days of burial is shown in Fig. 11. Here again attack appears to be predominantly of bacterial origin.

In the marine borer tests, the sample rods become heavily fouled in the water area, as may be noted in Fig. 12. Although these fouling organisms do not use the materials to which they attach as a source of food, it is well known that they can do mechanical damage or chemically influence the environment beneath them. The reader who is particularly interested in the broad subject of fouling and its effect on materials,

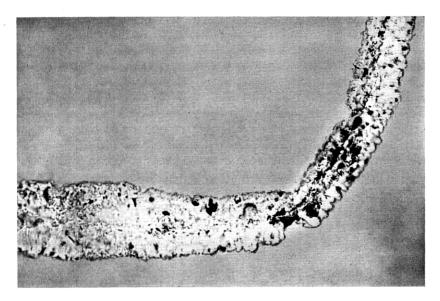


Fig. 11 — Cellulose acetate after 60 days in laboratory soil burial. Note characteristic surface erosion comparable to that shown in Fig. 10 for marine test sample. Original magnification 500X. Photo by F. G. Foster.



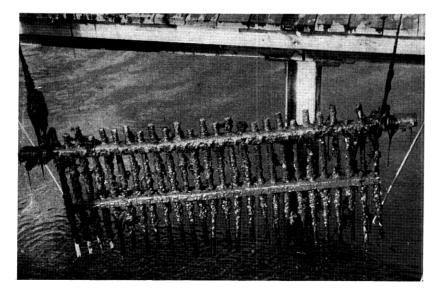


Fig. 12 — Test rack being lifted from water at Wrightsville Beach. Heavy accumulation of fouling on test rods in water-exposed area stops at point where rods entered the sediment.

structures and coatings, is referred to the report of the investigations conducted at the Woods Hole Oceanographic Institution during the years 1940 to 1946.17 The restricted areas beneath fouling, particularly under the bases of calcareous organisms such as barnacles, provide ideal cells for bacterial activity. Conditions of pH and aeration may be markedly different in these confined areas from those in the surrounding water. Some of the test rods made of polyvinyl chloride plastics containing basic lead stabilizers, illustrate the fact rather dramatically. Anaerobic, sulfate-reducing bacteria are common marine organisms which release hydrogen sulfide in the process of breaking down organic material. Under tightly adhering fouling, aerobic bacteria can utilize the free oxygen much more rapidly than it can be replaced by diffusion from the surrounding water. Once the oxygen has been depleted, the anaerobic organisms begin their activity and cause relatively high concentrations of hydrogen sulfide to be built up. The hydrogen sulfide reacts with the basic lead salts used as stabilizers and produces black lead sulfide. The sharp boundaries of the different environmental conditions existing beneath the base of a barnacle on one of the polyvinyl chloride test rods are illustrated in Fig. 13. Here the pattern of the barnacle base has literally been reproduced by the sulfiding which occurred under it. The black border and black radiating lines correspond to areas of exceptionally close contact. The radial extent of this sulfiding in the bottom end of the rod which was embedded in the sediment, as compared to the top or water end, is shown in Fig. 14. It must be emphasized that there has been no indication to date of any adverse effect on the physical properties of plastics which have been sulfided in this way.

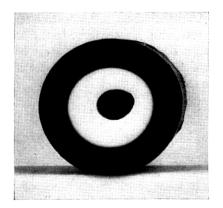
VI. CABLE SAMPLES FROM SERVICE

The samples of submarine cables which have been examined to the present time represent both telegraph and telephone cables. The samples of telegraph cable have been obtained through the cooperation of the Western Union Telegraph Company. It takes considerable time to assemble a large number of specimens during the course of routine repair operations. As a result, although some 22 different samples, the majority from the North Atlantic, have been examined, it is possible to make only



Fig. 13 — Sulfiding of Poly(Vinyl Chloride) plastic test rod beneath barnacles. The black, circular border and center area represent sulfiding at points of exceptionally close contact. Original magnification 2X. Photo by J. B. DeCoste.





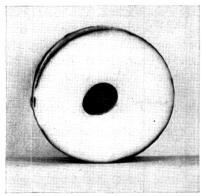


Fig. 14 — Cross-section of Poly(Vinyl Chloride) rod showing sulfiding due to sulfate-reducing marine bacteria. Bottom end was in sediment — top in water. Exposed at Daytona Beach for two years. Original magnification 1.6X.

general observations and broad comparisons. The locations and depths from which the samples were obtained are given in Table XIV. In most cases, a sample 3-feet long is obtained. Twenty-two different pieces of such size represent a rather small sample with respect to the total marine environment. Here again the program assumes more value as additional samples are obtained.

The procedure employed in examining one of these cable sections is about as follows. First, the over-all external condition is observed and recorded. Then, the outer jute covering, armor wires, inner jute bedding, and cloth and metallic tapes, if any, are removed progressively. The armor wires are examined in detail by electrochemists to determine the extent and kind of corrosion. The jute is tested in various ways. If sufficient material is available tensile strength is measured. Microscopic examination of representative fibers is also made. In the case of the inner jute which is not treated with tarry materials, damage counts are run according to the procedure of MacMillan and Basu.¹⁸ According to this method, deoiled and dewaxed fibers are permitted to swell in 10 per cent sodium hydroxide solution. Following this they are treated in a bath of 133 per cent weight to volume, aqueous zinc chloride solution over steam. Undamaged fibers swell as tight helices while damaged fibers swell as bundles of parallel fibrils. The fibers are mounted in zinc chloride solution on a microscope slide and counted to determine the per cent of damaged fibers.

To examine the integrity of the insulation on the conductor, the electrolytic procedure of Blake, Kitchin and Pratt¹⁹ is used. An electrolytic cell is set up with 20 per cent copper sulfate solution as the electrolyte, and a copper plate as the anode. The cathode is a loop of the insulated conductor from the cable. Any plating out of copper on the cathode indicates a break in the insulation. In this way the integrity of a relatively long length of conductor can be examined critically and simply.

One of the outstanding facts apparent from the examination of cable samples has been the evident importance of the outer jute in limiting the corrosion of armor wires. Galvanized steel armor wires which still retain the protection of flooding compounds, such as asphalt, tar or pitch, together with outer servings of impregnated jute, have shown negligible steel corrosion within 40 years, and in one case for as long as 66 years. On the other hand, most of the corrosion of armor wires which has been observed has occurred in cable from which a major part, or all, of the outer jute has been lost.

TABLE XIV — LOCATIONS AND DEPTHS FROM WHICH SUBMARINE
CABLE SAMPLES HAVE BEEN OBTAINED FOR
LABORATORY EXAMINATION

BTL No.	Location		Depth	
	Latitude	Longitude	Fathoms	
110	approx. 81° 30′ 00″N	24° 30′ 00″W	5 approx.	
111	approx. 81° 30′ 00″N	24° 30′ 00″W	5 approx.	
112	approx. 81° 30′ 00″N	24° 30′ 00″W	5 approx.	
113	approx. 81° 30′ 00″N	24° 30′ 00″W	5 approx.	
114	approx. 81° 30′ 00″N	24° 30′ 00″W	5 approx.	
135a	23° 45′ 00″N	81° 57′ 30″W	830	
136	Several miles south of Lo			
100	Exact location unknown.		90	
137	40° 13′ 40″N	71° 07′ 25″W	90	
163	48° 36′ 06″N	36° 23′ 36″W	2460	
164	51° 53′ 42″N	10° 37′ 18″W	54	
165	51° 40′ 42″N	13° 02′ 12″W	630	
166	51° 55′ 21″N	11° 58′ 18″W	387	
167	47° 52′ 24″N	38° 23′ 12″W	2460	
168	47° 22′ 06″N	42° 14′ 12″W	2175	
169	36° 41′ 46″N	25° 38′ 09″W	1180	
195	45° 28′ 21″N	60° 20′ 24″W	106	
196	46° 41′ 36″N	56° 18′ 18″W	37	
197	47° 00′ 32″N	56° 51′ 40″W	100	
200	44° 25′ 40″N	63° 25′ 15″W	46	
212	45° 08′ 38″N	54° 33′ 06″W	82	
281	43° 38′ 10″N	55° 07′ 00″W	2090	
282	39° 17′ 24″N	70° 12′ 15″W	1450	
283	53° 57′ 00″N	165° 50′ 00″W	Unknown	



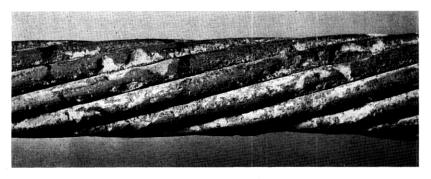


Fig. 15 — Corrosion pockets in galvanized steel armor wires of submarine cable after 12 years of service.

Of special interest is a particular type of corrosion which has occurred in two separate cable samples — one from Alaskan waters, the other from off the southern coast of Newfoundland. In one case the age of the cable was 12 years, and in the other 36 years. The Alaskan sample was located in an area characterized by water velocities of 5 to 9 knots. In both instances, the outer jute and most of the flooding compound was gone. Corrosion, instead of starting and progressing on the outer surface of the wires, had started, and been confined largely to the sides of the wires. Usually there are corresponding areas of corrosion on two adjacent wires to form "corrosion pockets." These pockets are illustrated in Fig. 15. In the case of the 12 year old cable, corrosion caused failure of the armor wires. In the case of the cable which was in service 36 years, failure was reported to have occurred from chaffing on a rocky bottom. Close examination suggests that failure may more reasonably be attributed to severe corrosion of the type just described. The exact cause of the corrosion pattern is still to be determined.

Sufficient samples have not been examined as yet to form a coordinated picture with respect to the inner jute. In the case of cable samples from the North Atlantic, the inner jute bedding was in good condition in cables which had been in service for as long as 30 or 40 years. Samples more than 40 years old showed the effect of deterioration. Although only a limited number of samples have been examined from the Caribbean, most of them from water about 50 feet deep, jute and cotton tape components were in poor condition in certain spots. It was evident that microbiological deterioration of the jute had occurred. In no case has there been any evidence of deterioration of the insulation of the central conductor of any of the cable samples. In the case of the older cable samples the insulation was gutta percha, but in the most recent samples it has been polyethylene.

VII. SUMMARY

A progress report has been presented on the results of a test program designed to determine the relative resistance of materials to marine biological attack. Specific test results have been reported wherever possible, predominantly from the laboratory test procedures. In the case of the natural exposure tests, which are intended to provide correlative data for the laboratory program over longer periods of time, the information which has been assembled thus far is of a more general nature. There follows a summary of the more important information which has been obtained:

- 1. In the biochemical oxygen demand-type test it has been found that polyethylene is not utilized by the aerobic bacteria or the anaerobic sulfate-reducing bacteria. Polyvinyl chloride plastics are attacked according to the way in which they are plasticized. All of the samples tested which had an added external plasticizer, including the rigid plastic, were attacked to some degree. In the latter case the attack was apparently due to lubricants. The semi-flexible polyvinyl chloride copolymers, and the polyvinyl chloride resin alone, were not utilized by the bacteria. The five elastomers assayed were all attacked by aerobic bacteria, neoprene being the most resistant. The epoxide casting resin did not serve as a source of carbon for the organisms, but further testing is required with a polyester casting resin.
- 2. Coiled conductors insulated in one case with a rigid polyvinyl chloride, and in the other with GR-S, have been exposed half in sea water and half in marine sediment in the laboratory for thirteen months. Capacitance measurements show that a considerable change has occurred in the GR-S insulation apparently as a result of bacterial attack. Although there has been a slight rise in the capacitance values for the polyvinyl chloride-insulated conductors during the last five months, further observations are necessary before attack can be considered definite.
- 3. In three years of actual marine exposure of plastics, elastomers and pasting resins, there have been definite penetrations by marine borers of only three materials a test rod of silicone rubber, a 0.0035-inch film of polymonochlor-trifluoroethylene wrapped on a Lucite rod, and on Lucite rods themselves. The first two cases represent single instances of penetration both by pholads. The Lucite rods were penetrated at many places by pholads as a result of the organisms getting started in an asphalt-impregnated jute wrapping and then progressing into the Lucite.

Secondary cellulose acetate yarn and tow have been deteriorated badly, apparently by bacteria, in as short a time as six months.

Natural fibers, notably jute, have been degraded extensively by borers and microorganisms. There is considerable evidence of fungus attack.

Under fouling and in the sediment area, rods of polyvinyl chloride plastics containing basic lead stabilizers have been blackened as the result of hydrogen sulfide produced by sulfate-reducing bacteria reacting with the lead salts to give black lead sulfide. This sulfiding has caused no apparent degradation of the physical properties of the plastics.

4. The examination of cable samples from service has indicated that the impregnated outer jute serves an important function in limiting corrosion of armor wires. Generally, when corrosion is present the outer jute has been lost.

Two unusual cases of extensive corrosion have been reported — one in a cable 12 years old, the other in a cable which was in service 36 years. In both cases, corrosion occurred in pockets between adjacent armor wires rather than on the outside surfaces (water side) of the wires.

The performance of the inner jute in samples from service has been generally good for as long as 30 or 40 years in deep water. In samples from relatively shallow water in the Caribbean, inner jute bedding was badly deteriorated in as short a time as five years.

ACKNOWLEDGMENTS

The data which have been acquired in this program are the result of teamwork by many different members of the Laboratories. Special thanks are due to Priscilla Leach for obtaining much of the data in the BOD test, and her general assistance on many phases of the program. Madeline L. Cook is responsible for the majority of the electrical measurements in the conductor tests. T. D. Kegelman, formerly of the Laboratories, and W. C. Gibson gave considerable assistance in setting up the equipment and establishing the procedures for measurement of capacitance and conductance. Many members of the Chemical Research Department cooperated in furnishing the materials which have been tested. J. B. DeCoste has been particularly helpful in assembling the required information on the materials. From outside the Laboratories, Professor Claude E. ZoBell of the Scripps Institute of Oceanography has made many helpful suggestions and comments with regard to the laboratory portion of the program, and provided supplementary enrichment cultures and samples of sediment. The marine borer test program has been executed with the cooperation of A. P. Richards, William F. Clapp Laboratories, Inc., who has furnished much valuable information in many discussions of the tests. The cooperation of C. S. Lawton, Western Union Telegraph Company, and the personnel of C. S. Lord Kelvin in

obtaining samples of telegraph cable from service is gratefully acknowledged.

REFERENCES

- C. Chilton, The Gribble (*Limnoria lignorum*, Rathke) Attacking a Submarine Cable in New Zealand. Annals and Mag. Natural History, Ser. 8, 18, p. 208, 1916.
- 2. G. E. Preece, On Ocean Cable Borers, Telegr. Jour. and Electr. Rev., 3, pp.

296–297, 1875. 3. E. Jona, I cavi sottomarini dall'Italia alla Libia, Atti della Soc. ital. per il

- Progr. delle Sci., 6, pp. 263-292, 1913.
 4. R. J. Menzies and Ruth Turner, The Distribution and Importance of Marine Wood Borers in the United States, presented at Second Pacific Area National Meeting, A. S. T. M., Paper 93, 1956.
 W. F. Clapp, and R. Kenk, Marine Borers, A Preliminary Bibliography, Parts I and II, The Library of Congress, Tech. Inform. Div., Washington,

- D. C., 1956. 6. F. Roch, Die *Teredinidae* de Mittelmeeres. Thalassia **4,** pp. 1–147, 1940. 7. Notes on Everyday Cable Problems. Distribution of Electricity, **8,** pp. 1896– 1898, W. T. Henley's Telegraph Works Co., Ltd., London, November, 1935.
- 8. P. Bartsch and H. A. Rehder, The West Atlantic Boring Mollusks of the Genus Martesia, Smithsonian Inst. Misc. Collections 104, Washington, D. C., 11, 1945.
- 9. L. R. Snoke and A. P. Richards, Marine Borer Attack on Lead Cable Sheath, Science, 124, p. 443, 1956.

 10. C. E. ZoBell, Marine Microbiology, Chronica Botanica Co., Waltham, Mass.,
- 1946.
- R. Y. Morita, and C. E. ZoBell, Bacteria in Marine Sediments. Off. of Naval Res., Research Reviews, p. 21, July, 1956.
 C. E. ZoBell and R. Y. Morita, Effects of High Hydrostatic Pressure on Physical Physical Pressure on Physical Physical Physical Physical Physical Physical Phy
- ological Activities of Marine Microorganisms, Off. of Naval Res., Contr. N6 onr-275 (18) Project NR 135-020, Semi. Ann. Prog. Rept., July, 1955.

 13. C. E. ZoBell and Josephine Beckwith, The Deterioration of Rubber Products by Micro-Organisms, Jour. Amer. Water Works Assoc., 36, pp. 439-453, 1944.
- C. E. ZoBell, Action of Microorganisms on Hydrocarbons, Bact. Rev., 10, Nos. 1-2, March-June, 1946.
 E. S. Barghoorn and D. H. Linder, Marine Fungi, Their Taxonomy and Bi-
- ology, Farlowia, 1, pp. 395–467, Jan., 1944.

 16. S. P. Myers, Marine Fungi in Biscayne Bay, Florida. Bull. of Marine Sci. of the Gulf and Caribbean, 2, pp. 590–601, 1953. 17. Marine Fouling and Its Prevention. United States Naval Institute, Annapolis,
- Marine Fouting and Its Freeenton. Cinted States Naval Institute, Minapolis, Md., 1952.
 W. G. MacMillan and S. N. Basu, Detection and Estimation of Damage in Jute Fibers Part I: A New Microscopic Test and Implications of Certain Chemical Tests. Jour. Text. Inst., 38, pp. T350-T369, 1947.
 J. T. Blake, D. W. Kitchin and O. S. Pratt, The Microbiological Deterioration of Rubber Insulation. Presented at A.I.E.E. General Meeting, New York, Lett. 1052
- Jan., 1953.
- 20. P. Deschamps, Xylophaga Marins. Protection de Bois Immergés contres les Animaux Perforants. Peint.-Pigm.-Vern., 28, pp. 607-610, 1952.
- 21. C. E. ZoBell, Some Effects of High Hydrostatic Pressure on Physiological Activities of Bacteria, Proc. Soc. Amer. Bact., pp. 26-27, 1955.

