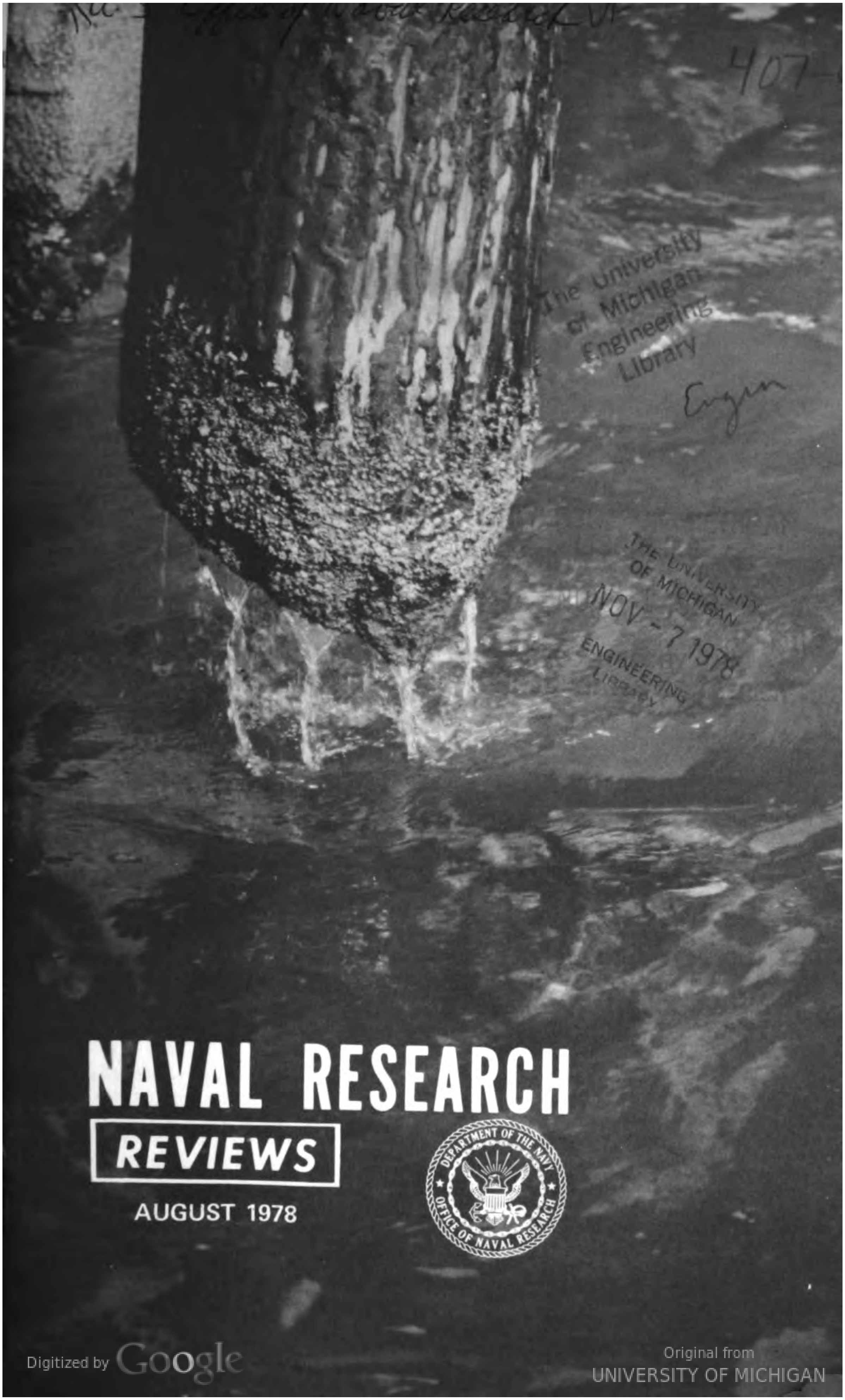

NAVAL RESEARCH REVIEWS

AUGUST 1978

PROFILES IN SCIENCE

Dr. Arthur L. Schawlow

Dr. Arthur L. Schawlow is the J.G. Jackson — C.J. Wood Professor of Physics at Stanford University. Before joining Stanford in 1961, he was a research physicist at Bell Laboratories. There with Charles H. Townes, he wrote the first paper to show that lasers were possible and how they could be made. Since then, he has been exploring novel kinds of lasers and their uses for investigating properties of matter. Also with Townes he is co-author of the book, *Microwave Spectroscopy*, an outstanding text in the field. Professor Schawlow's acomplishments include important research in the fields of optical and microwave spectroscopy and superconductivity. Today he is the principal investigator on an Office of Naval Research program for research on advanced laser sources.

Professor Schawlow was President of the Optical Society of America in 1975. He is a member of the National Academy of Sciences and of the American Academy of Arts and Sciences. In 1977 he was awarded the Marconi International Fellowship.

The Naval Research Laboratory and Marine Wood-Destroyers

John D. Bultman*
Naval Research Laboratory

Vignettes on Marine Wood-Destroyers

Since the dawn of recorded history man has been plagued by the depredation of his wooden ships and harbor installations by marine borer infestation and fungal decay. In ancient times the poet Ovid (43 BC-19AD) referred to borers (1), "For as the ship by hidden shipworm spoil'd," and Pliny the Elder (2) reported the "piercing of oak by teredos." Later, Marco Polo (3) described the practise of Chinese seafarers of protecting the planking of their ships against these creatures with a mixture of lime, chopped hemp, and a certain wood oil. Since then many accounts have appeared telling of unhappy encounters between mariners and marine wood-destroyers.

History tells us that wooden-hulled vessels often became so weakened by the boring activity of these organisms that they broke up even in moderate seas, or, more ignominiously, simply sprang catastrophic leaks and expired in sheltered tropic coves. Such was the shattering experience of Christopher Columbus. While returning from his fourth voyage to the New World in 1503, Columbus lost all four of Queen Isabella's caravels to the shipworm and its insatiable appetite for wood (4, 5). *Gallego* and *Vizcalina* were abandoned not far from Portobello on the Caribbean coast of Veragua, now modern Panama. By feverish bailing his crews were able to get the remains of his borer-infested and sinking fleet, *Capitana* and *Santiago de Palos*, to St. Ann's Bay, Jamaica, where they were run aground and converted into dwellings. Of course, the good Admiral, who had to make

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an inglorious journey home on what must have been the first Rent-A-Boat, probably had to answer to the Queen for the loss of her property. History does not record this confrontation – however it is known that the female is the deadlier of the species, especially when the equivalent of a good chunk of royal jewelry is lying irretrievably at the bottom of some distant sea!

And in 1588 the glorious and invincible Spanish Armada sailed confidently up the English Channel bent on the destruction of the "Sceptred Isle"; about half of these mighty vessels returned to Spain. Credit for this singular defeat is given jointly to the stout English navy, foul weather, and other causes. However it has been suggested (6) that part of the credit may also belong to unsung teredine allies of the English who signed on as deckhands while the Armada was becalmed, or as it stopped at warm-water ports-of-call on its nearly three-month journey to the English Channel. It is alleged that by the time this impressive array of fighting ships reached the scene of battle, the saboteurs had done their job well.

Seaside installations were not immune. For example, in the early 1700's the piling of the dikes protecting the Dutch lowlands from inundation by the sea were found badly infested by teredinids and limnorians. If the borers had succeeded in their attempt to destroy this piling, much of the Netherlands might have become one gigantic swimming pool (7). And perhaps the most infamous victory for marine wood-destroyers in modern times was the destruction of waterfront structures by teredinids between 1919 and 1921 in the northern reaches of San Francisco Bay (8). The damage was done primarily by *Teredo navalis*, aided and abetted by Mother Nature who arranged for a prior 3-year drought to get things started. The drought served to decrease fresh water runoff from the rivers and to increase the salinity of the northern Bay water to a tolerable level for the borers. By 1921, the wily little worms had taken the property owners for a staggering $25 million, as structure after structure crashed into the water at the slightest impact, or often because of their own dead weight.

Co-conspirators with the marine borers in the destruction of wood in marine service are the fungi whose diverse forms collectively attack wood above and below the waterline, and many were the accounts "of ships so rotten that it became necessary to strap their hulls with cables to keep the planking intact." In fairness to the truly marine fungi, most of the damage was done by terrestrial forms with an inclination to go to sea and who began their sea duty while their future homes were still under construction. For example, in 1810 the 100 gun *Queen Charlotte* (9) suffered such extensive fungal damage during construction and subsequent fitting that she had to be completely rebuilt before commissioning. Total cost of these repairs was more than three times the original cost of the vessel.

And more dramatically, while riding at anchor in Plymouth Harbor in 1782, one of the proudest ships of the British line, the 100 gun Royal George, "suffered her bottom to fall out" while heeled over for minor repairs; she came to rest on the bottom along with several hundred crewmen and the much less expendable Admiral Kempenfeld, thereby attesting to the lack of rank consciousness by the fungi responsible for this catastrophe (10). On the positive side, these organisms did provide the British Navy with a new, rapid, and unique scuttling technique which was amply demonstrated in the dispatch of the converted warship *Bute*; the act was performed by a sailor clenching his fist and "driving it without much pain to his knuckles, clear through her hull"(10).

Protective (?) Measures

The literature on marine wood protection, particularly from the borers, is filled with seemingly endless descriptions of attacks launched by man against these ancient enemies – most of which have ended in some degree of failure. It is not possible to review all the many schemes which have been employed over the centuries to protect wood in marine service from the boring animals. Deep charring of the wood was an ancient practice; another was the use of a sheathing material of animal skins, wood, or metal over the hull planking. Wood was used in the form of a thin, sacrificial outer cover usually separated from the main hull by a bituminous substance loaded with animal hair. Lead, used as sheathing material from very early times, caused galvanic corrosion of iron fasteners and fittings. This metal was superseded in the 17th century by copper which was fastened to the hull (in England) over a layer of tarred paper. Again iron fasteners could not be used because of their susceptibility to galvanic corrosion. Although quite expensive, metal sheathing apparently dealt the marine borers a grievous blow; the fungi continued to thrive happily because they attacked from a different quarter. Beside cost, the most serious disadvantage to metal sheathing seems to have been the susceptibility of the metal to mechanical damage. Breaches in the integrity of the metal barrier became points of infestation by borers.

One of the most interesting metal-related hull treatments was scupper nailing or "filling", the practice of driving large-headed iron nails into a ship's hull or sheathing boards (or into piling) so close together that the heads nearly overlapped. In theory, the nail heads corroded and the corrosion products filled the interstices between them. Apparently, this technique was less than perfect (11, 12); it must have been a most efficient means of splitting and weakening the underlying wood, adding weight to the vessel, and keeping the nail manufactures prosperous.

Coating the hulls of unsheathed vessels with pitch, tar, or other bituminous products, with or without such additives as crushed glass or cow's hair, or impregnating the wood tissues with a wide variety of chemical repellents or toxicants were also among the many remedies employed. Nor does man's modern arsenal of combative techniques provide complete protection – not even the nostril-titillating mixture of goat fat and lime smeared on the hulls of present day Arab dhows plying the coast of the Indian Ocean (13).

The Enemy

Wooden-hulled sailing ships are gone, but man's battle with these wood-degraders still continues. Fixed wooden structures which he still has the audacity to place in the marine environment are promptly set upon in spite of the protective measures used; not every battle is won as illustrated by Figures 1-3 (and other figures appearing throughout the text).

Figure 1 – Fender timber thoroughly infested by teredine borers. The outer surface of the wood gives the untrained observer little indication of the extent of internal damage that has occurred.

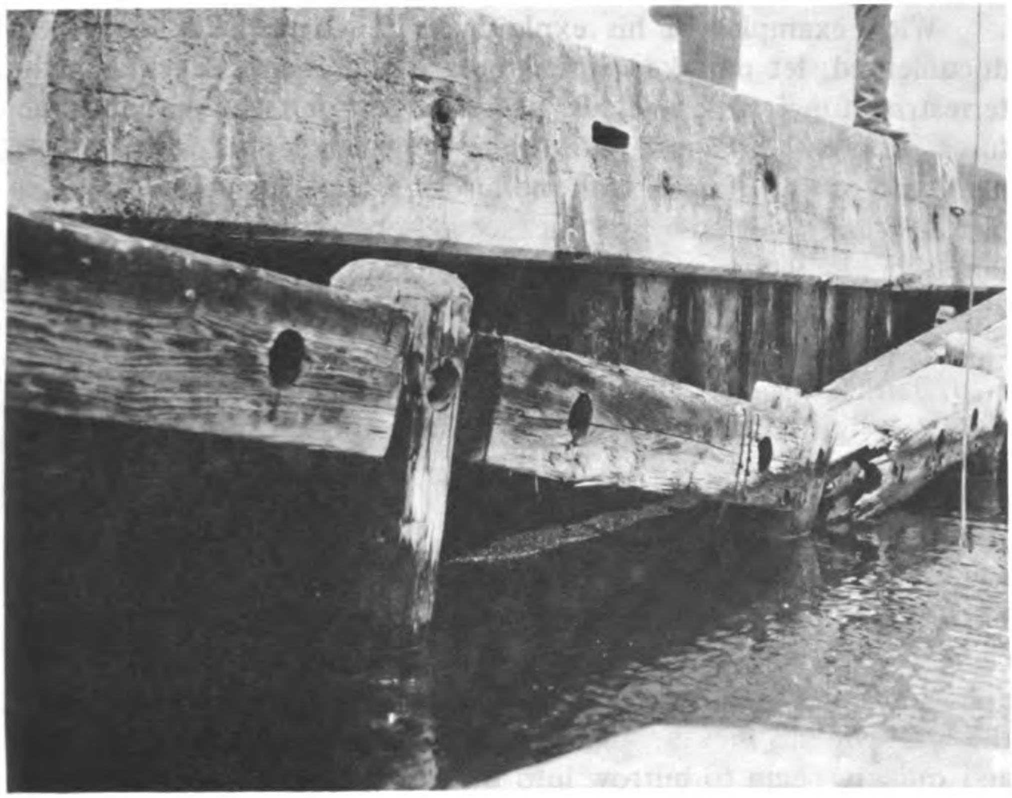

Figure 2 — Fender system at Coco Solo, C.Z. The piles have collapsed and torn away from the concrete pier, carrying the cross-members (wales and chocks) with them. The end of one chock is damaged by fungi.

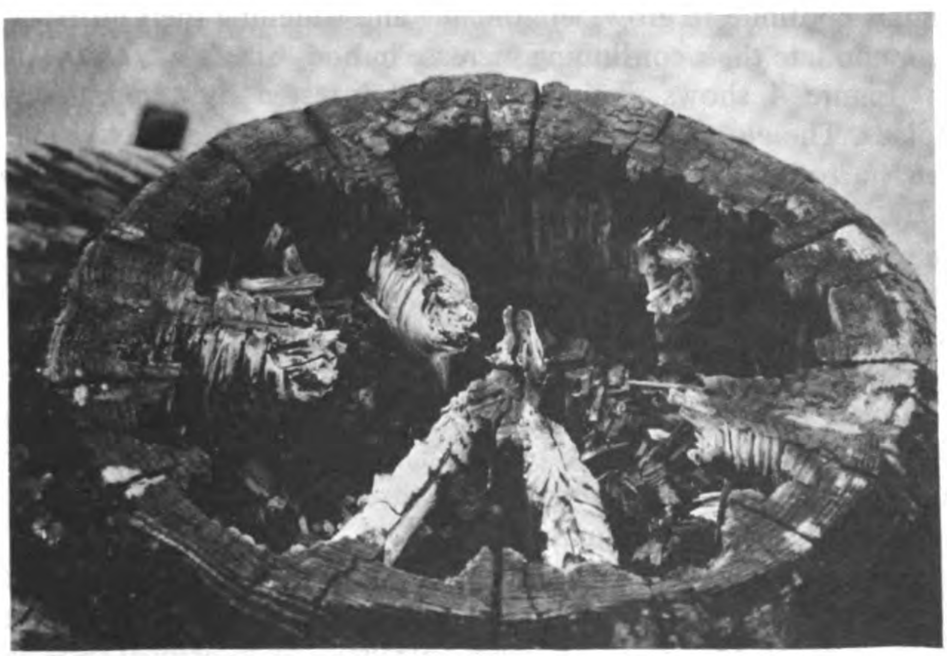

Figure 3 — Top of a creosoted fender piling showing extensive fungal damage. The wood is almost completely destroyed to a depth of 10 cm (4 in.).

With examples of his exploits on the battlefield adequately documented, let us take a brief look at the enemy. Excluding the terrestrial fungi which attack unsubmerged parts of marine structures, most wood damage in the marine environment is caused by the members of two families of molluscan borers, the teredinids and pholads, and one family of crustacean borers, the limnorians. Each family contains many species of differing genera, and nearly all have a craving for wood. For a detailed account of the life-style of these creatures, interested readers are referred to excellent monographs by R.D. Turner on teredinids (14, 15) and pholads (16) and by A.C. Oliver on limnorians (17). There are many others.

The Teredinids

The teredinids, known as teredos or shipworms, are molluscan borers of the family Teredinidae. These animals resemble very small clams whose "insides" are mostly outside of the shell which serves as a boring apparatus. From a free-floating larval stage in the water, those individuals lucky enough to find a wood surface settle upon it and quickly begin to burrow into the wood as they metamorphose; the entrance holes are tiny, nearly invisible to the casual observer. During the larval stage the teredinids are very vulnerable; predators and failure to settle on a suitable wood surface deplete the population. However once in the wood where they will remain for life, the animals continue to grow, lengthening and widening their burrows to accommodate their continuing increase in body size.

Figure 4 shows a piece of wood infested by teredinids and pholads. The elongated bodies of the teredinids are clearly visible in their burrows, and three points of entry into the wood are shown (A-C). Regardless of the number of teredinids in a piece of wood, or the extent to which they have reduced the interior of the wood to a confusion of intertwining tunnels as shown here, they somehow manage to avoid each other, nails, knots, and other impediments to their progress. And they never break through the outer boundaries of the wood. How these marvelous feats of navigation are accomplished is not known. However, the pholad has no respect for the teredinid and his tunnel and will burrow right through one if it happens to be in the way, killing the animal within.

The calcareous tunnel linings produced by the teredinids are shown more clearly as the white tubes in the wood in Figure 5; these linings thicken toward the burrow entrance. At their posterior ends the teredinids possess a very effective mechanism (pallets–Figure 6) for sealing off their burrows to protect against an external stress such

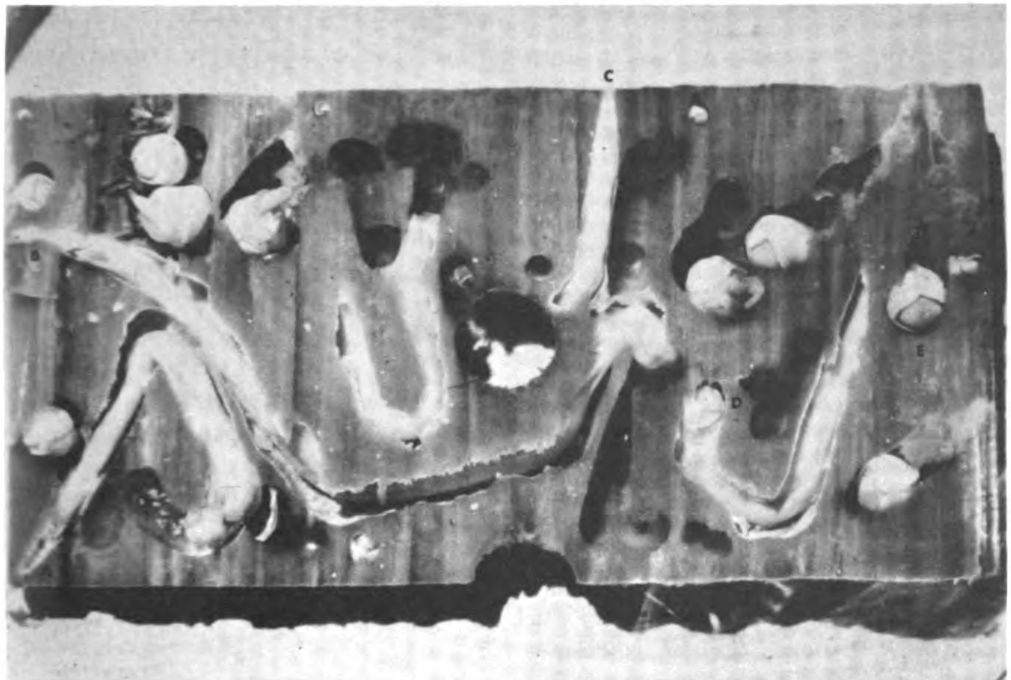

Figure 4 — Fir panel split open to show teredinids (Bankia setacea) *and pholads* (Xylophaga washintona) *in the wood. Teredinids entered the wood (A-C) as metamorphosing larvae and continued to grow, enlarging their burrows as they went. Their random-appearing progress through the wood is influenced by the proximity of other borers, physical obstacles, and the direction of the wood grain. A set of pallets is barely visible at A, a boring apparatus (shell) is shown at D and a pholad is identified at E. The photo was kindly supplied by Dr. R.D. Turner of Harvard University.*

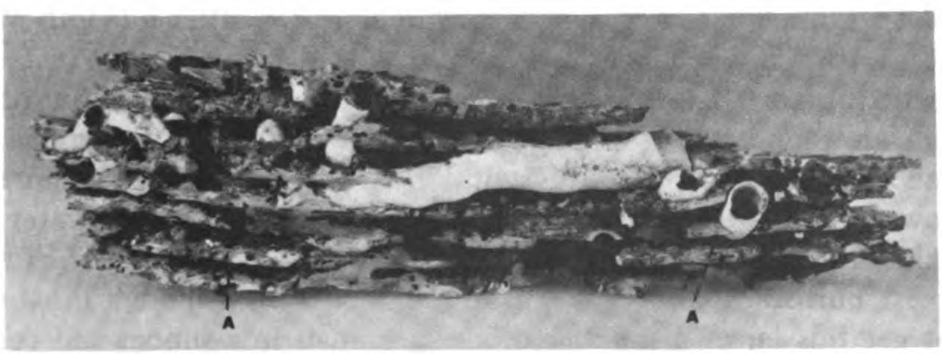

Figure 5 — A fragment of wood damaged by teredinids and limnorians. The white tubes are the calcareous burrow linings produced by the teredinids. The softer springwood was rasped by the limnorians (A).

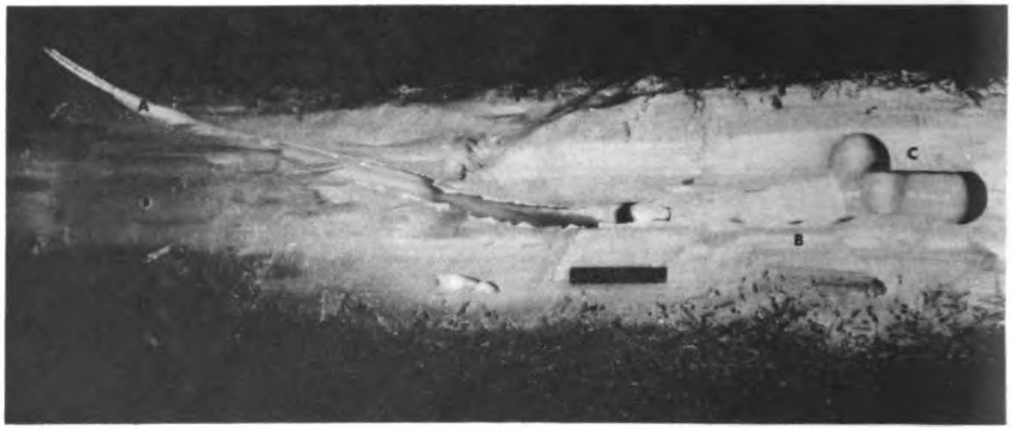

Figure 6 — The teredinid split wood is Bankia fosteria. *The animal entered the wood at the left where a pair of pallets are visible (A). During times of external stress such as a gross change in water salinity or the presence of a noxious chemical in the water, the pallets can be drawn snugly into the burrow opening, effectively sealing the burrow from the outside world. The animal can remain in seclusion for several weeks, if necessary, deriving it's energy by glycolysis. Some of the calcareous burrow lining is visible at B. The anterior end of the burrow at C shows the smoothness of the tunnel walls and two deviations in tunnel direction made by the borer. The black bar = 2 cm. The photo was kindly supplied by Dr. R.D Turner, Harvard University.*

as the presence of a noxious chemical in the water or gross changes in water temperature of salinity. They can remain alive for several weeks sealed in their burrows, even if the wood is removed from the water, and during this period of confinement they depend upon the anaerobic metabolism of stored glycogen (glycolysis) to meet their energy requirements.

With sufficient growing room, and depending upon the species and environmental factors, an adult teredinid can attain a length well over a 100 cm (39 in.) and a diameter of 2.5 cm (1 in.). In fact, lengths up to 6 feet have been reported. Creatures of these dimensions are found mostly in the south Pacific where they are prized as food delicacies by the natives, with or without condiments! Figure 7 shows a borer-infested section of a log removed from the water at Bikini Atoll. The borer species is not known, but the diameter of the largest burrow is over 2 cm (nearly an inch). Even though most do not get this large, a number of these animals in a timber can completely riddle it (and in a relatively short time) without any visual indication that anything is amiss, as illustrated by the camel section in Figure 8. The consequences of their boring activity may not become apparent until a catastrophic timber failure occurs; an unlucky pedestrian on a collapsing pier may find himself a sudden swimmer!

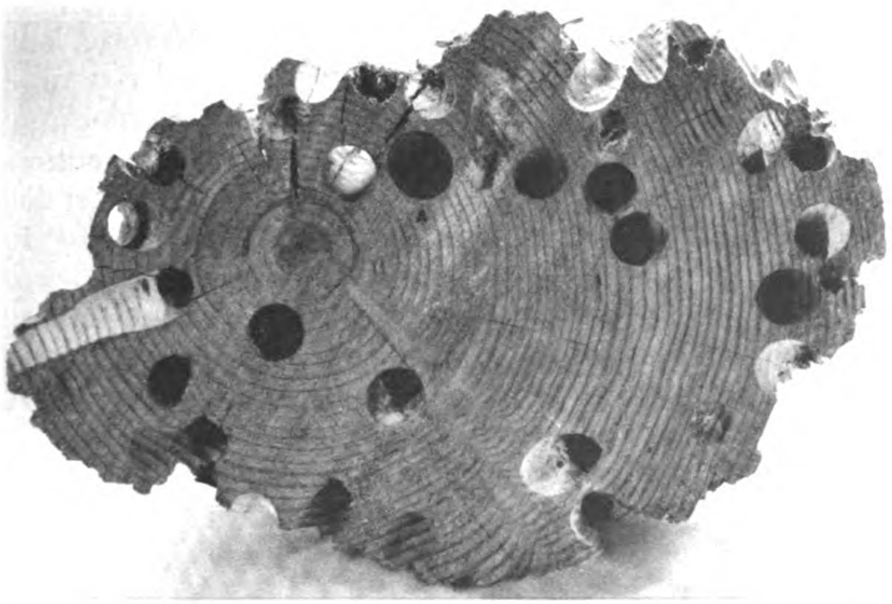

Figure 7 — Section of a log retrieved near Bikini Atoll showing tunnels made by unidentified borers; the largest tunnel (A) measures 24 mm (nearly 1 in.) in diameter.

Figure 8 — Section of a camel (used between ship hull and pier) showing extensive damage to a lower member caused by the combined action of teredinids, pholads, and limnorians.

The Pholad

Pholads are molluscan borers of the family Pholadidae. They are also called piddocks and have the ability to penetrate mud, shale, inferior concrete, hard stone (Figure 9), and other substances such as lead and wood. Attack on wood is performed almost entirely by species of the genera *Martesia* and *Xylophaga*, and the most destructive wood-boring species of these genera is the pantropically distributed *M. striata* (Figure 10). In those waters where the local concentration of wood-boring pholads is high, they can be as destructive to wood in marine service as the teredinids (16); generally, however, these creatures are not a serious threat to man's goods as are the teredinids and the limnorians.

Figure 9 — Pholads and mussels boring into Monterey shale taken from Monterey Bay, CA. The large white specimen in the center is a pholad (parapholas californicas) *and the dark-shelled specimen at A is a mussel* (Lithophaga plumula). *The circular (B) and elongated (C) depressions were made by the borers as they tunneled through the stone. The photo was kindly supplied by Dr. E.C. Haderlie of the Navy Postgraduate School.*

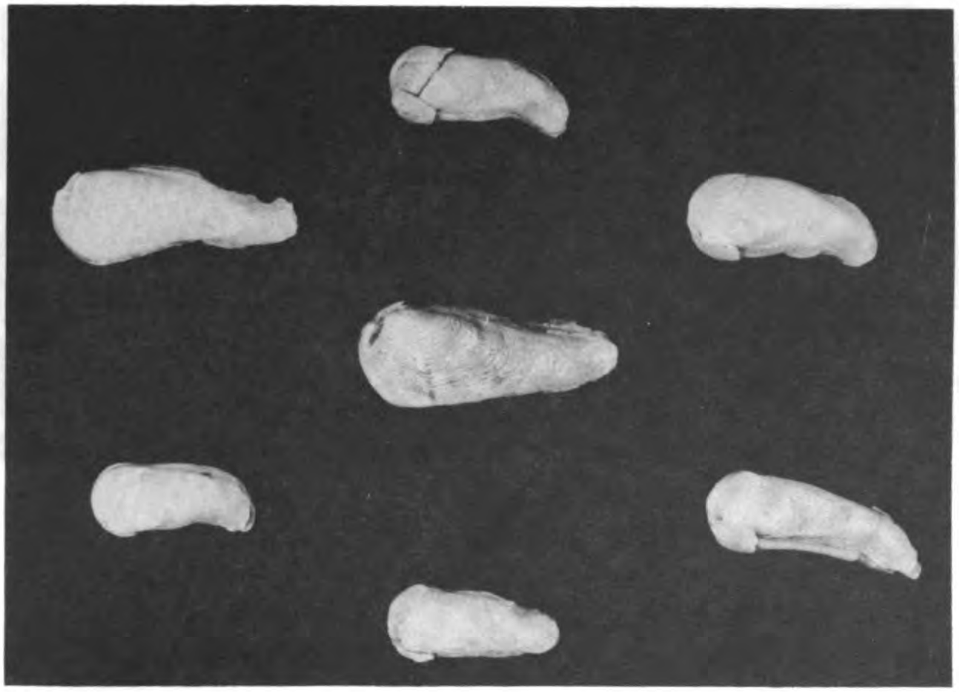

Figure 10 — Shells of the wood-boring pholad Martesia striata *(x 1.5). The largest shell is 38 mm (1.5 in.) long. These animals bore into the wood for protection only and do not penetrate much more than their body length. Their "kissing cousins" can bore into much harder substrates (see text).*

The larvae of pholads are subjected to the same survival stresses as the teredinids, and like the teredinids, once in the wood the adults are relatively secure. *Martesia* uses the wood only for shelter, and the burrow approximates the length of its shell. Since these borers do not develop the elongated body characteristic of teredinids, and since wood penetration is limited approximately to body length, the wood does not become deeply riddled by their boring activity. However, badly infested surface wood can become broken away by external mechanical forces in the manner of limnorian-damaged wood, thereby providing a fresh surface for reinfestation.

The other animal shown in Figure 9 is a mussel *Lithophaga* from the molluscan family Mytilidae. These creatures also have unusual boring talents as documented in this figure and in Figure 11 which shows *L. lithophaga* penetrating and perforating ¼"-thick plates of magnesium metal. These plates, in the water for 4 years, were part of a long-term (16 years) corrosion study (18) conducted by the Naval Research Laboratory (NRL). Just how long it took these persistent little bivalves to negotiate the metal is not known, however their activities confirm the dogged determination of creatures marine to evict man's works from their domain.

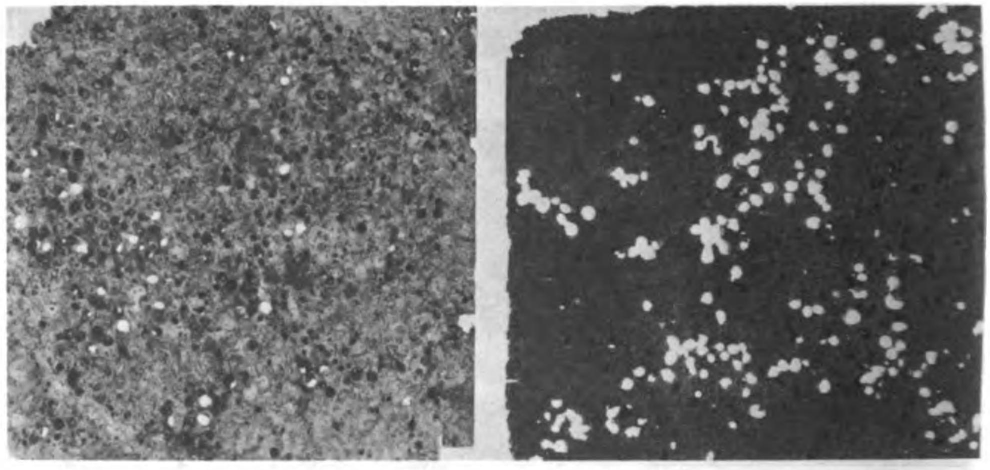

Figure 11 — Magnesium plates perforated by the mytilid Lithophaga. *The uncleaned panel on the left shows the animal shells still in the burrows; the plate on the right has been cleaned. The plates were in the water for 4 years as part of a 16-year marine corrosion study conducted by NRL in the Panama Canal Zone.*

The Limnorians

The limnorians, or gribble, are crustacean borers of the family Limnoriidae. Only a few mm long, these animals construct a maze of interconnecting galleries just below and parallel to the wood surface. Pieces of wood (Figure 12) can be turned into sponges within a matter of weeks by burrowing limnorians like those in Figure 13.

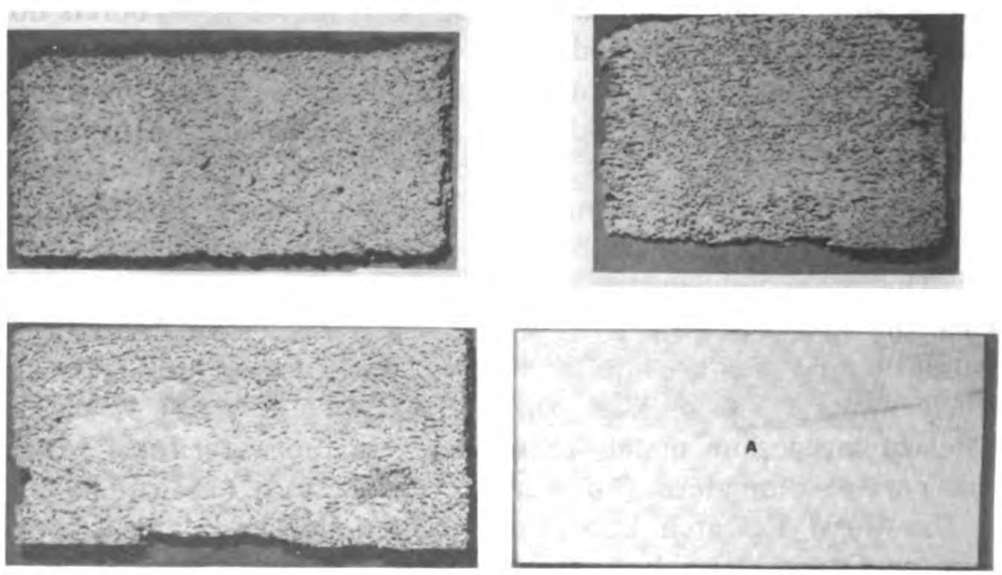

Figure 12 — Attacked from both sides, these pine panels were reduced from sound wood (A) to spongy masses after 3 months' exposure in a laboratory colony of Limnoria tripunctata.

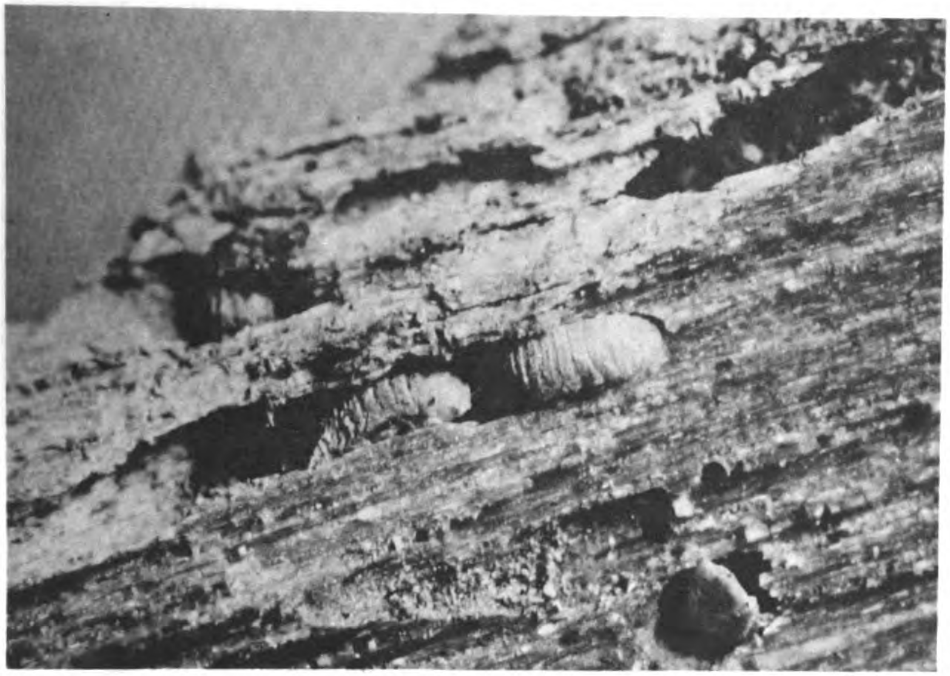

Figure 13 — Limnorians in a piece of greenheart (Ocotea rodiei). *These animals burrow preferentially in the softer springwood and just beneath and parallel to the wood surface, forming a maze of interconnecting tunnels. Heavily infested wood is easily broken away, and the animals are forced to "dig deeper" to reach sound wood. In this manner piles are eventually severed by Limnorians.*

The young are born within the parental galleries and commence burrowing galleries of their own within a short time. This is a much slicker way of getting their offspring out of the house and on their own than we humans have! Also, the young limnorians are quite fortunate; they do not have to rely on a chance encounter with a suitable wood substrate to ensure survival as do molluscan borer larvae. As the underlying wood weakens and is broken away by wave or other mechanical action, the animals are forced to burrow deeper. This sequence of events eventually leads to the formation of the familiar and characteristic 'hour-glass' shape within the intertidal zone which is acquired by limnorian-damaged piling as shown in Figure 14. Fortunately, this form of damage is readily apparent and remedial action can be taken before a piling collapses.

The Navy's Interest in Wood Biodeterioration

Navy Use of Wood

Not only is wood the only renewable natural resource available as a construction material (a point in its favor), but its many unique physical properties and relatively low cost, as compared to other

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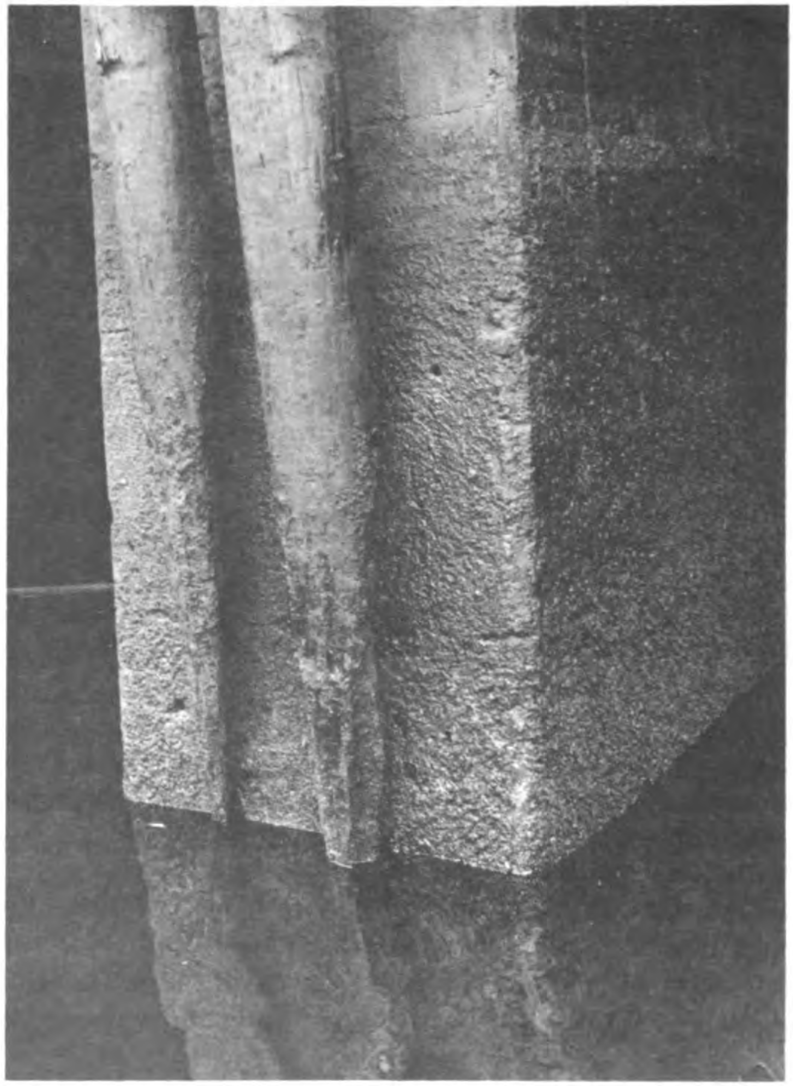

Figure 14 — Creosoted fender piling in Balboa Harbor at the Pacific entrance to the Panama Canal. The limnorians have severely reduced the diameter of the pile on the left; the other pile will be reduced similarly, and eventually both will be severed. The 13-foot tidal range at this site is responsible for the observed pattern of destruction of the piles.

construction materials, make it the best choice for many applications in spite of its susceptibility to biodegradation. Thus, the U.S. Navy has in service about 1.5 million utility poles, over 6 million cross-ties, over 100,000 buildings wholly or partly of wood, 1000 piers and wharves, innumerable camels and dolphins, and over 180 miles of fender system constructed of wood (19). Understandably, with this investment the Navy has an abiding interest in wood biodeterioration and in techniques for ensuring an adequate service life for this wood. It is difficult to assess accurately the cost of replacement or repair of biodamaged wood because cost accounting procedures often fail to delineate expenditures in this category from the total expenditure for replacement or repair which includes damage from other causes; the accounting department does not care if a section of fender system was damaged by borers or by a playful harbor-tug captain. Nevertheless, the latest estimate (20) places the annual cost of repair or replacement of biodegraded wood in marine service at $200 million. Obviously the wood-destroyers have not yet lost the battle!

Shortcomings of Current Wood Treatments

It is also obvious from the maintenance figure cited above that present treatments for wood in marine service are less than adequate. Pressure treatment with whole creosote or creosote-coal tar is one of the best methods and certainly the one most widely used by the Navy for marine wood protection. However, creosote-treated wood is not completely immune to attack by marine borers, particularly in tropical and semi-tropical waters populated by the crustacean borer *Limnoria tripunctata*. Also, creosote can be metabolized by certain microorganisms (21) which degrade it and leave the wood vulnerable to other wood-destroyers besides limnorians. Treatment of wood with chromated copper arsenate (CCA) or ammoniacal copper arsenite (ACA), with or without subsequent pressure impregnation with creosote, is very effective against borers, but it leaves the wood embrittled (22); thus, piling succumbs to the impacts of vessels because of wood-strength loss.

Environmental Pollution

The increasing concern for environmental pollution may provide wood-destroyers, particularly the marine borers, with an unexpected benefit. First, depuration of harbors is making it possible for marine borers to live once again in these previously polluted waters. They are finding, as in the case of New York harbor, wonderful, sheltered homes in untreated piling, or piling treated so long ago that it is no longer resistant. Second, because of the rise in pollution awareness, many of the current wood protectants may become unacceptable in the future because of their possible adverse environmental impact. Of course creosote is high on the list, along with some other wood preservatives, for review by the Environmental Protection Agency (EPA) as a potential toxic substance detrimental to the environment. Also, creosote has been declared an oil by EPA and is thus subject to the same stringent use regulations as other oils. It is very difficult to drive a freshly creosoted pile without creating an oil film on the adjacent water surface, and the presence of this film constitutes a reportable violation of the Water Quality Act of 1971 (23). The current attitude toward the use of copper, chromium, and arsenic in natural situations may eventually prevent the use of water-borne salts (CCA, ACA) as wood protectants, even if a new treating technique was developed which would prevent wood embrittlement. For these reasons the Navy seeks new, more effective, and environmentally acceptable wood protectants for marine and terrestrial use.

Marine Wood Protection Studies at the Naval Research Laboratory

Because of the multidisciplinary nature of this research, the collaboration of a number of individuals trained in a variety of technical fields was required to perform much of the investigative work reported here. These individuals collectively possess a background ranging from expertise in malacology, to expertise in the organic chemistry of natural products, to expertise in entomology. Their contributions will be recognized throughout the remaining text.

Marine Borer Control

For more than 20 years NRL has been a combatant in the struggle between the users of wood in the marine environment and those creatures dedicated to the proposition that man should not invade their domain with his wooden artifacts. Early work at NRL (24, 25) was concerned with an exhaustive study of the characteristics of whole creosote, certain arbitrarily defined distillation fractions, and certain chemically altered creosotes to determine the contribution of the components of creosote toward its ability to protect wood from marine borers. Briefly, this study showed that in whole creosote there was a synergistic effect between the toxicants in the various fractions; that the distillation residue, because of its very low leachability, apparently acted as a reservoir for the more toxic, lower-boiling fractions; and that the lowest boiling of these were the most ineffective, probably because they were more readily leached from the wood.

The current emphasis centers primarily on a search for bioresistant woods, the isolation of their bioactive constituents, the determination of the effects of these compounds on the physiology of the target organisms, and finally, on the feasibility of commercially producing these compounds or suitable analogs, as marine wood protectants. Although it is possible that a naturally bioresistant wood could be used directly in construction, factors such as the intra- and inter-tree variations in resistance often found for a given wood, adverse physical characteristics, or its limited availability in the forest frequently eliminate a bioresistant wood for such direct use.

A search conducted by NRL for such woods in the Panamanian forest and elsewhere culminated in the evaluation of a large number of tree species [112] for their inherent resistance to wood-destroying organisms. These woods were exposed to borer attack for periods up to 90 months at various marine locations within the Panama Canal Zone (26), and also to termite and fungal attack for periods up to 158 months at various forest locations (27). The heartwood of a few of the collected woods was naturally resistant to one or more of the wood-destroyers at these exposure sites, and cocobolo *(Dalbergia retusa)* was the most resistant wood among these to biodegradation in all environments. Unfortunately, its general physical form and its scarcity preclude the use of cocobolo directly as a source of construction wood. Because of its exceptional resistance to many kinds of wood-destroyers, its heartwood was examined chemically to isolate and identify the active constituent(s) for possible use as a marine wood protectant.

Subsequently, an orange pigment was isolated from the cocobolo heartwood and identified as obtusaquinone (28) by a collaborator, Dr. Leonard Jurd, and his colleagues at the Western Regional Research Laboratory, U.S.D.A. (Berkeley). When the native heartwood, or pine impregnated with obtusaquinone, was exposed to a laboratory culture of the teredinid *Lyrodus pedicellatus* by another collaborator, Dr. Ruth Turner of Harvard University, the larval pediveligers crawled about on the wood surface with no ill effects; however, when they attempted to enter the wood they quickly died (29). When the entry points on the wood surface were examined microscopically, the reason for their demise was obvious; the animals did not produce the calcium structures which normally are formed during this period in their metamorphosis. The chemical nature of obtusaquinone is such that it has the ability to bind calcium ions. This mechanism (chelation) was considered as a remote possibility to explain the obvious inability of the animals to produce the calcium-based shell material; subsequent studies by other collaborators, Drs. Herbert Waite and Karl Wilbur of the Duke University, showed that this was not the case (30).

The complicated process of shell formation in mollusks initially involves the conversion of a catechol into an orthoquinone by an enzyme phenoloxidase. This orthoquinone reacts with protein residues to form a scleroprotein matrix called the conchiolin network.

It is upon this quinone-tanned protein structure (which is somewhat analogous to mortar in a brick wall) that the deposition of shell material (the bricks in our analogy) occurs.

Kinetic studies by the Duke investigators (30) on phenoloxidase isolated from the mantles or the periostraca of the horse mussel *(Modiolus demissus)* showed that a chemically altered form of obtusaquinone was competing with the natural catecholic substrate for active sites on the enzyme surface. This competitive inhibition by obtusaquinone affected the normal formation of the conchiolin network and, hence, the normal deposition of shell material.

Subsequent field evaluation of obtusaquinone by NRL showed that it was not effective against limnorians and pholads. Also, laboratory synthesis by Dr. Jurd and his colleague, Dr. Gary Manners, indicated that its preparation on a commercial scale as a protectant against teredinids was not economically feasible. Consequently, several obtusaquinone analogs were synthesized in a search for a more cheaply and easily prepared derivative which would also be effective against the other borers; some related cinnamylphenols and benzylphenols were also prepared. The cinnamylphenols represent a new class of naturally occurring products found in *Dalbergia* and the related *Machaerium* species (31). One of the cinnamylphenols is obtusastyrene. Obtusastyrene was not found in the heartwood of cocobolo, but it does occur in the heartwood of a related species *Dalbergia obtusa*. The interest in this compound (and the cinnamylphenols, generally) is that it could exist in cocobolo as an undetected, transient intermediate in the biosynthetic formation of obtusaquinone. Studies by Dr. Waite (32) show that it would fit into the scheme outlined above for the inhibition of shell formation by the teredinids.

Except for the benzylphenols, subsequent evaluation of these compounds showed a relationship between their chemical structure and their efficacy against teredinids. Two structural criteria were necessary to confer bioactivity: the presence of a cinnamyl group in the molecule, and the presence of two oxygen atoms mutually ortho (on adjacent carbon atoms) on the quinoid (or phenolic) ring. These structural relationships are depicted in Figure 15. With the juxtaposed oxygen atoms, and the occurrence of a preliminary reductive reaction where necessary, the active members of this series of obtusaquinone analogs and cinnamylphenols either duplicate or closely approximate the catecholic structure of the natural substrate for the enzyme, and this similarity may account for their observed antiteredo activity.

ACTIVE COMPOUNDS | INACTIVE COMPOUNDS

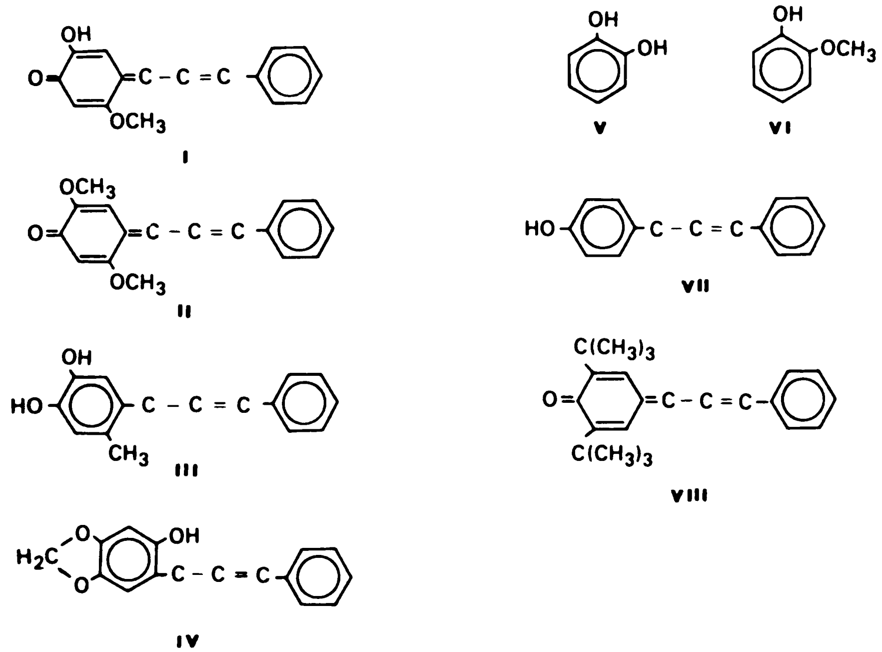

Figure 15 — Examples of active and inactive compounds showing the necessary structural relationships required for activity against teredinids. V and VI have the necessary oxygen-arrangment on the phenol ring but lack the "cinnamyl" group; VII and VIII do not have the juxtaposed oxygen atoms. Obtusaquinone (I), isolated from Dalbergia retusa, *and obtusastyrene (VII), isolated from* Dalbergia obtusa, *are discussed in the text.*

The benzylphenols which evolved as a consequence of the progressive structural alteration of the obtusaquinone molecule by Dr. Jurd are not directly related to the quinonemethides (obtusaquinone and analogs). Recent evidence, however, suggests that they may be converted *(in vivo)* to quinonemethides before becoming active (Jurd – private communication). One of these compounds, 2-benzyl-4, 6-di-t-butylphenol, was very active against teredinids and pholads as shown in Figure 16 but not against limnorians. Removal of one of the t-butyl groups on the phenolic ring (from the 6-position) completely destroyed this activity toward the teredinids but not toward the pholads.

The chief characteristic of the type of phenols represented by this compound is the presence of very large chemical groups on the phenolic ring adjacent to the hydroxyl (OH) group so that it is "boxed in" and the phenol is rendered relatively non-reactive. These sterically-hindered phenols are insoluble in aqueous media so that our compound must be assimilated by the borers by another mechanism, perhaps through a liproprotein membrane. We would like to know the mode of action of this compound upon the physiology of

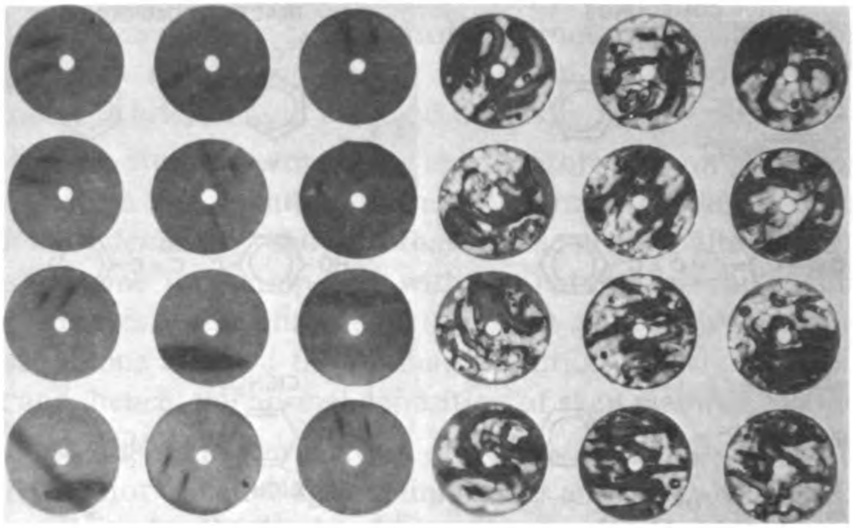

Figure 16 — X-ray photograph of pine sapwood disks. Those on the left contain 0.9% di-t-butylbenzylphenol (see text) and three small pholads which did not get the word; those on the right are untreated controls containing predominantly teredinids. When these animals are crowded as they are in these 2"-diameter disks, they do not attain full size, although they are complete in every other respect and perform their normal physiological functions. These animals are termed stenomorphs (dwarfs in our society). The darker regions of the burrows are caused by the calcified burrow linings which are more opaque to x-rays; the lighter areas are void spaces formed by the removal of wood.

these borers, why the alteration in chemical structure had such a pronounced effect upon its efficacy against teredinids, and if it must be activated by first converting to a quinonemethide.

Borer Control by Control of Marine Fungi

A secondary approach in the NRL search for new ways to protect wood in the marine environment shifts the emphasis from controlling the boring organisms directly to the control of marine fungal (or bacterial) infection which may influence borer infestation. This borer/fungus relationship is based upon a controversial hypothesis which holds that prior fungal degradation of a submerged wood surface must occur before settling marine borers can become established in the wood (33-36). The premise is that, at the time of settlement, the borers do not possess the necessary boring apparatus with which to penetrate the wood successfully; the wood surface must be presoftened presumably by the action of microorganisms. It is also hypothesized that the presence of fungi is necessary to fulfill certain nutritional requirements of the borers. The latter hypothesis is not addressed in the present work.

Limnorians probably do not require a preconditioned substrate surface because they infest new wood as young adults equipped with a pair of very efficient chewing mendibles with which they rasp the wood away. Also, limnorians do not contain any microflora in the gut (37), and recent work using the scanning electron microscope (38) confirms this and does not show any microbial infection at the site of boring. Therefore, if these tools are adequate for routing tunnels in uninfected wood, they must be adequate to the task of entering a new piece of wood. If so, this may account for some of the controvery; it seems to us that part of the disagreement arises often because one author is discussing limnorians, another teredinids. The molluscan borers, however, present a different case! Infestation of wood by teredinids is accomplished by metamorphosing larvae which have settled from the plankton and which do not yet possess the boring tools of the adults. It is easier to understand how the borer larvae in this stage of their development could benefit from the hypothesized borer/fungus relationship.

Except for some preliminary experiments which showed that a wood (mahogany) surface mechanically softened by exposure to a very hot, humid artificial environment for several weeks, was more heavily attacked by teredinids than an unaltered wood surface, no further work has been performed at NRL directly relating to this phenomenon. Instead, we are considering the possibility that some of the borer-resistant tropical woods from the earlier study in the Panama Canal Zone (26, 27) were, in fact, primarily resistant to marine fungal (or bacterial) infection which, in turn, conferred the observed borer resistance. Currently, extractives from the borer-resistant heartwoods, or their synthetic analogs, are being evaluated as marine fungicides. A more detailed study of the borer-fungus relationship will be performed in the future.

Obtusaquinone

The writer and another collaborator, Dr. D.D. Ritchie of Columbia University have shown (39) that obtusaquinone has some inhibitory effect upon the vegetative growth and reproduction of *Cheatomium olivaceum* and *Pestalotia oxanthi*, fungi isolated by Dr. Ritchie from wood exposed in a Panamanian estuary (40). The minimum concentration of obtusaquinone in the culture medium necessary to produce a substantial inhibitory effect upon vegetative growth of both organisms, and upon the reproductive activity of *Pestalotia*, was about 200 ppm; the reproductive activity of *Chaetomium* was inhibited at 125 ppm. From the amount of material necessary to produce the observed effects, obtusaquinone could not be considered a potent fungicide. In fact, in a later study (41) performed by another collaborator Dr. E.B. Gareth Jones, Portsmouth Polytechnic (England), it was shown that the concentration of obtusaquinone necessary to inhibit the growth of eight marine fungi was as much as three orders of magnitude greater than that reported for *Chaetomium* and *Pestalotia*; the quantity of material required to inhibit reproductive activity was about the same. Basically, the only experimental variation between these two studies was the organisms themselves. These diverse results illustrate the difficulty of finding a single preservative which will be effective in combatting the myriad species of wood-destroying organisms spanning several genera of differing families.

Obtusastyrene

As a group the cinnamylphenols exhibit antimicrobial activity, and obtusastyrene, in particular, is active against a wide variety of yeasts, molds, and gram-positive bacteria (42). At 8 ppm solute concentration in the culture medium, obtusastyrene was effective in retarding the vegetative growth in *Chaetomium* and *Pestalotia*, and in inhibiting reproduction in *Chaetomium*. Reproduction in *Pestalotia* was inhibited at 16 ppm solute concentration. Dihydro-obtusastyrene was nearly as effective as the parent compound, suppressing growth and reproduction of *Chaetomium* at about 13 ppm. It was, however, less effective by an order of magnitude against *Pestalotia*. Several additional analogs of obtusastyrene also were evaluated as fungicides. All possessed some activity although none were as active as the parent compound or its reduced form. The differences in activity are probably related to the differences in the functional groups on the aromatic rings of the parent compound. This aspect is being investigated.

Subterranean Termite Control

While the Navy's primary interest in wood biodeterioration is intimately related to the marine wood-destroyers (as the title of this work affirms), its terrestrial flank is being attacked simultaneously by equally aggressive wood-destroyers, the termites. Because of the Navy's large investment in wood in terrestrial service, these creatures are also being considered in the overall strategy. Accordingly, all of the natural wood extractives and their synthetic derivatives are evaluated for antitermitic activity in collaboration with Mr. R.H. Beal of the U.S. Forest Service, U.S.D.A. (Gulfport). Obtusaquinone, obtusastyrene, and lapachol isolated from the heartwood of guayacan *(tabebuia guayacan)* all protect pine from *Coptotermes formosanus* and *Reticulitermes virginicus* in a laboratory force-feeding situation. The force-feeding situation is one in which the animals are contained with a sample of wood impregnated with the candidate toxicant as their only food source: to paraphase Hamlet, the choice is "to eat or not to eat: is it better to die happily on a full stomach or to suffer the slings and arrows of hunger?" Often these creatures will prefer the "hunger" and succumb to starvation rather than partake of the treated wood.

All of the *C. formosanus* termites closeted with obtusaquinone-treated wood were dead within 6 weeks, and all of the *R. virginicus* termites were dead within two weeks. The animals survived five weeks and three weeks, respectively, with obtusastyrene-treated wood, before complete mortality occurred. *C. formosanus* lasted 7 weeks in contact with lapachol-treated wood while the less resistant species *R. virginicus* were all dead within 3 weeks. Pine controls were heavily damaged while the treated wood was only superficially damaged, if at all. The difference in resistance of these termite species reflects the nature of *C. formosanus*, a particularly vicious wood-destroyer that has immigrated from Asia and is now spreading through the Gulf states (43).

Other Bioresistant Tropical Woods

The extractive of cocobolo, its analogues, and related synthetic compounds have been the most extensively studied. Other tropic woods of varying degree of natural bioresistance which we are investigating are guayacan *(Tabebuia guayacan)*, laurel negro *(Cordia alliodora)*, cedro espino *(Bombacopsis quinata)*, pantano *(Hieronima alchorneoides)*, caimito *(Chrysophyllum cainito)*, carbonero de munición *(Columbrina glandulosa)*, and mata raton *(Gliricida sepium)*. Except for the first three woods, the phytochemical examination of the heartwood is just beginning, and no materials are yet available for evaluation as wood protectants.

Guayacan

Of those woods in the current series guayacan has received the most attention. The most abundant extractive isolated from this wood was a yellow pigment lapachol (44) which, because of its high concentration in the wood tissues, was expected to be the active constituent conferring borer protection. Subsequent evaluation, however, showed that it was completely ineffective as an anti-borer agent although it was an antitermitic as reported above. Four other extractives have been isolated from the heartwood of guayacan. These are olivil, iso-olivil, guayacanin, and guayin; iso-olivil is currently being evaluated as an antiborer agent in Canal Zone waters.

Laurel Negro

Laurel negro probably has the greatest potential for commercial exploitation of all the woods evaluated for natural bioresistance. It is relatively light, but strong; has other properties similar to Honduran mahogany; and occurs frequently throughout the tropical forest. It has been recommended as a reforestation tree (45) and as a plantation crop tree (46). In our study laurel was very resistant to attack by teredinids, limnorians, and subterranean termites; it was not resistant to pholad attack or to infection by terrestrial fungi. Laurel takes creosote exceptionally well, and because of its inherent resistance to limnorians, laurel wood treated with creosote should be very durable in the marine environment. Unfortunately, the chemistry of laurel is very complex; while several extractives have been isolated from the heartwood, only recently has one (alliodorin) become available in sufficient quantity for field evaluation.

Future Research Direction

The dibutylbenzylphenol mentioned earlier holds promise as a good preservative against the molluscan borers. This makes it a strong candidate as a creosote replacement should continued use of the latter material be banned. Also, early data indicate that this compound possesses antitermitic worth, and others have shown that it is a good sterilant for certain insect pests. This wide range of uses increases the market for this material. Since it is easily and cheaply synthesized on a commercial scale, certain manufacturers have expressed an interest, providing it can successfully negotiate the arduous trail of certification for these uses. Also, the ineffectiveness of creosote against certain limnorians is a short-coming which will remain even if continued use of creosote as a wood preservative is sanctioned. Consequently, future work at NRL will be more strongly oriented toward an investigation of those woods from the earlier study (24, 25) which were particularly resistant toward limnorians. Beside cocobolo, guayacan, and cedro espino of the present series of woods, lignum vitae *(Guajacum officinale)*, zaragosa *(Conocarpus erectus)*, quirá *(Platymiscium pinnatum)*, acapú *(Vouacapoua americana)*, and bongassi *(Lophira procera)* will be included. If an economically favorable anti-limnorian compound could be isolated from one of these woods, it might be possible to incorporate it into creosote, or to use it in conjunction with the dibutylbenzylphenol to provide complete borer protection.

Reflections

Marine wood-destroying organisms (and others, as well) have been around for millenia and will continue to inhabit our planet for as long as there is a planet to inhabit. Each has its place in the sun; each performs its specific role in Nature's scheme. Unfortunately, these organisms cannot distinguish between their natural substrates and the cellulosic goods man has placed in their environment. While protective steps must be taken, it is not our intention to eradicate wood-destroyers, but only to "educate" them to respect those things of man. This "education" must be accomplished by the development of better wood preservatives – preservatives which will not offend the environment more than is absolutely necessary to accomplish the protection of wood in marine service. To achieve this goal we need to develop preservatives as highly specific to the target organisms as possible to ensure that a minimum of non-destructives will be affected.

Certain biochemical systems are common to all living organisms; others are more specific, such as the cellulose-hydrolyzing systems most wood-destroyers possess, directly or symbiotically, to decompose their natural substrates. By directing our energies toward finding a means of disrupting these specialized biochemical systems, i.e., the decomposition of wood or the deposition of shell, then the range of non-target organisms adversely affected would be lessened. Thus in our studies it is important to relate the chemical structure of bioactive wood constituents with their physiological effects upon the target organisms, to determine which biochemical systems are being disrupted, and to determine how changes in molecular structure of the natural products might enhance or diminish this activity. With this information the possibility of engineering more specific wood protectants is increased.

Tailoring a preservative for a specific target organism is a tall order, a goal which probably will not be fully realized. So, as in all wars, the innocent suffer. It is our obligation to minimize any adverse environmental impact which our protective measures might generate against these innocents. In doing so however, we must not lose sight of the fact that man lives on this planet, too, and that our presence – our activities – will often be in direct conflict with those of lesser biological systems. While we cannot be indifferent toward the needs of these systems, we cannot allow nature to be served exclusively to the detriment of man. A suitable compromise must be achieved.

Acknowledgments

Again, we wish to acknowledge the collaborative efforts of Drs. L. Jurd and G. Manners of the Agricultural Research Service, U.S.D.A. (Berkeley), for their continuing work in performing the phytochemical examinations on the heartwood of the bioresistant woods; of Dr. R.D. Turner, Harvard University, for her laboratory evaluation of the response of *L. pedicellatus* toward wood extractives, and for providing much needed expertise in malacology; of Drs. H. Waite and K. Wilbur, Duke University, for their work on the effect of obtusaquinone on *M. demissus* physiology; of Drs. D.D. Ritchie, Columbia University, and E.B. Gareth Jones, Portsmouth Polytechnique (England), for many of the fungal studies; and R.H. Beal, Forest Service, U.S.D.A. (Gulfport) for the evaluation of various extractives as antitermitics. The author also wishes to acknowledge Dr. Eugene C. Haderlie of the Navy Postgraduate School, Dr. Ruth D. Turner, Harvard University, and longtime friend and colleague Dr. John M. Leonard (now retired) for their critical review of the manuscript and their invaluable comments and suggestions.

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System for Analyses of Earth's Magnetic Field

Scientists at the Naval Research Laboratory have developed a novel computer which provides real-time acquisition and processing of aeromagnetic data for studies of the dynamic processes which act upon the Earth's crust and upper mantle.

Robert Feden, principal investigator for the program, says his system allows rapid analysis and dissemination of information to the scientific community concerning anomalies in the Earth's magnetic field.

Magnetic anomaly interpretation is widely used in age dating the Earth's crust and permits researchers to correlate data on a global scale. An area north of New Zealand has been studied using the NRL's P3A research aircraft. The tests, designed to determine magnetic lineation, age and tectonic patterns (deformations of the Earth's crust and forces which produce them), covered the southern end of the Havre Trough and the South Fiji Basin.

A magnetic anomaly symmetry during the past 5 million years was detected over the axis of the Havre Trough and NE-SW trending anomalies from 27-28 million years old were found in the South Fiji Basin.

The data provide evidence for two major sea-floor spreading events north of New Zealand: the formation of the Fiji Basin and the later, continuing formation of the Havre Trough-Lau Basin System.

Research is continuing and NRL has recently completed additional studies in the region which will increase knowledge of the processes forming and transforming ocean features.

A more thorough understanding of these processes will enable Navy researchers to predict locations of topographic features.

This project is sponsored by the Office of Naval Research.

Acoustic Levitation for Studying Liquids and Biological Materials

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Introduction

This article describes some basic research on the properties of liquids. The novel technique of acoustic levitation can be used to make studies under conditions previously inaccessible to experimentation and as a new tool for separating materials (including biological ones) by their elastic property. Also acoustic levitation may provide new clues to the structure of water, information on the dynamics of explosions in liquids, clarification of the acoustic properties of the constituents of the porpoise melon, basic information on the explosion possibilities when hot and cold volatile liquids come in contact (e.g. LNG and water). Such applications of acoustic levitation provide a science base in support of diverse areas of research interest to the Navy.

We all have a natural fascination with objects suspended without obvious mechanical support. The word "levitation,[1]" itself, conjures up images of magic, but a closer look at the history of attempts to balance the gravitational force on an object by "invisible" and "silent", non-contact forces points to enjoyable research in the quest for knowledge.

The reasons for employing levitation in basic physics are straightforward. The use of fundamental (non-contact) forces to balance gravity means that some basic characteristic associated with that force can be determined. In the case of Milliken's near levitation

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of charged oil drops, the quantum of charge was determined.[2] And Fairbank and his co-workers have extended this work with electromagnetically levitated, superconducting niobium spheres in search of the elusive, if not mythical or unmeasurable, fractionally charged quark.[3]

Ashkin and Dziedzic have shown that light beams can be used to levitate particles and have suggested applications in cloud physics, aerosol sciences, fluid dynamics, and optics.[4] Studies of fission of rotated drops may be feasible due to an acoustical positioning module to be carried on a future space lab mission.[5] Another one of these missions will carry an acoustic levitation furnace which will allow for the container-less solidification of molten materials; resulting materials could be more than of scientific interest, with bulk processing of materials in space a conceivable outcome.[6]

But levitation needn't be at the low gravitational forces of space if sufficiently intense fields can be generated. These can be achieved acoustically by levitating objects in a liquid. Not only are gravity forces (or buoyancy forces) less in a liquid than in air, but also much stronger acoustic standing waves can be established in a liquid than in a gas owing to the liquid's cohesive strength.

Hertz and Mende clarified the nature of the acoustic forces in a simple experiment in which an acoustic transducer in water sends a beam of sound at a H_2O-CCl_4 interface (see Figure 1).[7] Near room temperature the acoustic impedances of the two are matched, suggesting that sound passes through the interface without reflection. A reflector in the CCl_4 reflects the sound back at an angle; once again there is no reflection at the liquid-liquid interface. But the interface does deform towards the water for both incident *and* reflected beams (i.e. independent of the direction of the beam). Why? The difference lies in the fact that although the impedances match, the sound velocities don't. Therefore, the energy *density* (a second order quantity) is lower in the water than in the CCl_4; and consequently the acoustic radiation pressure, which theorists tell us is just equal to the energy density for this case, is greater in CCl_4 than H_2O. The interface, therefore, deforms into the water.

The theoretical problem of the acoustic force on a compressible sphere due to radiation pressure is more difficult than the one dimensional wave problem, not only because we're dealing with three dimensions, but also because we have to take into account the scattering from the sphere and an oscillating translatory motion.

Large acoustic forces on objects can be established by strong acoustic standing waves in acoustically resonant systems. For the

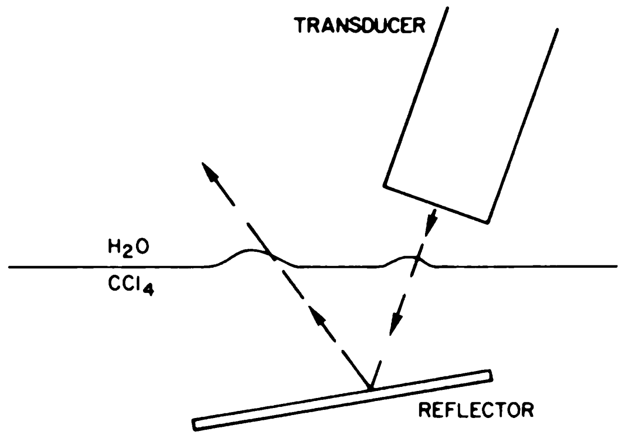


Figure 1 — The interface at a H_2O-CCl_4 interface deforms towards the water due to radiation pressure no matter what the direction of the sound beam.

case in which the acoustic wavelength is large compared to the size of the sphere, the theory for the acoustic force reduces to a simple expression in which the acoustic force is equal to the product K V p dp/dz, where V is the volume of the sphere, p and dp/dz are the acoustic pressure and vertical acoustic pressure gradient, respectively, and K is a constant which depends on the densities and compressibilities of the drop and surrounding fluid.

Levitation is achieved when this force is adjusted (by increasing the voltage of the driving transducer) to be equal to the gravitational or buoyancy force – a force that is *also* proportional to the volume of the drop. Since both forces depend only on volume, the volume cancels out from both sides of the equation and we get one of the most important features of acoustic levitation. This important feature is that the position at which objects are levitated in an acoustic standing wave field is *independent* of size and depends *only* on the relative densities and compressibilities of the two liquids. Another useful feature is that so long as the wavelength is large compared to the largest dimension of an object, the levitation position should also be independent of shape. The implications of these predictions will be clearer as applications of acoustic levitation are discussed. But first a word on apparatus for acoustic levitation.

Acoustic Levitation Apparatus

A simple apparatus for levitating objects by acoustical means is shown in Figure 2. A 30 mm o.d., precision bore pyrex tube of about 250 mm length and about 26 mm i.d. is fitted with a hollow brass piston with a 0.1 mm (or thinner) soldered-on, air-backed diaphragm. A 1.5 inch length, 1.5 inch o.d., 1.25 inch i.d. lead zirconate titanate

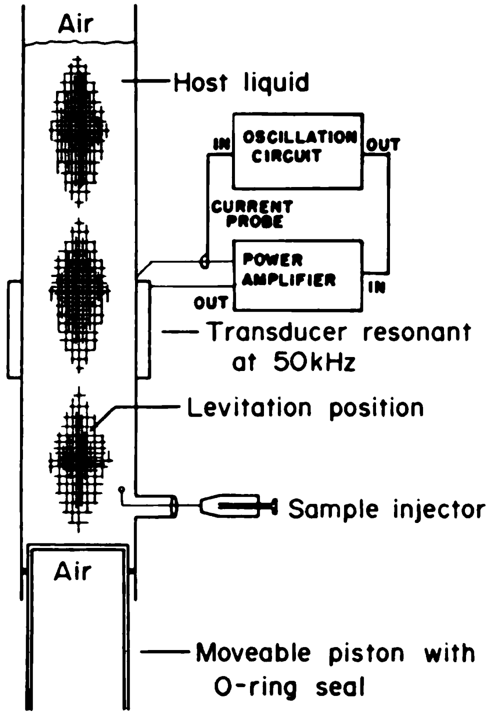


Figure 2 — Apparatus for acoustic levitation. In a typical application, the liquid resonates at about 50 kHz; at a transducer voltage of about 4 volts rms a peack acoustic pressure of about 2 bars can be produced, which is capable of levitating a hexane drop in water. The version shown here includes the self-oscillation circuit.

piezoelectric transducer epoxied about midway up the tube resonates in a length mode exciting standing waves in the "host" liquid. Once this standing wave has been tuned (by optimizing piston position and liquid height), an immiscible sample drop is injected and the voltage to the transducer is increased until the motion of the drop ceases. Drops more dense then the host are levitated below an acoustic pressure maximum and less dense ones above. In any case the drop must be more compressible than the host if the radial pressure distribution is to produce a centering action.

A minimum of apparatus is required to perform levitation experiments. An oscillator-amplifier drives the transducer, which resonates in its lowest mode at about 50 kHz. A current probe on one of the leads to the transducer can serve as a reasonably accurate probe of the liquid resonances if a low impedance power amplifier is used. Sometimes we use an inexpensive "hi-fi" amplifier with a response to 100 kHz. The voltage amplitude can be monitored on a scope or, for more accurate and convenient measurements, a digital A.C. voltmeter can be used. For experiments in which the resonance frequency of the system drifts due to changes such as temperature or liquid height, we have designed a self-oscillation circuit to track these changes.[8]

Applications

Now that we've levitated the sample, what can be done with it that can't be done easily with other techniques? An obvious answer would be experiments involving samples of limited quantity. A less obvious answer would be experiments relating to the properties of metastable liquids and their phase transitions.

Experiments with Metastable Liquids – Tensile Strength[9-11]

It is common knowledge that a liquid can be superheated, tensilely stressed, or supercooled. What is not commonly known is that at a given pressure the metastable range is far greater than the stable range. Figure 3 schematically displays this reality for water. For temperatures a little below the limit-of-superheat, a liquid can, in principle, sustain tensile stress.

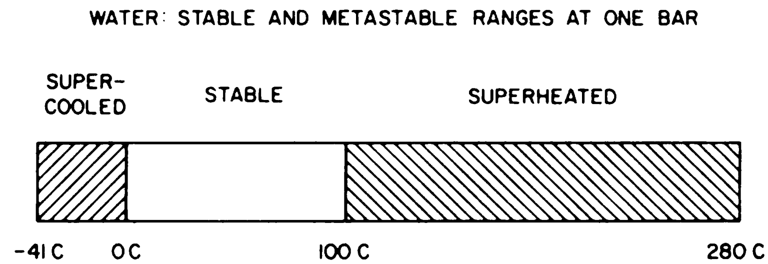


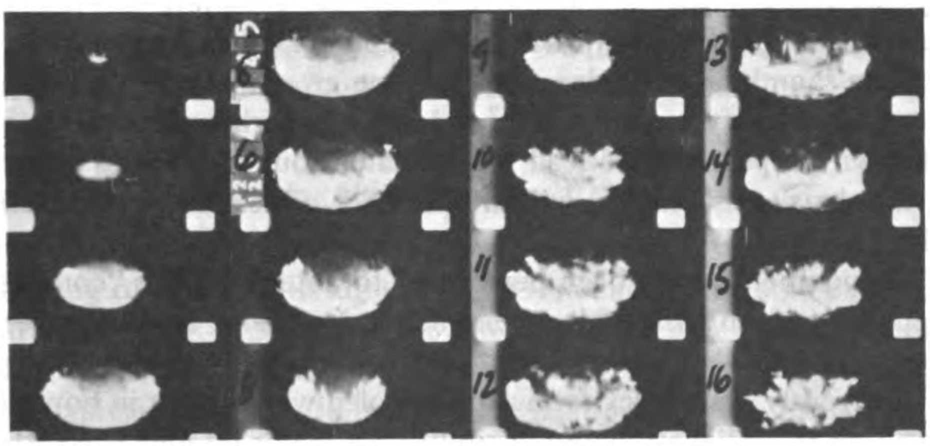
Figure 3 — Schematic of the stable and metastable range of liquid water at a pressure of one atmosphere.

Drops immobilized in another liquid provide an ideal system for tensile strength and superheat experiments, because the imperfectly wetted sites for bubble formation that usually limit the strength and superheatability of liquids are uncommon in small drops held by a smooth (liquid) container. Tensile strengths of superheated ether and hexane drops have been measured using acoustic levitation. The acoustic field serves two purposes: 1) the immobilization of the drop, and 2) the creation of negative pressures equal to the peak acoustic pressure minus the hydrostatic pressure. Strengths have been measured as a function of temperature and are in excellent (and uncommon) agreement with the classical theory of homogeneous nucleation. These strengths can also be viewed as cavitation thresholds except that the superheated drops explosively vaporize, unlike the expansion and collapse phases of traditional cavitation. The producable tensile stresses are, in fact, limited by the heterogeneously induced cavitation threshold of the host liquid and the radiation background.

This latter sensitivity points also to our ability to measure radiation-induced cavitation thresholds using levitated, superheated drops exposed to radiation of known type and energy.

Experiments with Metastable Liquids – Vapor Bubble Dynamics[1 2]

Observing the dynamics of the explosive vaporization of a superheated drop with high speed photography has been made easier by virtue of the ability to focus in close to the levitated drop. The explosion sequence seen in Figure 4 represents the vaporization a 1 mm drop of ether in a host of glycerin at 140 C. The acoustic field serves not only to levitate and produce the vaporization of the drop, but also maintains the integrity of the vapor bubble, which would otherwise shatter into smaller bubbles. Vapor bubble dynamics are characterized by symmetric expansion and by a collapse phase that readily becomes asymmetric and unstable. It is conceivable that experiments with superheated drops can be used to model underwater explosions.



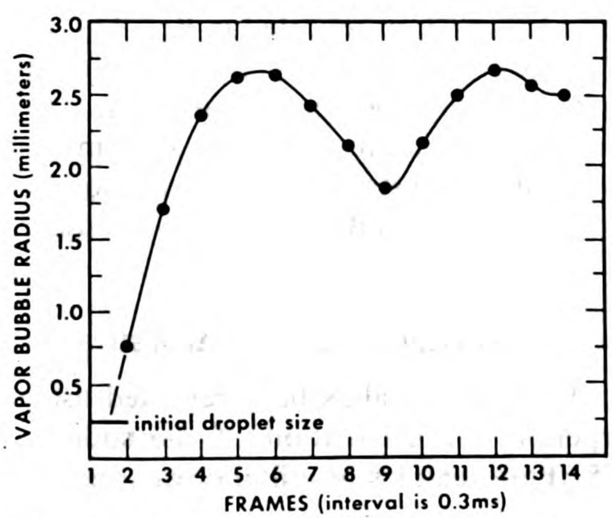


Figure 4 — Dynamics of a vapor bubble from the explosion of a superheated ether drop in glycerin at 140 C. Radius vs time curve is shown for the first 14 frames.

Experiments with Metastable Liquids – Elastic Properties[13]

The theory for acoustic levitation has been shown to be an accurate predictor for experiments, and therefore, it stands to reason that properly designed experiments can be used to predict the properties of the liquids which are responsible for the levitation. In brief, we compare the voltage required to levitate a drop of known properties (the reference liquid) at a given position with that required to levitate the sample drop at the *same* position. (Recall that the sample size is unimportant.) The ratio of these voltages is used with levitation theory to give a "compressadensity" factor – a simple function of the densities and adiabatic compressibilities of the host, reference, and sample liquid. Thus, if these properties are known for the host and references, (and these can be measured very accurately using standard techniques), then the experiment gives us a simple function of density ρ and adiabatic compressibility β_s of the sample. Knowledge of either one gives the other, as well as the sound velocity c, (through $c^2 = 1/\rho\beta_s$). Experiments with liquids of known properties have lead to calculated sound velocities (assuming the density is known) within about 1% of results of traditional techniques.

Experiments have been performed to determine the "compressadensity" of superheated n-pentane and hexane at atmospheric pressure to 140°C.[14]

Currently we are levitating supercooled water drops in hopes of measuring the adiabatic compressibility. Of major interest is whether this modulus, which anomalously *increases* with decreasing temperature (at least to −17°C as reported in Ref. 15), will have a strong turning point in the temperature dependence before the supercooled water reaches its limit of supercooling (at about −41°C) and solidifies. The importance of turning points to our understanding of the structure of water is demonstrated by the enormous amount of work expended by researchers in rationalizing the familiar density maximum at 4°C.

Experiments with Biological Materials – Acoustical Properties.

Varanasi, Apfel, and Malins have reported using the levitation technique to permit the calculation of the sound speed of small lipid samples.[16] (Pure samples in milliliter quantities are often quite time consuming to produce.) Of interest in some of these studies are the differences among isomers that are found in the porpoise dome, and the significance of these differences in influencing the acoustical properties of the dome.

Experiments with Biological Materials – Blood Separation.[17]

Red blood cells (rbc's) are less compressible than blood plasma and, therefore, move toward acoustical pressure minima (rather than maxima) in standing wave fields established in aqueous solutions in the levitation cell. We have, therefore, introduced an isotonic solution of rbc's into 1-2 mm i.d. pyrex tubes, sealed at the bottom, and have placed this tube along the axis of a water-filled, levitation cell. Moreover, we have used a high order mode of the transducer (at about 138 kHz) so that pressure gradients (and, therefore, acoustic forces) are increased without large increases in acoustic pressure.

The result is a system which separates a faint pink, dilute blood solution into bright red bands of rbc's and clear regions of aqueous solution. A significant feature of this size-independent separation is that the difference in the *elastic* properties of rbc and solution is of major importance in the separation. We must now study the implications of this observation to the science and technology of separation.

Interfacial and Damping Measurements.[18,19]

Another technology that poses new problems for society is the shipping of liquified natural gas (LNG) in enormous tankers. The potential problem arises when the LNG inadvertently comes in contact with the much warmer water. This sometimes results in an explosion. The explosion may be, in part, a superheating phenomena. An important parameter in predictions of superheating is the interfacial tension, but knowledge of the interfacial tension at a water/superheated liquid interface does not exist because the usual measurement techniques would cause the superheated liquid to vaporize. The acoustic levitation technique may offer a solution to this problem.

If surface waves of the right frequency are excited at the interface between the levitated drops and the host liquid, shape oscillations occur. Knowledge of the frequency of these shape oscillation resonances and the size of the drop, as well as the densities of the liquids, allows for the prediction of the interfacial tension. Furthermore, measurement via rainbow photometry of the phase of the shape oscillations relative to the driving signal which produces the shape oscillations (by radiation pressure) provides information on the viscosity of the drop material. Since the drop doesn't come in contact with solid surfaces, this technique can be used for a drop of liquid in its superheated and supercooled states and, therefore, extends the range over which interfacial tensions heretofore have been measured.

Summary

We have described how acoustically levitated drops can be used in the measurement of mechanical properties (bulk and surface) of stable and metastable liquids, and biological materials, and in the observation of the liquid-to-vapor and liquid-to-solid phase transformation. The results have been useful in the basic and applied sciences.

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Oceanic Interaction with Ozone Layer of Atmosphere under Study

Man's activities produce compounds that could be a threat to the ozone layer of the atmosphere. Research by chemical oceanographers funded by the Office of Naval Research at Oregon State University is directed towards understanding of the global cycles of these compounds, some of which are also produced naturally on land and in the sea. The work by Yuval Cohen and Louis I. Gordon concentrates on nitrous oxide (N_2O). Like some other compounds used in aerosol spray cans that are being banned, this gas can contribute to chemical breakdown of the atmospheric ozone layer that protects the earth against the penetration of ultraviolet radiation from the sun. A substantial increase in the amount of ultraviolet radation reaching the earth's surface would result in more skin cancer in humans. According to some statistics, a 2 percent increase in ultraviolet radiation would cause an additional 10,000 skin cancer cases per year in the U.S. alone.

The OSU scientists have been seeking to determine whether the oceans are "a source or a sink" for atmospheric N_2O. This information is critical for assessing the impact of the N_2O produced by man through the burning of fossile fuel and also as a result of the use of nitrogen fertilizers. Measurements in the Pacific Ocean showed that there is an excess of nitrous oxide in the ocean over what might be expected from just equilibrium with the atmosphere. The OSU investigators have concluded that the oceans are a significant source for N_2O in the atmosphere. Their work also indicates that the microbial processes responsible for nitrous oxide formation in seawater are not the same as those most commonly operating in soils.

Research Notes

Proton-Beam Pumping of Gas Laser

The first intense proton-beam pumping of a gas laser has been demonstrated by a team of scientists at the Naval Research Laboratory. They report preliminary measurements which suggest that proton-beam pumping may be more efficient than its electron beam counterpart because of the large number of ionizations per unit path length for protons in rare gases. Strong stimulated emission in the Argon-Nitrogen laser system at 358 and 381 nanometers (nm), and in Xenon fluoride at 351 and 353 nm has been observed.

The laser gas mixture was irradiated by a 450 kiloelectron Volt pulsed beam of protons from a reflex tetrode powered by a Seven Ohm Line (SOL) generator.

XeF laser pulses exceeding 4 millijoules were obtained for nonoptimized cavity conditions when 0.5 Joules of proton energy were deposited in the laser cell, yielding a laser efficiency of 0.8%. The use of neon along with higher operating pressures and an optimized optical cavity is expected to increase the laser efficiency.

Scripps Scientist Receives Navy's Conrad Award

The U.S. Navy's highest honor for scientific achievement, the Captain Robert Dexter Conrad Award, was given to Walter H. Munk in a ceremony at Scripps Institution of Oceanography, University of California, San Diego, July 13, 1978. The award, in the forms of a medal and certificate, was presented by Rear Admiral Robert K. Geiger, USN, Chief of Naval Research, on behalf of the Secretary of the Navy.

In presenting the award, Admiral Geiger said Dr. Munk had made "great contributions to the field of geophysics, particularly to physical oceanography." Dr. Munk is a professor of geophysics at Scripps and associate director of LaJolla Laboratories.

The admiral commended Dr. Munk for service both as an individual advisor and as a member of numerous committees, "which have advised the entire spectrum of the Navy community from the Secretariat level down through the various commands and naval laboratories."

The Conrad award is presented annually to an individual "for outstanding scientific achievement of significance to the Navy." It commemorates the service of Captain Robert Dexter Conrad, who was one of the primary architects of the Office of Naval Research (ONR), which was established in 1946 to support research at universities and research institutions on a permanent basis. The award has been described by the Navy as the "highest recognition that the Department can bestow on any scientist engaged in research and development for the Department."

Among the major accomplishments that helped earn Dr. Munk the award was his recent work in air/sea interaction and the role of ocean processes in

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determining the variability of sound transmission through the ocean. Such information is vital to the monitoring of the world's oceans by acoustic means.

In collaboration with Scripps Director William Nierenberg, Dr. Munk also initiated the study of ocean waves and currents using over-the-horizon and synthetic aperture radars.

His diverse interests have led to work on storm-surge protection for Venice, Italy, the cleaning of valuable sculptures by laser, and the holographic photography of famous statuary so their three-dimensional images are preserved for posterity.

The admiral said, "He has been a leader in understanding our earth from its oceans to its center and out beyond to the moon and planets."

Dr. Munk is the 21st recipient of the Conrad award, and the second scientist to receive it in the field of oceanography. The other oceanographer is Dr. Fred N. Spiess of Scripps, who was given the award in June 1974.

Director Nierenberg said, "Scripps is proud of the achievements of Drs. Munk and Spiess and appreciates the more than 30 years of basic-research support from ONR that have enabled these and other Scripps scientists to make great advances in marine sciences."

The award citation reads as follows:

> "In recognition of outstanding technical and scientific achievement in research and development for the United States Navy ... for outstanding contributions to Naval Ocean Science and Engineering. His dedication to the solution of Naval problems began with his first efforts on operational aspects of forecasting waves for World War II amphibious landings. This initial work was further developed and led to our present day understanding of wave generation, propagation and dissipation ... Dr. Munk has generously shared recognition for these accomplishments with many colleagues and students and through his own dedication and effort he has inspired and motivated them to greater achievements. Many of these associates are now applying his theories and methodologies at centers of excellence throughout the world. During his career, Walter Munk has been well attuned to the needs and interests of the Navy ... Because of his scientific contributions guidance, he has become an essential part of the national defense."

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Fender piling cut through by Limnoria. A section of the piling is visible below the water. *See article on page 1.*

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