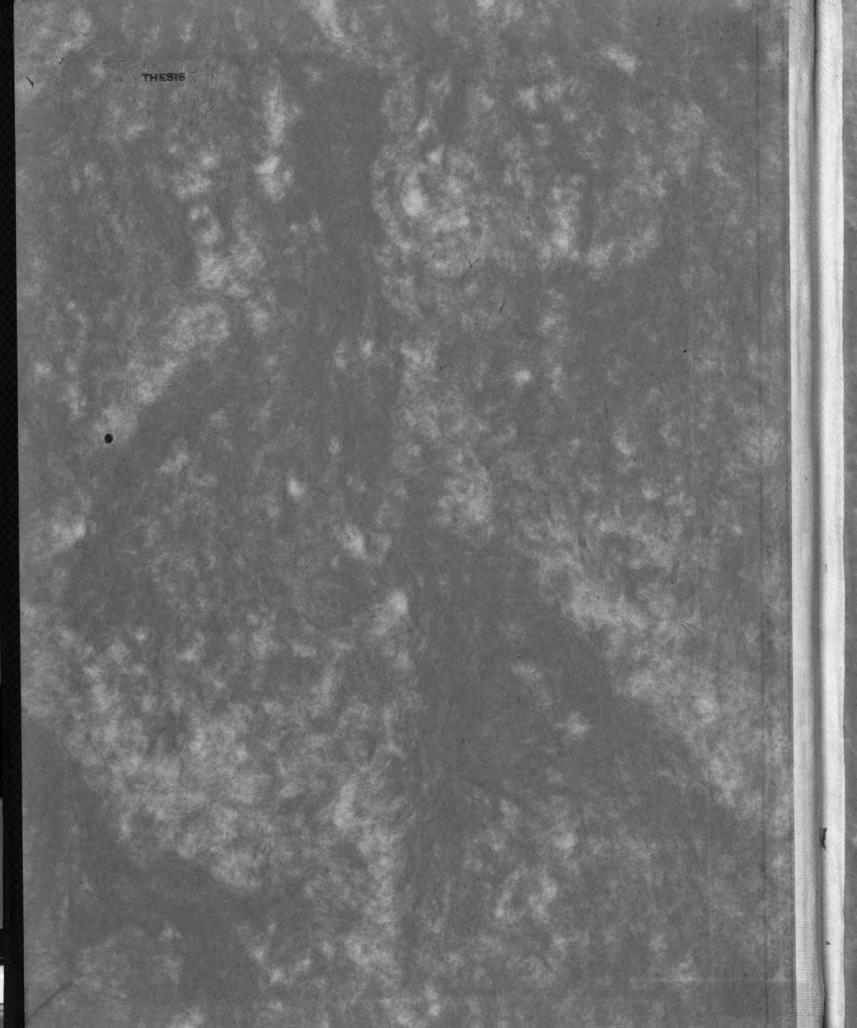
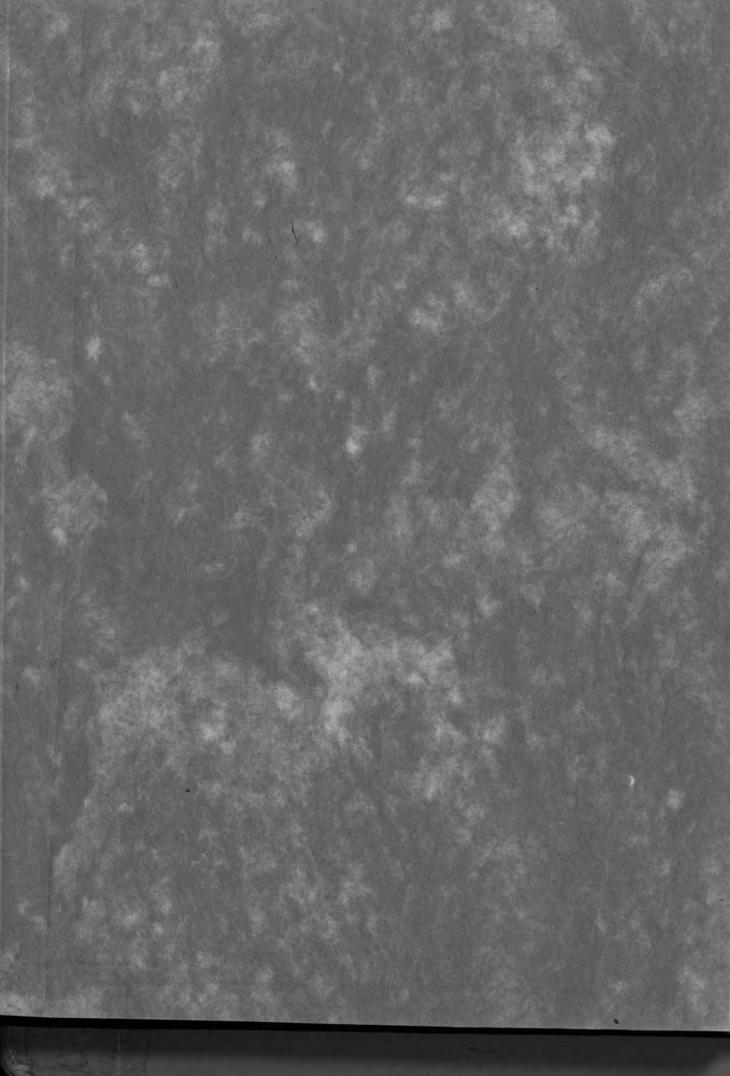
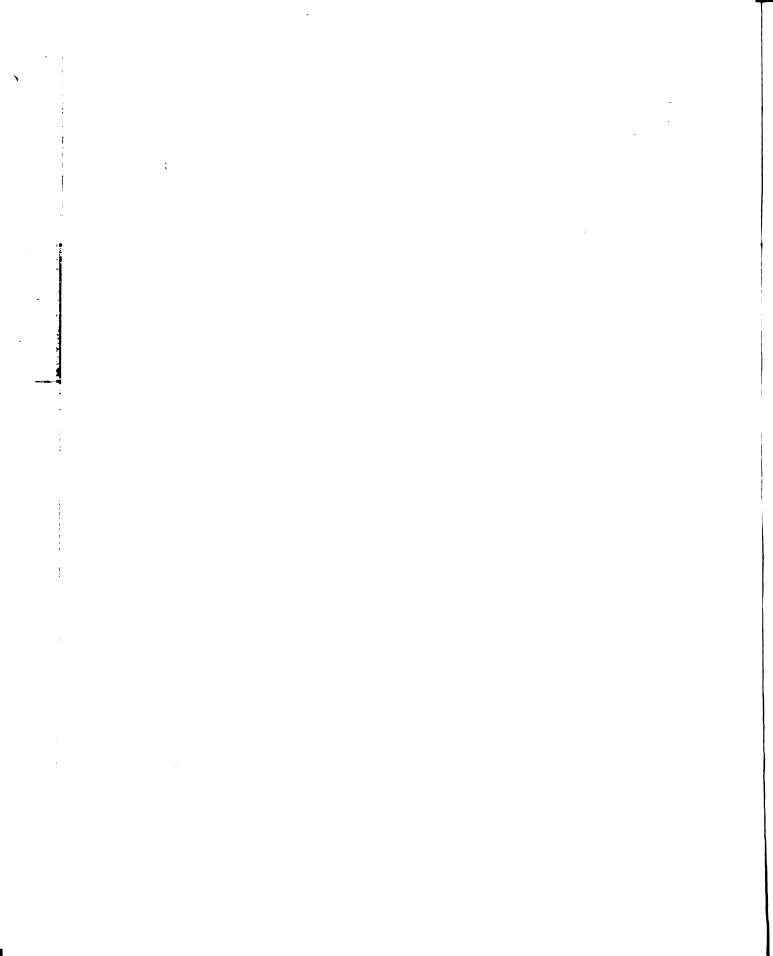
A STUDY OF THE DECAY
RESISTANCE OF COPPER-METAARSENITE TREATED WHITE FIR
LUMBER
(ABIES CONCOLOR LINDLEY
AND GORDON)

Thesis for the Degree of M. S. MICHIGAN STATE COLLEGE Frederick H. Vogel







A STUDY OF THE DECAY RESISTANCE OF COPPER-META-ARSENITE TREATED WHITE FIR LUMBER (ABIES CONCOLOR LINDLEY AND GORDON)

by FREDERICK HAROLD VOGEL

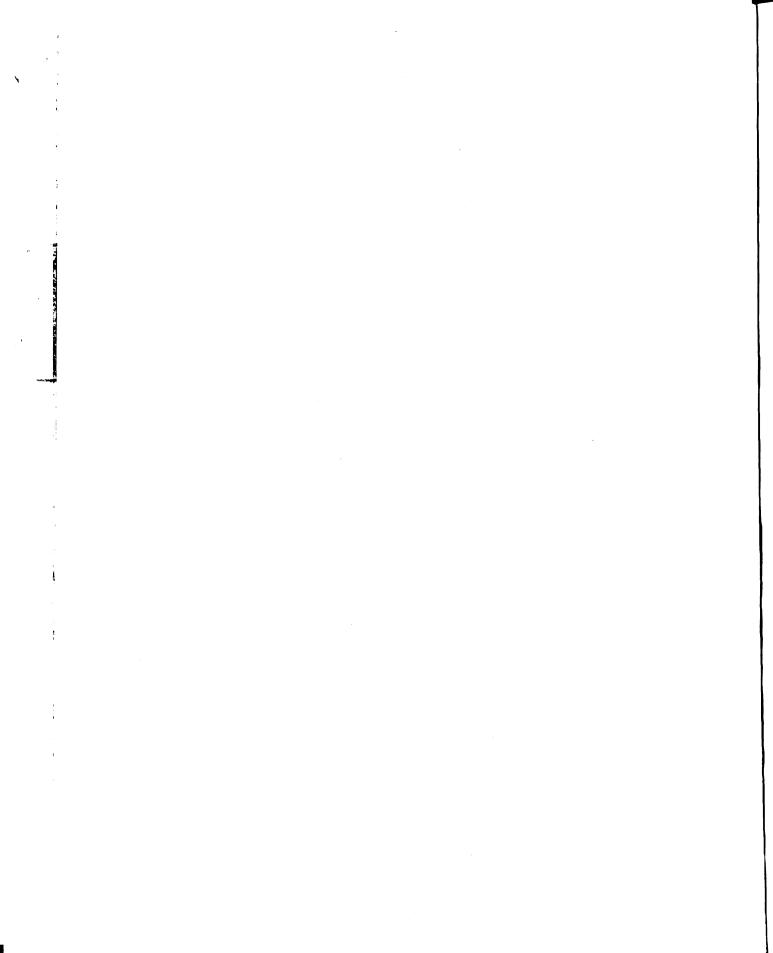
Submitted in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of Michigan State College

Department of Forestry

June 1939

THESIS

To John Vogel (1874 - 1938)





Acting Head of Department of Forestry, In Charge of Major.

Head of Botany Department, In Charge of Minor, and Dean of the Graduate School.

ACKNOWLEDGMENT

It is with a feeling of deep and growing respect for the talents of his guiding professors that the candidate submits this thesis. His attempts in the realm of pure research and especially his analysis of the results bring most forcibly to mind the fact that his guiding professors have long ago surmounted equally difficult problems and have progressed to attainments far beyond a project of this scope.

edged to Professor Forrest C. Strong, whose grasp of the subject and whose ability to demonstrate it clearly have lightened the work. To Dean Ernst A. Bessey it is wished to acknowledge credit for an absorbing course in Mycology, the very foundation for understanding the organisms used in the work. To Professor Stanley E. Crowe there is owed a debt of gratitude for extra personal help and advice in courses on the mechanics of statistical analysis. To Professor William J. Baker there is acknowledged a manifold debt: for his constant inspiration from the inception of the project to its fruition; for his aid in surmounting the curricular problems which have arisen from time to time; and for his counsel in matters pertaining to industrial applications.

Were the entire graduate project to have produced no more than the friendship of these men, it would have more than repaid the candidate's investment of time and effort.

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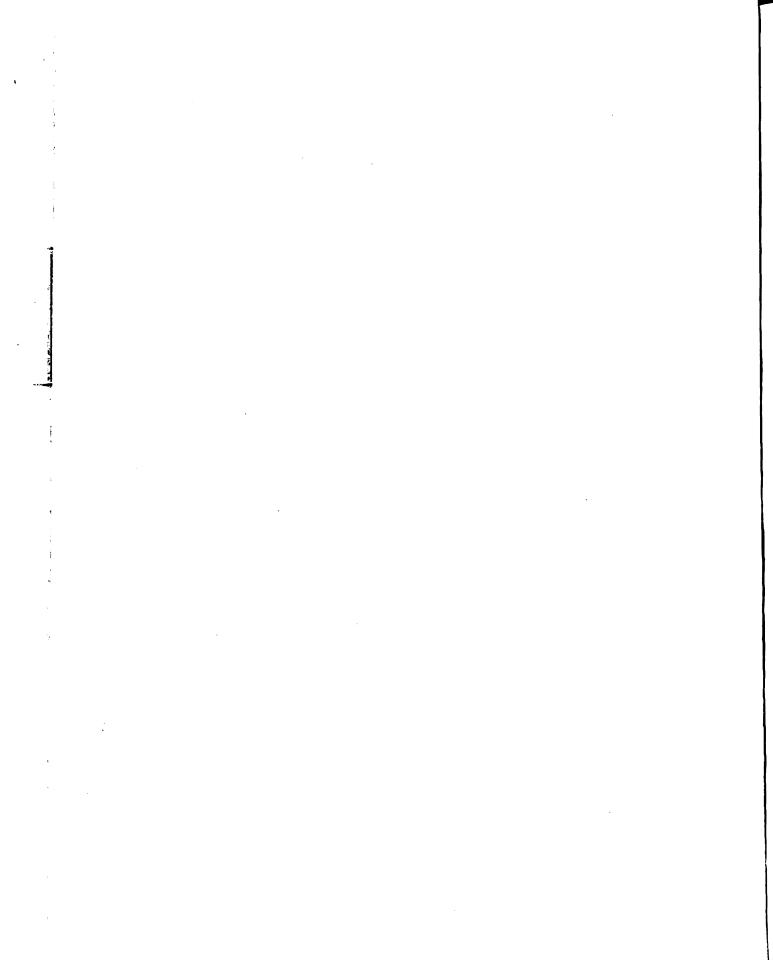
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INTRODUCTION

Until recent years the lumber industry was like an orphan child who grew to maturity without guidance or care. The industry did not realize the economic basis on which it was builded; it did not realize its potentialities; it failed to realize (almost disastrously) that it must fight competition with knowledge, improvement and trade promotion.

While competitive industries -- iron, steel, brick, concrete and fiber building board -- grew tremendously on the strength of the more dependable physical data they could and did make available, our lumber industry stood complacently by and watched the path to its door grow less and less traveled. When the industry's leaders did awaken, they were faced with a dual problem: that of holding their remaining markets, and that of fighting to regain lost markets vital to the existence of certain branches of the production industry.

Markets lost because steel and concrete could be relied upon to conform to certain physical specifications (while timbers varied widely within the same grade, and were seldom sold with engineering data to guide their use) are being fought for with the aid of conferences on uniform grading, with modern physical testing apparatus, and with research laboratories. Markets lost because of slipshod manufacture and careless handling are being regained through the adoption of uniform standards and attention to eye appeal such as labeling and packaging. Markets lost because of lethargic salesmanship are being contested with nation-wide sales promotion campaigns, advertising, contests, legislative lobbying and vast credit facilities. And that which concerns this paper most, markets lost because wood lacked the

necessary durability, are being regained through the development and application of dependable wood preservatives.

For wood preservatives the last hundred years has been a period of juvenile trial and error; only in the very last two decades has the scientific approach been evident. Many preservatives on the market today would be discarded, at least for certain specific applications, if there were complete studies made on them. Some preservatives or systems of application would be revived after their discard through the same means.

Most widely known and used of all wood preservatives, and with good reason, is coal-tar creosote, with service records extending back as long as ninety years (19). But creosote, with all its proven service records, has certain inherent qualities which render its use impractical in some applications. As a result, a great body of competitive preservatives has sprung up to fill the gap left by those unsatisfied demands, and incidently, to compete with creosote where possibly the coal-tar product would serve as well or better.

Copper-meta-arsenite is a relatively new wood preservative. The chemical nature of it is discussed in the body of the paper. There are many additional questions to be answered in regard to copper-meta-arsenite, but this paper concerns itself with but one — the decay resistance to nine different fungi of white fir wood treated with it.

In order to present a coherent paper, it has been deemed advisable to survey, cursorily, most of the field of wood preservation, and to present the story in logical order from the beginning of history to the culmination of this experiment.

⁽¹⁹⁾ See citation 19 in list at end of this paper.

A STUDY OF THE DECAY RESISTANCE OF COPPER-META-ARSENITE TREATED WHITE FIR LUMBER (ABIES CONCOLOR LINDLEY AND GORDON)

HISTORICAL BACKGROUND

The practical application of wood preservation is not new; it is not even comparatively new. Its experimental beginnings are shrouded in remote historical antiquity; in the heyday of Egyptian embalming; in the wooden sculpture and architecture of Greece. There is ample evidence on hand today to show that wood was intentionally preserved thousands of years ago, notably that of museum specimens of wooden articles found in Egyptian tombs and about Grecian excavations.

Several investigators, among them S.B. Boulton (19), believe that the five great orders of classical architecture were derived from wooden ancestors. On the stone columns of these orders may be seen vestigal remains of the block of stone upon which the wooden pillar used to sit to ward off decay; of the slab or tile that used to cap the wooden pole or pillar to throw off the rain; and even of the metal hoops which were placed around the pillars to prevent them from splitting, evoluting now to decorative moldings.

Early scientific data are lacking - as we define the term "scientific" today - but there are Egyptian papyrus fragments in many museums which record some phases of the preservation of organic material, as the bodies of kings, with "natrums" (68) (120a) (122a), spices, oils and "bitumens" (67) (68). We cannot chemically reproduce these substances, since the ancients left no exact formulas, but we believe that the preserving solutions and oils must have been the concentrated waters

^{(19).} Numbers in parentheses refer to citations at end of thesis.

• of certain salt-bearing lakes still existing near Cairo (in which are found mixtures of sodium-sesqui-carbonate, sodium chloride and sodium sulphate)²; the natural oils or asphaltums found in seepage pools or lakes, such as we know in Iraq and Trinidad today; and many natural aromatic oils and spices.

It is interesting to review what little is known of Egyptian embalming. Herodotus (67) and Diodorus Siculus (41) wrote that bodies were steeped in natrum for seventy days and then imbued with oils.

Rouyer, who was in Napoleon's Egyptian foray of 1798, believed that the bodies were oven baked to take up oils after the long natrum treatment (38) (122b), although no ancient author records that opinion. It seems more probable, however, that the bodies were dried naturally by the low humidities prevalent in the country back from the Nile, otherwise the kiln drying of the bodies must have been recorded as significant.

According to Howard Weiss (The Preservation of Structural Timbers. N.Y.: McGraw-Hill. 1916), the Egyptian wooden coffins were not preserved artificially. Their durability was to be accounted for only by their very low moisture content. Weiss states that sycamore was largely used in the construction of these coffins, and he pictures an almost perfect Egyptian specimen in the Metropolitan Museum of Art, New York. On the other hand, Balfour states that the wood used in mummy cases came from the species Cordia sebestena L. Dr. Ernst A. Bessey points out the fact that Cordia sebestena L. is a native of the American tropics and could not have been used in Egyptian mummy cases.

The American Society of Civil Engineers in its timber preservation Report of 1885 says: "Chemical analysis of the mumnies of Egypt shows arsenic in large quantities in every portion -- and even in linen vestments . . . (3. page 285).

Pettigrew (122) worked on mummies in his analyses of embalming materials. He found such a thorough penetration of preservatives that even the bones were saturated (page 62). He also found (page 60), significantly, that the stony heart from an Egyptian mummy began to putrify when the preservatives were withdrawn by maceration after 3000 years!

One of the earliest Gree's objects of value to be preserved was Phidias! wooden statue of Zeus (19). It was said to be located in a damp forest at Olympus, and had its wooden base protected from decay by saturation with certain preserving oils. The statue of Diana at Ephesus was entirely of wood, which Pliny records (183b) (according to Musicianus, an eye-witness) was kept from decaying by the application of oil of Nard-bush in numerous small bore holes.

Pliny recommended rubbing wood with oil of cedar to protect it against decay and worms. According to his writings (123c &123d), forty-eight different kinds of oils were extracted from various trees, plants and fruits to preserve wood, and Pliny details the various processes of extraction(123d). There was probably no recourse to other preservatives except the aforementioned Egyptian natrum and bitumens. Herodotus (67) records many oils, resins, tars and pitches which were extracted and prepared from trees, plants and mineral deposits. Various Greek and Roman authors have written that the astringent portions of olive oil (amurca) (27) (123a), and oils from cedar, larch, juniper and Nard-bush (Valeriana) (123a) were used as preservatives. Probably many of the oils employed were of doubtful value.

According to S.B. Boulton, who made an exhaustive study of the subject, there was no mention of salts of metals for wood preservation by the ancients (19).

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It is interesting to learn that considerable was known, practiced and written about the art of wood preservation years before the Christian era. But we find no mention of further progress, nor hardly a mention of the wood decay problem at all, until after the time of the world scientific reawakening, less than three hundred years ago. 3

And although the ancients knew and practiced the art of wood preservation thousands of years ago, they left no record which might indicate that they had a theory of what wood decay actually was. Apparently they considered it in the light of a natural phenomenon, like night which naturally follows the day, but which can be alleviated with the aid of oil or candle lamps.

Actual theories are not apparent until the 18th century, toward the end of which scientists generally indicated that they believed decays and putrefactions were due to fermentations of some kind. Zallinger (178), according to Whetzel (177), believed that fungi found associated with plant diseases were only abnormal growths of the plants themselves, resulting from the disease rather than being a cause of it. His ideas influenced pathological thought for a long time. Liebig and Pasteur fought out the theory of ferments until Pasteur finally convinced the world that Liebig's theory of "eremacausis" was wrong -- but he failed to convince Liebig (106).

In the period in which the "phlogiston" theory was in vogue, many eminent scientists subscribed to the belief that decay was due to the escape of an unknown substance called phlogiston. Scheele and Priestley subscribed wholeheartedly to it. Dr. Priestley, who first discover-

^{5.} Aristotle (384-322 B.C.) and Theophrastus (371-286 B.C.) wrote on tree diseases. Plinius Secundus (23-79 A.D.) has already been cited. Colerus, in 1600; Laurenberg, in 1631; and Hesze, in 1690, wrote further on the subject.

Caesalpinus (1583) was the first to gather together the known fungi in his "De Plantis."

ed oxygen, called it "dephlogisticated air." Dr. McBride (44a) wrote later that decay was caused by the liberation of carbon dioxide.

Leading up to our modern concepts of the phenomenon, we find Theodore Hartig in Germany in 1833 seeking the cause of wood decay. His analysis was faulty, as we see it today, probably because of the weight of the current line of thought - spontaneous generation.

In 1839 we find that Weigmann published a quaint statement of similar vein in regard to fungi associated with certain tree diseases:

"The pus of the blight as well as that of the canker contains putric and humic acid . . ."(148). In 1840 Unger (160) came forward with the theory that fungi, conidiophores and spores were transformed morbid sap of diseased tissue. From 1837 to 1854 Corda brought out his <u>Icones fungorem</u> which did much to show the light on fungi. In 1841 Meyen, in his <u>Pflanzenpathologie</u>, refuted Weigmann with the statement, "smut mass is not to be compared with animal pus." In 1851 Bonorden's <u>Handbuch der Mykologie</u> gave to the potato famine in Ireland credit for the development of fungus study.

In 1866 Anton de Bery brought out his Morphologie und Physiologie der Pilze, Flechten und Myxomyceten, a contribution that was to lay the foundation for real scientific mycology. Hubert Martin (116) says that the definite recognition of parasitism of fungi dates from 1853 when de Bary published his work die Brandpilze. In 1866 M. Willcomm published a comprehensive analysis of the causes of decay, verifying Theodore Hartig's belief in spontaneous generation(73). It remained for Hartig's son, Robert, to fathom the secret and to bring to light the true relation between decaying wood and the fungi which are

By "true" relation, the writer abides by the broad conception of the term. Pathologists today still debate upon the exact physiological behavior of wood-attacking fungi.

always present. In 1878 Robert Hartig's first publication on the subject caused a storm of controversy, but he had known the truth for many years before he made it public.

Paul Sorauer (148) led a strong school of thought that held to a "predisposition theory": Sorauer believed that wood had a natural tendency to succumb to wood rot fungi when external conditions were of the requisite kind.

In 1768 there was recorded the first British patent on a wood preservative, and in 1770 Sir John Pringle published a list of antiseptics, being copied later by Dr. McBride(44b).

Toward the close of the 18th century and early in the 19th, the pressing needs of the British Admiralty Department for ship timbers began to stir the first research on wood preservation. Good ship timbers were growing steadily scarcer and delays in repairing rotted ships were becoming alarmingly frequent. Many English writers record all too plainly the price that England was paying for her lack of knowledge on timber protection. The records of the Admiralty Department are choked with dusty correspondence relating to rotted beams and knees and decking, and delays in replacing them.

Samuel Pepys (121), author of the famous diary, who was a Secretary to the Admiralty in the reigns of Charles II and James II, left a record that lays the problem as bare as the bedrock disclosed by a mountain avalanche. Pepys (121), Ramsbottom (127) and Albion (1) have covered the subject in dramatic style.

In 1812 Lukin tried an experiment of injecting ship timbers with resinous vapors at the Woolwich Dockyard (45b), but the results proved the method a failure. Nevertheless, it was a step in the right di-

rection because highly resinous woods had been observed to be, and are still known to be, generally resistant to decay. Even the ancients recorded that woods with highly resinous odors lasted the longest(123e).

Sir Humphrey Davy (45a) suggested the use of corrosive sublimate, and Thomas Wade, in 1815, suggested salts of copper, iron and zinc - thereby making himself one of the earliest proponents of the compounds represented by the preservative studied in this thesis.

When the iron and steelclad ship came into its own and spelled the end of the romantic old wooden ships-of-the-line (and the end of the Admiralty's worry over the depleted ship building resources) it did not spell the end of research on wood preservation; far from it, the seeds of research had been sown and the first meager harvests arrived in time for the birth and rise of the railroad industry, an outlet, ultimately, for more wood and more species of wood than ever was dreamed of by the British Admiralty Department. Oliver Evans' Philadelphia steam wagon of 1782, and James Watt's Birmingham engine of 1784 have laid the foundations for a vast network of railroads over the world. The growth of railroads in this country may be traced from a humble beginning on the Baltimore and Ohio in the 1830's to a climax in 1890, when new track laying began to slack off noticeably. Slow expansion occurred until 1916, when over 254,000 miles of railroad line were actually being operated. (119).

Few students of the history of wood preservation fail to note the tremendous influence of our railroads on the rise and growth of the preservative industry. Thus Hartley (59) lays the great impetus of preservation to the railroads, as does Schmitz (140). Evidence is not lacking in the long lists of patent specifications that a large percentage of them were aimed specifically at railroad ties, as for

instance citation (105). Schmitz (140) says that wood preservation in the United States began seriously in 1838 when the North Central Rail-road of Maryland, now a part of the Pennsylvania system, erected a plant to Kyanize chestnut ties with mercuric bichloride solution. Ten years later the first commercial plant was erected at Lowell, Massachusetts, to treat wood with mercuric and zinc salts for the locks and canals on the Merrimac River.

In the 1850's preservation plants were erected by the Vermont Central, the Chicago, Rock Island and Pacific, the Boston and Albany, and the Erie Railroads to treat ties with zinc chloride.

In the 1860's the Philadelphia and Reading, the Old Colony, and the Chicago, Burlington and Quincy Railroads began treating ties. The Old Colony Railroad plant, erected in 1865 at Somerset, Massachusetts, was the first in the United States to use creosote.

The first wood preservation plant in Michigan was erected in 1867 by Seeley of New York at the St. Clair Flats government project. It was across Lake St. Clair from Detroit, at the mouth of the St. Clair River.

The first copper-sulphate treated ties were laid about 1870 in the United States by several railroads, but without marked success. Thilmany treated with this process for the Wabash, the Pennsylvania and Ohio, the Lake Shore and Michigan Southern, the Cleveland and Pittsburgh, and the Baltimore and Ohio Railroads.

Modern timber preservation probably began in the United States in 1875 with the installation of a creosote plant at West Pescagoula, Mississippi. This plant was erected for the Louisville and Nashville Railroad, and it met with success from the beginning. From that time until the present, the preservation industry has grown steadily.

Wooden railroad ties, universally next to the ground except on trestles and on the pavement in cities, were subjected to the severest conditions favorable to decay. Research begun for improving wooden ship construction fell naturally into that for prolonging the life of railroad ties.

Rundreds of chemicals and compounds were recommended by as many investigators⁵, and a flood of patent applications began to inundate the British Patent Office, to be followed by similar floods of patent applications in France, Italy, Germany and the United States. An idea of the trend of the times may be gained by a superficial study of less than a decade of patent abstracts in one technical paper, the Journal of the Society of Chemical Industries.

In 1882 we find three disclosures worthy of mention: Cross (35) describes a process utilizing powdered asbestos in silicate of soda as a preserving and fireproofing treatment; Card(26) patented a process using chloride of zinc followed by a hot creosote bath to prevent leaching; and Glazer(55) describes a coating formed by the use of zinc vitriol followed by chloride of calcium.

Three years later we find Gardner (53) patenting a complicated material called "Ceralin" in which are mixed linseed oil, colophony, doubly rectified American petroleum, levigated litharge, zinc sulphate, potash alum and carbolic acid. The whole was to be boiled two hours and let stand for two days, whereupon it became an excellent preservative paint. Lake(103) describes an improved Thilmany process⁶, in which the

Chapman (29) wrote in 1817 that almost everything under the sun had been tried as a wood preservative in the past five years.

^{6.} Mr. W. Thilmany in 1870 worked on putting copper sulphate into tree trunks, and later perfected the process by first injecting muriate of barytes followed with copper sulphate by Boucherie process. Finally Thilmany adopted the pressure treating tank.

modern system of running trucks into the treating cylinder on rails is used, complete with provision for keeping the loads from floating. He recommends the use of barium chloride followed by cupric chloride.

Another Lake (104) patented a system in which steaming and drying was employed before treatment with antiseptic vapor. The same man (105) was allowed the first patent for treatment of whole trunks of felled trees, using a hollow cap and pump to get the preservatives into the timber. Adaptations of this system are still in use (36).

In 1886 Mancion (114) patented a process utilizing arsenic acid, carbolic acid and ferrous sulphate. In the same year we find in Germany some work by Filsinger (48) on the value of aluminum chloride for preserving oak and fir. Filsinger decided that while the crude aluminum salt was all right, it was much improved by the addition of salts of iron. Free hydrochloric acid was proved to be detrimental to wood, and the whole aluminum chloride system was judged to be rather expensive.

In 1837 four patents show the trend that was developing: Royle (138) describes a system of treating green wood by boiling off the excess water in heated oil similarly to the modern Boulton system, and then treating the wood under air or liquid pressure. Stevenson(152) patented a preservative for wood block pavement, consisting of wood tar, oil of resin and colophony. It was claimed to be proof against frost injury and to resist slipping when wet. Quarente and D'Escalonne (126) describe another complicated mixture of acetate of alumina or sode, subacetate of lead, pyrolignite of lead, glycerine and water. This mixture was either overenthusiastically described or the industry is overlooking the answer to its prayers, for it was deemed imputrescible, uninflammable and nearly incombustible. The inventors claimed, as a

side blow at competitors, that creosote destroyed the fiber of wood and that sulphate of copper decayed wood in contact with iron or gal-vanized iron. Under severe conditions, there was claimed to be no sign of decay in ten years. McLea and Punshon(112) obtained a patent, for both preserving timber and rendering it non-inflammable, in which calcium chloride and ammonium phosphate were the chemicals named.

One patent, added in 1888 to the growing list of new compounds and improved processes, included Avenarius'(7) patent for chlorine treatment of tar oils to make "carbolineum", a preservative with no bad odor, said to be better all around by the inventor. Modifications of this compound are still to be found on the market today. A German writer, Rittmeyer(137), published in this same year a historical description of various methods and results of wood preservative treatment. Rittmeyer described, among others, sulphate of copper, sulphate of iron, sulphate of zinc and sulphate of barium; chloride of mercury and chloride of zinc; creosote and tar oils; and mixtures of these. He also included a table of costs that should be interesting to investigators who are exploring this field. (Compare with (111) and (156)).

In 1889 McMahon(113) took out a patent on a mixture of mercuric chloride, ammonium chloride, soft soap, methylated spirit, water and Venice turpentine. The race to patent every possible preservative or combination of preservatives was especially marked curing the middle and last thirds of the 19th century, and these few examples serve only to show the variety of patentable ideas.

By 1838 there were already four great basic patents extant, upon which foundation the vast preservative industry has largely been builded (85) (19): J.J. Lloyd Margary's sulphate of copper(115); Sir William Burnett's chloride of zinc(24); and John Bethell's heavy oil of tar(16),

which did not even mention the name "creosote".

These patents were not the result of sudden brilliant inspirations by the inventors, but were rather the crystallizing of a century's random thought and experiment. Thus Boulton writes(19) that bichloride of mercury, a very poisonous compound, was successfully employed as early as 1705 by Homberg, a French savant; it was also recommended by De Boissieu in 1767, although the Dutch Government was unsuccessful in official trials with it in 1730, according to the same author, and others (85). The Encyclopaedia Brittenica of 1824 says that Sir Humphrey Davy recommended it for timber, as mentioned before. Kyan's patent in 1832 (101) is thus seen to be the culmination of more than a hundred years of other men's work. While still used in certain applications, mercuric salts are looked on with disfavor for open use, as on railroad ties where cattle have poisoned themselves by licking the salt (3, page 286).

And similarly for sulphate of copper, since DeBoissieu and Bordenave first recommended it (120c) (85) in 1767, just seventy years prior to its patent by Margary in 1837 (115). Thomas Wade (45a) officially recommended its use in 1815. It was tested by Evans on the Southern Railway of Chile in 1857 (3). Copper salts are still popular in France today, not only as wood preservatives but as general fungicides. It is well known that many genera and even orders of lower fungi are killed outright or at least severely inhibited in growth by low concentrations of copper salts, and many of the higher fungi react similarly. Dr. Boucherie patented a trunk injection method in 1838 under French Patent No. 11061.

It should be noted in passing that Margary's original patent covered a mixture of sulphate and acetate of copper.

Dr. Boucherie was a celebrated French chemist who made many experiments on the timber preservation problem between 1836 and 1846.

Chloride of zinc was recommended first by Thomas Wade in 1815 (45a) and by Dr. Boucherie in 1837 (120d). It was patented in the United States by Sir William Burnett as a steeping process in 1838 (24), and it remains popular to this day for many uses where the treated wood is not subject to direct leaching. Of all the common preservative chemicals, it is the most economical to use from the standpoint of first cost.

Heavy oils, tars and creosotes follow the lead of the Egyptians who employed "bitumens" in their embalming. According to Boulton (19), Knowles described the use of tar oils as early as 1756. Franz Moll patented in Germany a heavy oils process in 1836 (117) in which patent was the first use of the word "Kreosot." John Bethell's American patent of July, 1838 (16), although covering the field fully with the mention of eighteen different antiseptics, makes no mention of creosote by that name.

Boulton (19) refers to a report of the East Indian Railway Company for 1867, which records the pronounced success of creosoted sleepers after sixteen years experience with them. Mr. Boulton also cites papers by McMaster in 1859 and 1863 on the subject of Permanent Way materials in India, and by Danvers in his annual report to the Secretary of State for India for 1863.

The history of wood preservation is still being made, and it is being recorded in numerous technical journals as this thesis is written; it is impossible to write "finis" to a study of it. The various publications of the American Wood Preservers' Association (4) (5) (6), the magazine Phytopathology, the Journal of Forestry, the Review of Applied

Mycology and others carry a never-ending history of the development of wood preserving.

For students interested in the history of wood-preserving patents, one of the finest sources of information lies in three volumes of the Proceedings of the American Wood Preservers' Association; 1915, 1916 and 1935.

Great names have become engraved on the roster of researchers in the field of preservation and pathology, names such as the Hartigs, Boulton, Bethell, Kyan, Chanute, Burnett, Willkomm, Falck, Moller, Kühn, Munch, Mayr, Tubeuf, Neger; Ward, Biffen, Bayliss, Hiley, Buller, Faull, White; Berkeley, Smith; Von Schrenk, Spaulding, Atkinson, Rankin, Long, Whetzel, Weir, Bessey, Meinecke, Hunt, Humphrey, Hubert, Boyce, Richards and Schmitz. Not a name here but what carries meaning to an enthusiastic student of the field in which many hundreds of names might have been cited.

DISCUSSION OF CREOSOME VERSUS METAL - SALT PRESERVATIVES

It has been brought out clearly in the historical introduction that coal-tar creosote has long been a major factor in wood preservation, at least since the art and science of preservation began its enlightened growth about a hundred years ago. There is a reason for it just as there is a reason for the popularity of water as a solvent. Creosote serves the purpose cheaply and dependably, for all its homely nature.

But just as we turn to other solvents for special solutes, we turn to special wood preservatives to fit certain specific applications where other factors outweigh the cheapness, the availability, and the ease of handling of creosote. We can hardly pass on to a consideration of copper-meta-arsenite without a brief dissertation on creosote and how it fits into the economic scheme.

The first recorded mention of ters and related compounds is credited by Knowles with having occurred in 1756 in England and America (19). First mention of the use of distillation products of gas-tar for preservatives was by Franz Moll (117) whose German patent in 1836 first made mention of the word "KREOSOT."

Bethell is responsible for the practical introduction of the creosote process, according to Boulton, even though Bethell's basic patent of 1836 (16) did not mention creosote by that name; it included instead a list of eighteen oils, tars and metallic salts, alone and in mixture. The pertinent mixture which most concerned this paper was one of coal-tar thinned with dead oil of coal-tar.

Of course, technically correct nomenclature would confine the term creosote to a product of the destructive distillation of wood, but

modern usage gives the name to the coal-tar product, not chemically identical. Wood crossote is seldom used as a wood preservative, although it has merit, chiefly because it is not available in sufficient quantity with uniform characteristics. It is also likely to run highly acid and to attack metals.

1834 Runge, a German chemist, discovered carbolic acid, an active ingredient of coal-tar creosote. Experience seemed to bear out theories which laid most of the value of coal-tar to that acid (which is not corrosive to iron or steel). Later it was demonstrated that while carbolic acid was a valuable constituent, it could not have been alone responsible for the long preservation records; it was too volatile. The heavier toxic oil constituents must have been responsible for the longest service records.

The active preserving ingredients of coal-tar creosote are known to be multiple, consisting of carbolic and cresylic acids, naphthalenes, and many other related toxic compounds and alkaloids (13) (19).

It may be worthwhile to brief the process of coal-tar manufacture: coal is heated in the absence of air or presence of steam for the production of gas. Four products are derived from the process: commercial or illuminating gas, ammoniacal liquor, coal tar and coke. The antiseptic products are all obtained from the distillation of the coal-tar, a black gummy substance; thousands of very valuable chemicals, dyes and flavorings have also been recovered from the same material.

Light fractions distil off the coal tar first, running strongly to crude naphthas, of negligible value in preservation; next come the heavy oils in which the preserving factors are concentrated; and finally come the pitches and residue.

Disregarding a long technical discussion of creosote, we will confine our remarks instead to the physical properties and attributes which place creosote where it is - at the head of the field - and to the physical drawbacks which have lead to the introduction of numerous competitive preservatives such as copper-meta-arsenite.

First and foremost, creosote is cheap to produce in tremendous quantities with comparatively uniform characteristics. True, every coal region produces a distinct type of creosote oil, but since commercial coal fields are extensive, great quantities of coal-tar over decades or even centuries of time are normally available from each district.

And were one lot of creosote to be substituted for another from a different region, the difference in preservative value would be of small significance. Not so with wood-tar creosote, which varies greatly between producers in the same area, and which is not normally available from a given manufacturer in large enough quantities to satisfy the demands of even one large treating plant. Wood-tar creosote is also comparatively expensive.

Secondly, and with almost equal weight with cheapness and availability, is creosote's toxicity per unit of weight. Creosote is an excellent fungicide, not only cheap in bulk cost, but cheap per-unit-toxicity cost.

Creosote is fairly easily handled and it penetrates wood acceptably well, both rapidly and deeply. It is permanent in its effect and resists washing and leaching almost, but not quite, ideally. (The phenols and cresols will leach out to some extent in water, but other insoluble toxic agents remain in the wood.)

It does not corrode metals, and to all practical purposes does not decompose wood fiber, Quarente and D'Escalonne (126) to the contrary.

It is not deliquescent.

But (and here lies the answer to the growing popularity of salts of metals) creosote has certain inherent faults, not cheaply remedial, which preclude its use for many specific applications:

Creosote has a strong, objectionable odor; a black, ugly color; it leaves a dirty, oily surface to handle; it is irritating to many people's skins; it often tends to bleed out of heavily treated timber on hot days; it can be painted over only with considerable difficulty and added expense; it adds to the heat of burning timbers and throws off a thick, black smoke; and lastly, some of the toxic ingredients are volatile, as the phenols, cresols and naphthalenes.

Various salts of metals overcome all these difficulties without trouble, but they fail on one or two very important points wherein creosote gains its enviable record - cheapness and freedom from measurable leaching. A few salts of metals fail on only one point; they may leach badly, but most compounds which come so close to the ideal are high in cost, are deliquescent, add color to the wood, are corrosive to metal or are extremely poisonous.

Bateman and Baechler (11, entire series) and Waterman, et al, (176) have analyzed many wood preservatives, with the following recommendations:

All mineral acids and acid reacting salts such as the soluble salts of aluminum, iron and tin are toxic to fungi but they attack wood, too, and slowly decrease its strength. The same criticism holds true for strong alkalies and strongly alkaline salts such as sodium carbonate and trisodium phosphate.

Some salts attack iron and steel. These salts include some of those of mercury, copper, nickel, cobalt and antimony.

Many toxic compounds are unstable, including catechol and pyrogallol.

Some preservatives fail because they are too volatile. These include benzene, toluene, xylene, phenol, ortho-, meta-, and paracresol, chlorobenzene, nitrobenzene, benzaldehyde and iodine.

Many compounds are too expensive: thymol, pyridine, mercuric chloride, benzyl aniline, mercurochrome, alpha naphthol, benzoic acid, picric acid, soluble molybdates and soluble salts of cadmium, cobalt, uranium, thallium, thorium, silver and gold.

Preservatives must be toxic below 28°C. to come within the range of fungus growth, and they must be toxic to all the wood destroying fungi rather than to a selective few.

Hundreds of proprietary compounds have been placed on the market to compete with creosote, but none has so far succeeded as well on its own merits as has creosote. The writer may be questioned on this point, but let the questioner look into the capitalization behind the most successful proprietary salt preservatives on the market; names like Bell Telephone, Western Union, General Electric, American Telephone and Telegraph, Weyerhaeuser, Mellon and the like are identified with funds for active trade promotion, lobbying and advertising. Many preservatives on the market are sustained only by the pressure of the money behind them — and not by their merits. Wood preservation is big business today; copper-meta-arsenite is only one of a crowd.

It is easily seen why competition with creosote is logical, and why the place of any competitor in the field depends upon two supports:

1. the physical characteristics in which it happens to be superior to creosote, and 2. the confidence of the public.

Unfortunately up to the present, the claims of certain promoters have misled the public on the question of the actual physical superiority of their preservatives. Freedom from leaching has been claimed for metal salts which were still soluble after treating; greater depth of penetration has been claimed for preservatives that have been found to penetrate no farther than does creosote, and occasionally not as far; complete protection to the very core has been claimed for treated lumber with no more than a superficial protection; fireproofing, rodent proofing and insect proofing has been claimed for treatments of doubtful value. In many instances the justifiably shaken faith of the public has been bolstered anew with fresh financial reserves for high-pressure promotion to get a turnover out of an unwise investment. The confidence of the public very nearly has to be bought under conditions such as these. A new proprietary preservative could hardly be expected to compete with creosote and its fellow competitors without promotional backing. Hence the claims of advertisers must be taken with a grain of salt, and nothing should be included in a scientific report on such a product unless it has been attested to by reliable researchers. It might not be amiss to follow Lord Kelvin's advice in this respect: to measure everything in order to know what you are talking about. Definite longtime service records should be the strongest criteria by which a preservative is judged.

COPPER-META-ARSENITE

Copper-meta-arsenite is really a cross between two major groups

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of non-gaseous fungicides and insecticides. These groups are, broadly:

1. antiseptic oils; 2. coal-tar antiseptics; 3. violently poisonous

mercury compounds; 4. violently poisonous cyanides; 5. copper compounds;

6. poisonous arsenic compounds; 7. sundry metal salts; and 8. the

poisonous alkaloids (as nicotine). In contrast to these, the gaseous

compounds, or fumigants, include the hydrocyanic group, naphthalenes,

tetrachlorethane, sulphur dioxide, carbon monoxide and formaldehyde.

Copper-meta-arsenite is represented in its best form by the patented basic process held by the University of California and leased to a
commercial enterpriser. Although the actual commercial processes are
secret, it was the writer's privilege to observe every detail of them
and to study the behavior of many species of wood under treatment.

Concisely, the chemical preparation involves mixing copper sulphate solution with arsenic trioxide solution under favorable conditions in the presence of aqueous ammonia and stabilizing compounds such as sodium hydroxide and glycerine. The resulting preservative resists leaching to a remarkable degree.

According to Dr. Aaron Gordon⁹, inventor of the process, the above mixture reacts to form a group of stable, non-soluble compounds in the presence of water. These compounds include copper arsenite, CuHAsO₃; copper-meta-arsenite, Cu(AsO₂)₂; and copper hydroxide, Cu(OH)₂, of which the first two are salts of very weak acids, hence they dissolve by hydrolyzing to form weak meta-arsenious acid, HAsO₂, and arsenious acid, H₃AsO₃.

^{9.} Chemist, California Forest Experiment Station, Berkeley, California.

But copper hydroxide reacts with these to reprecipitate them thus:

In contrast, the soluble zinc-meta-arsenite, $ZnAs(O_2)_2$, reacts as follows with acetic acid commonly used to bring it into solution:

2 HAC¹⁰ + ZnAs(O₂)₂ = H₂AsO₂ + Zn(AC)₂O, both products soluble.

Many copper-bearing fungicides have been placed on American and

European markets under such proprietary names as "Bordeaux", "Forstite",

"Sulphsteatite", "Bordorite", "Kupferpasta Bosna", "Caffaro", "Kurkakol".

"Nosperal", "Vitriolin", "Coposil" and "Chemonite".

The non-technical reader may question why copper-meta-arsenite (which is injected in a water solution in the first place, and which is made partly from soluble copper sulphate in the second) will not leach out of treated wood as freely as copper sulphate or zinc chloride. It is a reasonable question, and one easily answered: First, the aqueous solution is not water alone, but contains ammonium hydroxide; second, the copper sulphate has lost its identity in the reactions already illustrated. The writer has helped to prepare commercial charges of copper-meta-arsenite and has observed in several instances that it took five hours of stirring in the presence of aqueous ammonia under pressure to get the solids into solution. On one occasion when a leak developed in the mixing tank, allowing ammonia gas to escape, considerable of the solids immediately precipitated and were rediscolved only with difficulty by the introduction of ammonia gas.

⁽AC) represents the complex acetate radical in acetic acid.

It is a simple matter to precipitate the solids from liquid solution by releasing the ammonia, but almost a disheartening task to redissolve the precipitate which is the toxic factor. In other words, copper-meta-arsenite mixture is not soluble in water to more than the slightest extent. Of that much it is certain, but of other factors such as fire resistance and rodent repulsion there remains to be done more research before any additional claims will be upheld.

Some readers, familiar with the handling of copper sulphate as a preservative, may question the cost of treating equipment for handling copper-meta-arsenite, since copper sulphate is so corrosive to iron and steel 11 that wood, concrete or alloys usually must be employed for its handling. Not so with copper-meta-arsenite, for the first step, only, involves the need for a wooden tank - that of dissolving the copper sulphate crystals in water. The patented process involves the subsequent neutralization of the weak corrosive acids and the admixture of ammonia, so that succeeding steps and transportation can be handled in ordinary steel pipes and tanks.

Before proceeding further with a discussion of copper-meta-arsenite, it is almost necessary, from the standpoint of a clear understanding, to trace back the history and records of both the copper and arsenic salts which go to make up the finished products. Copper-meta-arsenite is relatively new, having had its birth and inception only about fifty years ego, but the parent salts are old in history.

Copper sulphate (bluestone, blue vitriol, etc.) is a pentahydrate, CuSO4.5H2O. It is soluble in water, the solution having a slightly acid reaction which evidences itself by attacking many metals. This acidity is probably caused by the formation of sulfuric acid, H2SO4. by hydrolysis, although some investigators say it is caused by the formation of mono-hydrated copper sulphate, HO.Cu.O.SO2.OH.

Martin (116) says that the cuprammonium group was known in 1885 to Audoynaud, who called it "Eau Céleste"; later it was known as "Azurin". The group is formed by an excess of ammonium hydroxide added to a solution of copper salt, whereupon a peculiar reaction occurs. The ammonia combines with the copper to form a cuprammonium salt. Copper sulphate, CuSO4, first hydrolyzes to free electropositive ions and the equivalent number of free electro-negative sulfate ions; next, traces of basic copper compound and free sulfuric acid, H₂SO4, are thought to form. Added ammonium hydroxide, NH4OH, neutralizes the sulfuric acid and precipitates basic copper compound, which finally redissolves in ammonia to form deep blue cuprammonium sulphate solution, possibly Cu(NH3)4. It then forms negative sulphate ions and positive cuprammonium ions. It never breaks down to free sulfuric acid again.

The earliest history of the use of fungicides and insecticides is obscure, but there must have been much random experimenting. The first recorded successful history dates from the accidental discovery by Millardet in 1882 of the action of lime-copper sulphate solution, although Martin (116) says that Robertson used soap-wetted sulfur as a fungicide in 1821. After the efficacy of Millardet's discovery was generally known there came into use a myriad of materials, many of which harmed the plants they were to protect. (The knowledge of wood-decay fungicides grew jointly with the knowledge of plant-disease fungicides.)

Fungicidal and insecticidal action are manifold: fungicides may act to kill fungi outright; to stop fungus growth; to repel fungi by chemotropic action; and to inhibit germination of spores. Insecticides may act as direct killers, as deterrents, or as ovicides to stop the hatching of eggs.

The largest and most important group of fungicides at present (in phytopathological use) contains as its active agent some form of copper; and the most successful group of insecticides contains arsenic in some form.

Arsenic salts have long been known to be poisonous to insects, but they have been used as insecticides generally only since about the middle of the nineteenth century. Their rise was not without obstacles to overcome, since France passed a law in 1846 prohibiting their use in the interests of public safety. After some time the arsenic group proved so successful in the United States that the French law was repealed. Today there is still a question in the minds of some investigators (20) (85) (154) concerning the liberation of poisonous arsenical gases by certain molds on arsenic treated wood. In 1867 Markham found Paris Green to be a dependable control for Coloredo beetle, which for a time threatened the world's potatoes. Paris Green, called "Schweinfurter Grun" in Germany, is a complex compound of copper acetate and copper arsenite (closely related to our copper-meta-arsenite) to which has been given the formula (CH₃COO)₂Cu.- 3 Cu(AsO₂)₂. It was originally made from verdigris, which was in turn made by the action on sheet copper of the acid "marc" or residue of wine manufacture.

Arsenious oxide (white oxide of arsenic) is obtained as a by-product of the roasting of arsenical ores of many metals. It is cheap to purify by sublimation into both the amorphous and crystalline forms, but it cannot be kept in the amorphous condition for long, as it changes to the crystalline form on standing. The arsenic atom is trivalent in arsenites; pentavalent in arsenates.

The arsenic salts are not more than slightly soluble in pure

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water, but are perfectly soluble in water-solutions of carbon dioxide or ammonia, precipitating when the gases escape. Both arsenites and arsenates are toxic to insects, including termites, wood borers, carpenter ants and to marine borers.

According to Fink, as reported by Martin (116), the toxicity of arsenic is based on a lowering of oxygen consumption by poisoned insects. That action is probably a result of inactivation of the oxydizing enzymes, perhaps by interference with the normal functioning glutathione in the oxygen-reduction phenomenon in cell tissue. Some writers have attributed the trypanocidal action to the remarkable affinity of arsenic for organic combined sulfur.

Other excellent insecticides may be mentioned in passing: lead chromate and ground rhizomes of white Hellebore (Veratrum album L.) which were used as far back as 1842; cuprous cyanide; cuprous thiocyanate; dinitro-o-cresol; dinitro-ortho-cresol; and thiodiphenylamine.

Arsenic salts, although excellent as insecticides, have not so much to commend them as fungicides, at least when compared with copper salts.

Although there has been a wide variety of materials suggested for plant fungicides, only sulfur and copper, in the main, survive for general use. Mercuric chloride is more toxic, and ferrous sulphate, zinc chloride and zinc sulphate are very good, but copper salts prove to be the best all around according to most authorities. Silver salts are about equal to copper salts but are expensive per unit of toxicity.

Lead arsenate is fungicidal, as is calcium arsenate, according to numerous authorities (M.B. Waite, W.J. Morse, H.H. Whetzel, S.E.A. McCallan, T.C. Loh, E. Salmon and E.S. Horton).

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THE AGENCIES DESTRUCTIVE TO WOOD

AND A GENERAL DISCUSSION OF THEIR CONTROL

THE AGENCIES DESTRUCTIVE TO WOOD:

GENERAL BACKGROUND.

There is a tremendous amount of published work bearing on the subject of wood preservation and laboratory tests related to it. The U.S.

Department of Agriculture publishes lists relating to the field (162)
(163) which should help a beginner to survey the literature at hand.

The Superintendent of Documents at Washington publishes two excellent catalogues (generally available in public libraries) (170) and (171), and there is a number of technical indexes relating to current literature. Phytopathology, the Agricultural Index, the Engineering Index,

Journal of Agricultural Research, Chemical Abstracts, and the Review of Applied Mycology supply nearly all the source data that any researcher may need. In this study, the problem is not so much how to find pertinent literature as how to select the best material from the field at hand.

SOME NOTES ON THE STRUCTURE OF WOOD

The mechanics of wood preservation and wood decay are so closely allied to wood structure that an understanding of the basic structure of wood is necessary before further investigation is advised.

Numerous available references cover the subject of wood technology, as (25) (34) (54) (98), so that it should not be necessary here to go into more than a skeleton outline. Current work by Record, Harrar, Brown and Panshin, Koehler, Lodewick and others may be found listed in library catalogues and indexes.

Abies concolor, Lind. & Gord., the species from which the white fir lumber has been selected, is, of course, one of the conifers, or softwoods. Like all other softwoods and hardwoods, its basic structure is not homoge-

neous, like glass, but heterogeneous (168). The wood, instead of being a uniform, solid mass, is composed of innumerable cigar-shaped cells, filled with air when the wood is dry. The great bulk of these cells is longitudinally disposed in the tree trunk.

There are in a softwood tree no continuous vertical tubes or vessels to conduct the sap as there are in hardwoods. Most liquid movement in a softwood tree is through the membranous pits in the walls of the cells. Since the cells are very long in relation to their diameter, it follows that lengthwise liquid travel will be facilitated by capillarity, while lateral liquid travel will have no such advantage, except in the small percentage of ray-cells. (*i.e., in our commercial lumber species).

There are certain cells radially disposed in a tree to carry food materials laterally between the inner bark and the internal wood. These radially disposed cells constitute the wood rays, which in some hardwoods like oak and sycamore, add a beautiful figure to the grain. Wood ray cells form only a small percentage of all the cells in a tree, so that their aid to total lateral liquid movement is not very significant.

In many trees, white fir excepted, there is a marked difference between the outer portion of the wood and that toward the center of the tree. Usually the outer, newer wood is light in color while the center portion is dark. This difference in color is significant.

The center, dark wood of a tree is called heartwood (duramen in some old texts); it is all dead, even in living trees, and it is marked by deposits of "foreign" substances not present when the wood cells were first laid down by the cambium. If a wood is durable, it is these substances which render it so, for there is no native durability in wood substance itself. Hence only the heartwood of a tree can ever be

considered to be durable in the presence of wood-decay fungi, and that durability may vary widely in a given species.

The outer portion of wood on a tree trunk is usually white, or only slightly colored. This zone is known as sapwood (alburnum in some old texts) and it contains only a small portion of living cells, those food storage cells known as parenchyma, and the very outer layer. Sapwood varies in thickness between species, and even between trees in a given species. It is never naturally durable unless it is rendered full of resin by reason of a localized injury to a section of living cambium.

It stands to reason that the outer portion of forest-grown trees will be the highest quality, at least on the clear bole below the crown. Limbs have pruned themselves and the sapwood is clear and free from knots. It is economically unsound to fail to protect this excellent part of a tree from decay and insects after it is converted to timber products.

In certain species of trees, moreover, neither the sapwood nor heartwood is durable. White fir is one of these. The deposits in the heartwood cells of white fir are neither toxic nor particularly repellent to fungi or insects. If white fir (or any of the many perishable species) is to be used in locations favorable to decay, it is important that every piece be treated with a desirable preservative.

THE MECHANICS OF DECAY

As discussed in the historical introduction, the mechanics of wood decay was not understood until Robert Hartig's time in the late nine-teenth century. Even then, only the broad principles were seen and understood. For the purposes of this study, however, a conception lit-

tle more advanced than Robert Hartig's will suffice (58).

Wood decay (known variously as rot, punk, dote and doze) is usually described according to its physical appearance as one of a number of kinds; viz: white pocket rot, white spongy rot, brown ring rot, yellow ring rot, brown stringy rot, brown mottled rot, brown pocket rot, red ray rot, brown cubical rot, and the like (20) (73)(95)(128)(162)(166).

Regardless of the type of rot - white or brown, ring or ray - it is all caused by the same general agency, a fungus. Variations between the different rots are caused primarily by attacks of different species of fungi. Thus, the same species of wood may exhibit both brown and white rots if attacked by two types of fungi.

That the structure of wood and the mechanics of decay are closely allied is plainly seen when the difference between white and brown rots is analyzed. Basically the difference lies in the breakdown of more of one wood element than another; more cellulose broken down and used as food in the case of brown rots; more lignin utilized in the case of white rots.

The physical properties of a given wood, attacked by each of the two broad groups of wood-rot fungi, vary widely even in the early stages of attack. Hence the basic structural composition of wood becomes a factor in advanced studies on the decay problem (21)(22)(23)(34)(58)(74) (77)(132).

The cells of wood are attacked directly by the invading fungus hyphae which are microscopic, threadlike organisms having the faculty of piercing the cell walls of living or dead wood, or both, depending on the species of fungi. Although there is no general agreement on the exact process of attack, investigators are agreed that wood-destroying fungi must secrete a dissolving enzyme from the growing tips of their hyphae, result-

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ing in a chemical breakdown of a small portion of the cell wall at the point of contact. When hyphae are present in sufficient mass, a complete breakdown occurs. Almost every text on forest pathology is illustrated with photomicrographs of this phenomenon (20)(29)(42)(57)(53)(64) (73)(74)(128) and (150).

If a partially decayed piece of wood be sectioned and viewed under the microscope, perforations in the cell walls will be observed distinct from the cell pits. These perforations, almost always irregular in outline, are the scars left by the penetrating hyphae. Very seldom will fungus hyphae be observed in and through these perforations, except on the freshly attacked wood specimens. Old hyphae either dry up and disintegrate, or they are absorbed and drawn shead to the growing tips as part of the food supply required for growth of the fungus. Authorities are not fully agreed on this point.

As the hyphae of the fungi anastomose throughout the tracheids of a softwood like white fir, they usually tend to align themselves in the path of least resistance, parallel to the long axis of the tracheids. The basic structure of the wood thus determines the direction of most rapid spread of decay.

An unfortunate phenomenon, economically, is that of the hidden nature of the advance zone of decay which may be detected in many fungionly with the aid of a microscope and staining technique (40)(75)(129) (136). Since wood is often weakened severely by the initial stage of certain decays, and since it is impossible to detect the extreme boundaries of fungus attack with the naked eye, there is seen an added advantage to treated wood - the certainty that no decay fungus can attack it unknown to the property owner (70).

Alternate drying out and wetting will not destroy most wood fungi; in fact Hubert (73) cites instances of decayed wood which, dried for over seven years in a laboratory, was dampened again only to find that the fungus revived to full vigor.

Fruiting bodies may form on the surfaces of attacked wood after the progress of decay has arrived at the advanced point where sufficient reserve food is available. In every case where a fruiting body (conk, toadstool, etc.) is evident on a piece of wood, it may be taken for granted that the piece is already badly decayed near the point of fruiting.

How far the decayed zone may extend is indeterminate externally (15)(20) (21)(22)(52)(73).

In summary, then, it is seen that the decay of wood is the chemical dissolution of wood lignins and celluloses by enzymes secreted by certain fungi. The fungi reabsorb the enzymes and their dissolved organic matter for food. When both fungi and bacteria are found on decayed wood it may be assumed that fungi are the primary organisms, and that bacteria are secondary, working on altered wood tissue.

WOOD DECAY FUNGI

Fungi are primarily responsible for the condition we know as wood decay. In addition to being only secondary organisms on decayed wood, certain bacteria may actually slow down the rate of decay by inhibiting the growth of wood-decay fungi (172); others may hasten the rate of decay(20).

Without exception the wood-rot organisms are confined to the higher fungi. A few belong to the Ascomyceteae and more to the Heterobasidize, but most are found in the Basidiomyceteae (Eubasidiae). It would be effort wasted to outline mycological classification here. Numerous references are available to cover that field (15)(39)(42)(47)(57)(145)

(150) (151) (162) (177).

Molds of woods, distinct from rots, and some stains are centered in the lower fungi, notably in the Mucorales. Stains work normally in sap-wood only. Although they do ramify throughout the wood cells, and enter them as do the rots, their method of entrence and their food habits are dissimilar. While rot-fungi hyphae dissolve portions of the cell wall, stain hyphae seem to seek out the thin pits and to enter through them—to dissolve and take up the cell contents rather than the substance of the cell walls. The strength of wood bears little relation to the contents of its cells, hence a bad staining by fungi such as Ceratostomella spp. may not affect the strength of a timber, whereas a barely perceptible attack by wood-rot fungi may render a timber worthless. Mold fungi appear to grow only on the surface of wood (139)(162).

The color of molds and stains caused by the lower fungi may be caused by masses of ripened, colored spores, by colored hyphae in the mycelium, or by a slight chemical reaction. In contrast, the discoloration of wood under the action of wood-rot fungi is due to a chemical dissolution of the substance making up wood cells - augmented, in advanced cases, by colored mycelial mats. (23)(32)(39)(72)(167).

Fungi propagate by several means, both sexual and asexual. Most effective from the standpoint of dissemination is spore production, although growth in a limited area may be carried on by other means entirely.

The higher wood-decay fungi produce myriads of spores, all capable of infecting new wood. Chief among the spore producing structures are the large sporophores which are known variously as conks, brackets, toad-stools, mushrooms or puffballs, depending on the species of fungus. A single large fruiting body may produce literally trillions of microscopic spores (15), each fertile and capable of starting a new infection. Only

a very small percentage of the spores ever germinate and find favorable conditions for growth. The air, almost everywhere, is charged with fungus spores, as may be easily proved with a sterile agar plate open for a few seconds. Wood is constantly exposed to these spores and will be sure to develop decay if external conditions are favorable.

Beside the method of spore propagation, fungi may spread by broken pieces of mycelium or infected wood. A piece of decayed wood in which are living hyphae may serve to carry the fungus across a continent. Fungi in dried wood have been known to revive upon dampening after over seven years of storage in a dry laboratory (73). Contact between sound wood and decayed wood may serve to bridge active fungus hyphae across to the sound wood. Decay in one member of a wooden structure may spread from piece to piece by contact.

Certain wood-destroying fungi, notably Merulius lacrymans (Wulf.)

Fr., Poria incrassata (B.&C.) Burt., Armillaria mellea (Vahl.) Fr., and

Cyathus stercoreus (Schw.) de Toni, may develop specialized mycelial

strands which stretch out along any surface and carry the living hyphae

to new sources of sound wood many feet away from the original infection.

Moisture may also be carried to dry wood by means of these strands.

The vital processes of fungi, as well as of other forms of life, depend upon several conditions: a supply of food, water and air (although certain forms of fungi approach an anaerobic existence, deriving their oxygen from decomposition products). In addition, the temperature must fall between certain definite limits to facilitate growth.

It may be seen therefore that wood decay is likely to develop in any piece of unprotected wood which meets the moisture and temperature conditions favorable to decay. Spores may be considered always present.

Some retain their viability for great lengths of time and are ready to

germinate when conditions favor their growth.

Preservatives like creosote, copper-meta-arsenite and others act both to kill fungi which contact them, and to inhibit the germination of spores by a chemotronic action. C. Audrey Richards says, however, that different species of wood-destroying fungi vary greatly in their resistance to toxic agents. Even within a given species, different physiological strains or races exist which also show considerable variation in their resistance to the same toxic agent.

Moisture sufficient to promote decay in dwellings may be trapped in wood joints by capillarity, or it may be accuired through leaks in plumbing, condensation of moisture, scrubbing water, or absorption from the soil.

The most important physiological factor in regard to either stain fungi or wood decay fungi, at least from the standpoint of control, is that of their habit of secreting acids and enzymes which dissolve the food substance, and which are then reabsorbed by the fungus hyphae.

Wood preservation aims at this week point in the fungus life cycle; the powerful dissolving action of the acids also encompasses the ability to dissolve a wide range of chemicals which may be harmful or fatal to the fungus responsible for the secretion.

Schander, Ruhland, Barker and Gimingham worked on copper fungicides in 1904. They all came to the conclusion that fungus secretions may dissolve insoluble copper. Exosmosis of this substance by hyphae or spores brings about their death.

As early as 1896 Swingle thought that the germ tube of a fungus is killed by copper absorbed from the cuticle of the host or substratum. He thought that there might have been a chemotropic action which discouraged penetration.

Martin (116) believed that copper salts dissolve in the slightly acid secretions of fungus spores, depositing a cupric phosphate layer on the spore membrane and making it impermeable. Martin proved that copper on spores stops germination; cleaning with hydrochloric acid results in renewing the power to germinate.

Actually, it takes a higher degree of toxicity to kill fungus spores than it does to kill higher plants (8) and a higher degree of toxicity to kill bacteria than to kill fungi. Molds are harder to kill than are wood-rot fungi. Concentrations of copper salts sufficient to protect wood from decay, seldom are sufficient to protect wood against surface molds.

Thus it may be seen that to kill fungi, a poison must be soluble in the fungal acids. It need not necessarily be soluble in water to more than the slightest extent. In fact, solubility in water is a poor quality, as leaching may remove all or most of the preservative before fungi ever find other conditions favorable to begin an attack.

Wood, of itself, does not "break down." It is stable, and will last indefinitely unless external agencies destroy it. These agencies include fungi, insects, marine borers, fire and mechanical wear.

MARINE BORERS

Of late years we have been hearing more and more of the danger of attacks on marine structures by a group of organisms called marine borers. Wood preservatives have been called upon to protect wood against marine life as well as against fungi and insects.

Several factors have brought this question vividly to the public mind, most prominent among them being the sudden and severe "epidemic" of marine borers in San Francisco Bay from 1917 to 1921, when an estimated

\$25,000,000 of demage was suffered by dock, wharf, bridge and warehouse owners.

At the time of the San Francisco epidemic a commission was set up by the National Research Council to study and combat the menace, and the commission made its recommendations in an exhaustive report in 1924.

Other excellent discussions of the question may be found in various commercial advertising literature (30)(97), and in several government publications (163)(164)(170)(171).

Marine borers, unlike decay organisms, are quite rapid destroyers of wood, and they may completely destroy an unprotected wood pile in from six months to a year or more, depending on the location and the warmth of the waters. In the Gulf of Mexico, the tropical waters of the Panama Canal, The Hawaiian and Philippine Islands, and Guam, the Teredo may be expected to reduce small piling to a fragile shell in six month's time. In the colder waters of the North Atlantic and North Pacific Oceans, the time would be increased to at least a year, and possibly four or five years.

There are two general groups of marine borers; the Molluscans, related to oysters and clams, and the Crustaceans, related to lobsters and crabs. The two groups are quite different in their physiological structures and life processes.

Of the first group, the Mollusks, American representatives include the Teredo, the Bankia and the Martesia genera.

Teredo and Bankia are the most destructive of all our borers from the standpoint of both speed and unsuspected damage. They are commonly known as shipworms, and have been a scourge of ocean shipping for ages past. Alexander the Great was known to have been plagued with them,

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according to Pliny the Elder (123g).

Teredo will grow to a maximum length of four feet and a maximum diameter of one inch, although at the time of infestation the young Teredo is only of pin-head size. Teredo and Bankia hatch from eggs, and the larvae are free swimmers, which finally become attached to wood and begin to burrow in with their hard, shell-like cases. As the borers grow, the excavating shell remains attached to the anterior portion and grows in diameter, too. Thus the borer becomes imprisoned in a long tunnel of ever-increasing diameter. As the Teredo grows, it secretes a calcareous substance which forms a hard lining around the tunnel. Its food consists of both minute marine life called plankton and the wood which is excavated.

The <u>Martesia</u> genus is not included in the ship worms, but is clamlike, its body being always encased in a lime shell. It is smaller than <u>Teredo</u> or <u>Bankia</u>, seldom attaining a length of $2\frac{1}{2}$ inches or a diameter of one inch. <u>Martesia</u> occurs at present in American waters only on the shores of the Gulf of Mexico.

The Crustacean borers include, in our waters, Limnoria, Sphaeroma and Chelura. The Limnoria and Sphaeroma belong to the Isopoda, among which are included the common sow bugs or wood lice. The Chelura spp. belong to the Amphipoda which includes the common sand flea. All have the general appearance of free moving soft insects, suggesting sow bugs and young shrimp.

over all United States coasts. Like the other Crustacea, and unlike the Molluscan borers, wood constitutes all the food of Limnoria. The young hatch from eggs, but have no free swimming stage, so that the spread

is quite slow. At maturity the <u>Limnoria</u> attain a length of from one-eighth to one-quarter inch. Its attack is external only, so that the damage is easily seen and appraised, and it extends only about one-quarter to one-half inch deep. But the pounding of ocean flotsam wears away the riddled outer portion at the water line and continually exposes new wood for the <u>Limnoria</u> to attack. The damage from <u>Limnoria</u> is increased tremendously when water conditions favor a heavy increase in animal life. That these conditions may come about through changes in sewage disposal, industrial waste disposal and changes in current is well known. Attacks in San Francisco Bay were experienced suddenly, after years of seeming immunity.

The Sphaeroma is larger than the Limnoria, often reaching a length of one-half inch and a width of one-quarter inch, but it is not so prevalent as a rule. It produces one-half-inch burrows.

The Chelura, which is a member of the Amphipoda, does not occur in our North American waters. It is found in the warm, tropical waters of the Canal Zone and around our tropical possessions.

Creosote has generally been conceded to be a dependable marine borer safeguard, although it has failed in many instances in San Francisco Bay against the ravages of the Crustacea, according to Atwood and Johnson's "Marine Structures" (Wash: Natl. Res. Council. 1924) 12.

The writer has observed creosoted piles in the Bay area with the centers completely riddled by Teredo, so that only a thin shell remained.

Entrance was gained through the creosoted shell, which was, however, little damaged in itself. Only the heaviest injection of creosote served to protect piling in these waters, but heavy injections did prove 12.

Report of the Committee on Marine Piling Investigation, National Research Council, Washington, D.C.

effective.

Matched piling treated with copper-meta-arsenite was observed (in comparison) to have survived over eleven years of constant exposure without attack by any of the borers. The only large dock installation of copper-meta-arsenite-treated piling¹³ of which the writer is aware, has not yet been in service long enough to show conclusive evidence of its marine borer protection.

As with fungus control, the basic principle in marine borer control is the killing of borers by rendering their food poison. The preservative must be sufficiently soluble in the digestive juices of the borer to result in toxic quantities being absorbed, but in this application above all others the solubility must not be such that the preservative would leach out in water.

TERMITES

A group of insects responsible for tremendous losses in the United States is that known as "white ants" or termites. The common name of "white ant" is a misnomer, for the termite is neither an ant, nor is it always white. Termites are, in fact, more closely related to roaches than to ants. They live in colonies like ants, with definite castes of workers, soldiers and reproducers, but there the similarity ends.

Termites are found all over the United States, but particularly in four areas: the South Atlantic States, the Gulf States, the Southwest, and the Pacific Coast. They attack all kinds of wood and wood products, from wooden dwellings to bridges, telephone poles and vineyard stakes.

Dr. Thomas E. Snyder (147) estimates that they are responsible for an annual loss of over \$40,000,000. In many sections of California the

^{13.} Private dock of Henry Kirchmann, Berkeley, California.

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termite has infested nearly 100% of all the unprotected wooden structures, a condition which the writer can verify at first hand through nearly six thousand miles of official travel in the area.

It is reported that there are over two thousand species of termites throughout the world, and fifty-six species in the United States. (In contrast, Europe is reported to harbor only two species.) There are, broadly, three main groups of termites which live and work under characteristic environments: 1. Subterrane an or soil inhabiting; 2. Dry wood, and 3. Damp wood termites. Each group is distinct enough to require different methods of control, but all termites have life histories and habits that show considerable similarity (43)(60)(97)(99)(147)(153).

Concisely, a single pair of king and queen termites start a new colony, and no other reproducers will be found in that colony until after the death of the original king or queen or both, or at the time of seasonal flight migrations.

The eggs, laid by the queen, hatch to nymphs which develop by stages involving the shedding of successive skins. In two groups the workers responsible for actual damage to wood include only the young nymphs in their earliest stages of metamorphosis, while in the subterranean group a permanent worker class is maintained. Some nymphs mature to the soldier or guard class with enormously developed heads and mandibles. (The soldiers are sterile, wingless, colored and blind; some species develop soldiers which fight by secreting a sticky fluid). The size of mature termites varies from one-quarter inch long in the subterranean group, through one-half inch for the dry wood group, to a maximum of three-quarters inch for the damp wood order.

All termites eat wood substance as a main item of diet, but they cannot digest wood without the help of one-celled intestinal Protozoa (and other bacteria and fungi) which secrete enzymes for the digestive process. The mandibles of termites look small and weak, but they suffice to bite off innumerable tiny pieces of wood.

After a sufficient length of time, when the successive growth transformations have occurred, termites are found to develop wings and to be able to fly for a short period of time. Swarms of flying alates (the sexually mature, winged forms) may be seen about April or May, although on the Pacific Coast another swarm usually occurs after the first warm fall rains. The alates fly for varying distances, possibly up to several miles in a wind, and shortly descend to the ground where their wings drop off, they find mates, and crawl into places of concealment to consummate their mating and establish a new colony.

Very few swarming alates survive these mating flights; those which escape birds have still to find a mate and favorable location for a new colony. (Winged termites, or "flying ants", are poor fliers, lacking maneuverability).

Termites, like the Molluscan marine borers, invade wood for a twofold purpose: to gain shelter and to utilize the wood for food. The

nymphs cannot stand exposure to strong light, high temperatures or low
humidities, consequently timbers are always excavated to a hollow shell.

External evidence of termite damage may be entirely lacking and unsuspected until an increased load on a timber or board causes it to fail.

Termites have many natural enemies, and if they do make an opening from
their galleries, they quickly close it with a pasty substance.

Termites eat each other's partially digested excreta, cast-off skins, sweet secretions, and their dead fellows. In addition they constantly groom each other in the colony - a habit called trophallaxis -

for a purpose thought by most investigators to be directed toward personal sanitation.

Several investigators lip have been able to kill an entire termite colony by dusting one termite with arsenic trioxide. Successive grooming, or trophallaxis, accounted for the deaths of the balance of the colony.

SUBCERRANEAN TERMITES inhabit the soil, and attack wood only in the soil or in contact with it, except under conditions where the termites build their own contact galleries. Unlike the dry wood and damp wood termites, these have a definite worker caste.

Like other termites, these shun light and low humidities, hence their work is seldom in evidence until a failure occurs. Sometimes, however, the contact tubes may be seen in semi-hidden locations, or seasonal flight swarms may give evidence of attack. The subterranean termites have been officially reported in every state in the Union except North Dakota, and it seems probable that they will be found there.

In the United States at least eight species of Reticulitermes, and one lone species of Heterotermes (in the Southwest) have been reported.

DRY WOOD TERMITES are entirely wood inhabiting. They need very little moisture 15 to carry on their life processes, and they enter wood directly from the air at swarm periods. Points of entry include checks, cracks and open joints in pieces of wood or in dwellings.

These termites form fecal pellets and discharge them periodically

^{14.} Including Schrader of the University of Washington.

Hunt and Garratt (35) estimate that dry wood termites will work in wood of 10 - 12 % moisture content or higher; no upper limit is noted.

from temporary openings, which habit often serves to indicate their presence.

Only one genus, Kalotermes, is represented in our country. It is found only in a narrow strip across the southern tier of states and up both coasts, as far as Virginia and Central California. It is much less injurious than the subterranean group, and requires several years to do appreciable damage.

Subterra nean termite damage is often incorrectly appraised as dry wood termite damage when the manner of entry is unknown. Upper floor damage in dwellings has often been traced to direct contact with the soil through hollowed grape vines, wistaria, Virginia creeper, and ivy.

DAMP WOOD TERMITES, like the dry wood group, require no contact with the soil, but they must have wet wood to continue their operations. In almost every instance the wood will be found to be decayed as well as wet, but whether the damp wood termites select decayed wood or cause it, is yet to be determined. It is known, however, that their operations do extend into sound wood.

This group belongs to the genus Zootermonsis (or Termonsis), and it is found only west of the Rocky Mountains, usually in damp forests. Occasionally wet wood termites extend their work into buildings from an old decayed stump left under a house, in contact with foundation members.

Very few native woods offer much resistance to termites. The heartwood of redwood, cypress, Port Orford cedar, and some very resinous pines has shown marked resistance, but at times even these species are attacked severely. Termites will work in the sapwood of any species.

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Preservatives may act to kill the termites outright, to kill the fungi in the termite galleries, 16 to poison the Protozoa in the termites intestines, or to discourage the termites by rendering the wood unpalatable.

Heavy injections of creosote accomplish these purposes, as do various arsenic salts. Copper-meta-arsenite has proved itself a termite resistant treatment for wood, but only in the zone penetrated.

Termites may bridge over treated wood, or enter the center, untreated portions of timbers which have checked or cracked deeply.

POWDER POST BEETLES include several genera of beetles which are responsible for a tremendous amount of damage to wood products in the United States.

Adult beetles either bore holes in wood or bark to deposit their eggs, or they utilize natural openings such as pores in the hardwoods. The larvae, or grubs, hatch from the eggs and begin to bore into the wood for food and shelter. They leave behind, as they bore, a fine powder which consists of undigested wood particles. Usually the presence of wood borers is indicated by this dust or powder which falls out of the small openings.

In time a metamorphosis occurs, pupation beginning in the early spring, and the adults bore holes to escape in late spring or early summer. They repeat the life cycle in other pieces of wood, or even in the same piece.

The worst beetles, from the standpoint of total damage, are in the genus Lyctus, which occurs all over the United States. They concentrate their operations on hardwoods with large pores such as the oaks,

^{16.} Some investigators believe that termites cultivate fungi to use it for their protein intake - a vital dietetic factor.

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ashes and hickories, but they also attack maple, walnut, persimmon, elm and sycamore.

Since the starch content of the wood seems to determine its liability to attack, most of the damage occurs in the sapwood. More damage occurs in fast dried wood than in very slowly dried material. Kiln dried furniture woods are often seriously damaged by these beetles, as are untreated interior trim and flooring.

The arsenic component of copper-meta-arsenite is the active control factor in beetle protection.

CARPENTER ANTS are true ants which excavate wood in contact with the soil, but they do not utilize the wood for food. Their excavations serve for shelter only, and may be easily distinguished from termite excavations because carpenter ants maintain absolutely clean galleries. Termites leave pasty excreta, frass or pellets in their workings.

Carpenter ants prefer to work in springwood of posts, poles and timbers that are already partially decayed. They take years to do any appreciable damage. Copper-meta-arsenite will control them two-fold: first, it will prevent decay, a condition which they prefer; and, second, it will kill the ants which excavate in the treated wood.

For every living agency of wood destruction the same fact holds true — that exterior protection alone is not the final answer. Wood is too prone to check or crack, exposing the inner, untreated portion. When that is the case, any one or all of the agencies can proceed to attack the inner portion without harm from preservatives in the outer shell.

FIRE is one of the major factors in the destruction of wooden products.

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but it has been capitalized to excess in the claims of commercial preservatives.

No preservative on the market today is fireproof, but some are fire resistant, at least to a degree. In the quantities in which metal salts are injected into wood, there could be very little pronounced fire resistance. On the other hand, certain widely used metal-salt preservatives would actually harm wood if they were present in sufficient quantity to prevent burning.

Oily preservatives, such as creosote, actually add to the heat of combustion when a treated timber burns. Creosoted timber, in addition, produces an objectionable, dense black smoke when burning.

Proprietary compounds as a whole offer advantages over creosote from the fire standpoint, but mostly in the fact that they do not add to the heat of combustion. Their fire resistance is usually far over-rated. For a complete discussion of this problem, see the files of the Annual Proceedings of the American Wood Preservers' Association (4); Hunt and Garratt (85); Prince (125); Truax (158)(159); and the technical indexes and catalogues in public libraries (170)(171).

LABORATORY METHODS OF PRESERVATIVE TESTING

LABORATORY METHODS OF PRESERVATIVE TESTING

There are three general approaches open to the experimenter by which the comparative preservative value of a given chemical may be determined: first, by putting full-size wooden timbers in ordinary construction and watching them to see how they compared in durability with matched untreated timbers, or by using smaller pieces of the same materials exposed to more severe natural rotting conditions; second, by carrying on the test in the laboratory, using equipment which would rot treated wood under optimum conditions; and third, by growing wood-rotting fungi on artificial media with varying concentrations of preservatives (9)(10)(20)(42)(49)(50)(69)(131)(135)(142)(172)(176). Snell (143) gives an unusually clear discussion of the problem.

The first broad test method is too slow and cumbersome for the tempo of our times, except for poor preservatives on the least durable wood species. It is, however, the truest test of the value of a preservative or the relative durability of a species, showing in from one to fifty years what might actually occur under ordinary service conditions in about the same time. The third method is too theoretical to rely upon without practical substantiation.

The second method, although artificial, is probably most often employed by researchers in the field, giving results in from one to six months that would require up to ten times that many years under natural conditions. The accelerated results may or may not indicate what can be expected in service; several investigators using the same technique may disagree on their findings because wood and its treating are so variable. Nevertheless, the American public is attuned to a tempo of living and working which demands speed in everything - in development,

in production and even in research - hence the almost universal acceptance of the fast, variable, non-standardized laboratory technique of testing (142).

Photography and increasing dissemination of technical journals have aided much in the gradual trend toward the standardization of technique, but the goal is yet to be reached. It is, of course, impossible to standardize every variable because of the heterogeneous nature of wood itself and the uneven depths of penetration in even a single piece of timber.

Taking the matter of the test fungus alone, considering tests with a single fungus, there are today advocates of at least a half dozen fungi to be used against an array of wood species, wood preservatives or concentrations of one preservative. The Forest Products Laboratory at Madison, Wisconsin, recommends strongly their strain of test fungus No. 517, an unidentified isolate from a decayed mine timber (133). The Western Pine Association Research Laboratories in Portland, Oregon 17, have based considerable work on tests with Lenzites trabea (Pers.) Fr., an active dry-rot fungus encountered in actual service conditions. In some European laboratories Merulius lacrymans (Wulf.) Fr., vies for first honors, being a troublesome timber destroyer on the European continent. Poria incrassata (B.& C.) Burt., Coniophora cerebella Pers., and others are preferred in some laboratories in this country for the reason that they are common, either here or where our timber is shipped.

All the fungi named have their merits from one standpoint or another, whether it be that of actual danger of attack by them under natural conditions; that of broad adaptibility to wood species (102)

^{17.} Wood decay studies directed by Dr. Ernest E. Hubert.

and conditions; that of rapidity of growth and attack (172); or that of ease of growing and propagating the fungi in pure culture in the laboratory. Some fungi attack lignin most strongly while others seem to concentrate on wood cellulose; some attack softwoods and some prefer hardwoods (102). Factors such as these may determine the choice of organisms.

Some investigators prefer the use of Petri dishes for culture work while others, with equally good reason, prefer the use of Kolle flasks.

Each type of culture chamber has its peculiar advantages (109)(142)(175).

A great volume of literature covers the subject of preservative testing, and many investigators have devoted their time to studies in the field. Bateman, Findlay, Fleming, Harsch, Hatfield, Hirt, Hubert, Humphrey, Kaufert, LaFuze, Long, Reeve, Richards, Schmitz, Snell and Waterman have covered the technique quite thoroughly. See citations (9)(10)(11)(49)(50)(51)(62)(63)(69)(73)(80)(81)(83)(96)(102)(109)(131)(135)(142)(143)(163)(172)(176).

One of the most significant steps toward standardization of technique in the field was taken in Missouri in December, 1929, when a group of interested workers headed by Henry Schmitz met to discuss the problem (142). Although no clear-cut standards resulted from the meeting, considerable progress was made.

Two broad testing systems are extant, the American and the European.

In the American system fungi are cultured on agar with various concentrations of preservative to find the total inhibition and killing points.

Every fungus shows different points with the same preservative, making

^{18.} The group included E.E. Bateman, R.H. Colley, S.R. Church, Carl Hartley, E. Waterman, A.L. Kammerer, H. von Schrenk, E.B. Fulks, E.E. Hubert, C. S. Reeve, W.H. Snell, C.A. Richards, D.H. Linder, J.D. Burnes and Henry Schmitz.

it necessary to compare different chemicals against the same organisms.

Madison No. 517 is often used.

The European method relies on tests involving treated blocks of pine sapwood, with a matched untreated test block. The small wood cubes are laid over a fungus mycelium mat on agar and allowed to remain for an arbitrary period.

GENERAL PROCEDURE

SELECTION OF WOOD

In order to eliminate the human element as far as possible, it was decided to select commercially treated lumber rather than to treat the lumber by hand. Accordingly, the lumber yards of the Diamond Match Co. at Stirling City, California, were used as a source of supply for treated wood. In September, 1937, random samples of commercial 2"x4" white fir sapwood (Abies concolor, Lind. & Gord.) were cut by the writer from mid-sections of treated full-length scantling, and brought to East Lansing, Michigan.

The surfaced 2"x4" material varied in ring count from six to twelve rings per inch.

From the same lumber yard, untreated 1"x4" white fir strips were taken for check samples. Every piece in the yard was of the current year's sawing, sound and air-dried.

At East Lansing the samples of lumber were sawed into about 1/8" thick cross-sections which were numbered with pencil consecutively from 1 to 36, with a key letter preceding, as A-1, A-2, B-1, B-2, etc.

After sawing and numbering, the sections were bound together in packets of similar key letter and allowed to come to equilibrium in a closed box in a warm inner room of the Plant Pathology Laboratory.

After two months several specimens of each bound set were weighed carefully, dried in an oven at 212°F., and weighed again. The loss in weight, expressed as a percentage of the oven-dry weight of the sample, was taken as the initial M.C. (moisture content) of each piece. The several M.C.'s were then averaged together and that figure was used as the average M.C. for the packet.

Using the average M.C. as a basis, oven-dry weights were calculated for each numbered wood wafer, and recorded for future reference.

SELECTION OF GLASSWARE

Early in the experiment it was decided to use the so-called European system of preservative analysis and rating. For an authoritative evaluation of this and other methods of procedure see Schmitz (142), Hunt and Garratt (85), Riker and Riker (136), Boyce (20), Richards (135), and Long (109). Dr. Ernest E. Hubert, of the Western Pine Association Laboratories in Portland, Oregon, had shown the writer the advantages of the cotton-stoppered Kolle flask some time before.

Thirty Pyrex Kolle flasks and one hundred Pyrex test tubes were made available for experimental use, together with other necessary equipment for mixing media, making transfers and sterilizing.

SELECTION OF CULTURES

On the written advice of Dr. Hubert, the following wood-rotting and wood-staining fungi were selected for the study:

- 1. Poria incrassata (B.&C.) Burt. (78)(79)
- 2. Merulius lacrymans (Wulf.) Fr.
- 3. Lenzites trabea (Pers.) Fr.
- 4. F.P.L. Madison No. 517 (133)
- 5. Trametes serialis Fr.
- 6. Lentinus lepideus Fr. (174)
- 7. Coniophora cerebella Pers.
- 8. Graphium rigidum (Pers.) Sacc.
- 9. Ceratostomella pluriannulata Hedg.
- 10. Certostomella pilifera (Fr.) Wint.

A request for cultures of each fungus was directed to Miss C.A. Richards, Pathologist of the Forest Products Laboratory at Madison, Wisconsin. (Miss Richards maintains the public stock of wood attacking fungi for the United States Department of Agriculture.) All were furnished except 2 and 7, which Miss Richards was unable to supply.

Later in the study several additional fungi were tried in a limited way. These included <u>Cyathus stercoreus</u> (Schw.) de Toni (172), <u>Chaetomium sp., Penicillium sp., Armillaria mellea</u> (Vahl.) ex Fr., <u>Aspergillus sp.</u> and <u>Mucor sp.</u>

With this selection of organisms it was possible to determine the inhibiting or killing action of copper-meta-arsenite on typical mold-, stain-, and wood-rot fungi.

Stock cultures of the various fungi were kept growing on malt agar in test-tube slants by transferring to fresh agar slants as the preceding ones began to dry out after one to two months. Later in the study it was found that test tube cultures could be kept almost indefinitely without transfer by sealing the cotton plugs with a skin-like product called Parafilm 19. Even aerobic fungi seemed to grow about as well when sealed as when unsealed, although the moisture was kept from escaping for as long as a year.

EXPERIMENTAL PROCEDURE

Malt-agar media were prepared according to advice from Miss C.A.

Richards. From 1.0% to 2.5% bacto-agar, and from 1.0% to 2.5% Trommer's liquid malt²⁰ were tried with little variation in the growing rate of fungi. Higher concentrations of bacto-agar were found to be desirable,

^{19.} Made by the Menasha Products Co., Menasha, Wisconsin.

^{20.} The Trommer Company, Fremont, Ohio.

however, in that less media breakdown occurred. (The necessity for careful sterilization of agar resulted in several cases of advanced temperature breakdown. Although the fungi would grow well on liquid media, the technique employed in this study would not accommodate it) (109).

Sterilization of Kolle flasks and media was effected with an autoclave run at approximately seventeen pounds of steam pressure. Temperatures at over twenty pounds of steam often were sufficient to break down the agar completely. Even at seventeen pounds pressure, partial breakdown sometimes occurred, and it was necessary to let the flasks sit hot for about twenty minutes to allow the precipitate to settle. If this were not done, the flocculent precipitate would interfere with the detection of contaminants in young cultures.

The concensus of opinion among laboratory technicians is that several intermittent heatings at about twenty-four hour intervals are more efficacious in sterilization than is one equal, prolonged heating.

Intermittent heating allows heat-resistant spores to germinate between successive heatings and to become sensitive to high temperatures.

After sterilization, the agar plates were carefully inoculated in several places from the stock cultures of fungi. Gummed labels were marked, placed on the necks of the flasks and covered with Parafilm to prevent loss of legibility. While the inoculated areas grew, the plates were watched carefully for evidences of contamination.

Efforts to remove contaminants proved fruitless. Attempts were made to lift out contaminated areas bodily; to burn them out with red-hot spatulas; to kill the contaminants with alcohol, mercuric bichloride, carbolic acid and copper-meta-arsenite. None proved entirely successful. The mechanical method was unreliable; it seldom caught all the contamin-

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ants. The red hot spatula served to spatter spores or pieces of agar and hyphae. Alcohol in any concentration seemed only to inhibit temporarily the growth of foreign fungi and bacteria. The several poisons made permanently sterile areas on the agar plates. If contamination were found to occur, it was deemed best and fastest to start over again with a new culture.

After several days to a month (depending on the species of fungi) the several inoculated areas coalesced to a single mycelial mat which covered the entire surface of the agar. When this had occurred, sterilized wood wafers were laid flat on the mycelial mat and allowed to remain undisturbed for the test period of from two to eight months.

For wood sterilization, it was decided to use the method suggested by Schmitz, von Schrenk and Kammerer (141, page 68). This method employs boiling water entirely, rather than an oven, and it is much more flexible and desirable from many standpoints than the oven sterilization method described by Hirt (69):

Hirt oven dried one-inch cubes of locust wood at 104°C, until they reached a constant weight. Then they were left twenty-four hours longer in the oven to kill fungus spores. Next the cubes were placed in cold, sterilized water and aspirated for two hours, after which they were allowed to soak for sixteen hours more. Finally the sterilized wood was put into culture flasks over mycelial mats, and left for the duration of the test period.

Schmitz, von Schrenk and Kammerer found it much simpler, faster and more satisfactory to sterilize wood wafers for decay resistance tests by employing boiling water and dipping the specimens into it intermittently for only a few seconds. They report the method effective in a vast majority of cases.

The experiment described in this paper followed the water sterilization technique with entire success, after several simple tests were made to determine just how much immersion time was required to insure complete sterilization of the wood. Plate 1, Figure 1, shows the rank growth of fungus hyphae growing from an unsterilized wood specimen placed on malt-agar media. Figure 2 shows the result of insufficient immersion time — bacterial growth in evidence although all the fungus spores were killed. Intermittent dipping which totalled about fifteen seconds in rapidly boiling water was sufficient to kill all fungi and bacteria present.

When the first test series was conducted, full cross-section wafers were employed intact, with the outer zone of treated wood surrounding an inner untreated core comprising about half the area of the section.

It was apparent that if the copper-meta-arsenite were soluble in hot water, then not more than a few pieces of wood could be sterilized in the same water without the possibility of partially treating the center core. Subsequent leaching tests proved that only minute quantities of metal salts leached during the few seconds of sterilization, but no more than three pieces were sterilized in the same water, regardless.

The cross sections of untreated 1" x 4" white fir sapwood used as check samples were always sterilized in a separate beaker of distilled water. No limit was placed on the number of pieces which might be sterilized in the same water.

As each treated and untreated sample was sterilized, it was allowed to cool for a few seconds, and then was quickly transferred directly onto the mycelial mat of one of the culture flasks. (If laid on too quickly, the high temperature served to kill the mycelium under the test specimen or to melt some of the agar. In some cases the specimens sank so

deeply into the agar that the moisture content of the wood remained too high for fungus growth.)

The Kolle flasks were plugged again and the cotton stoppers were sealed with Parafilm to retard drying out. This method of sealing cotton plugs with Parafilm proved highly successful, for it dispensed with the need for expensive humidity chambers. Cultures were kept in moist condition for as long as a year in the dry atmosphere of an inside laboratory.

Near the close of the first test series it was found that certain fungi²¹ sent their hyphae out through the damp cotton plugs (kept damp by the Parafilm), under the Parafilm seal and onto the paper labels. The cellulose of the labels was attacked and several of them were rendered illegible.

Subsequently all labels were affixed near the bottoms of the flasks rather than near the necks where fungus hyphae could reach them. Incomplete experiments indicated that preservative treatment of the cotton plugs (as with a volatile-solvent preservative such as Permatol²²) would discourage fungi from working in the plugs. Poria incrassata was found in several cases to have reduced the untreated plugs to a pulpy, sodden mass, impossible to remove in one piece or to replace tightly.

When the visual evidence of the first series was reviewed, it was apparent that the central cores of the treated wood were affected as much as the untreated check samples. It was then decided to collect further data of a quantitative nature, comparing the loss in oven-dry weight of the treated zone to that of the inner core. The boundary be-

^{21.} Poria incrassata and Madison No. 517.

Formula developed by Dr.E.E. Hubert.

· • . tween treated and untreated zones was arbitrarily set as the limit of visual penetration.

As already described, the average moisture content for each packet of wood wafers had been determined at equilibrium weight, so that oven-dry weights could be calculated for each wafer at any given air-dry weight. Assuming that the moisture content was equal throughout each wafer (the wafers had been sawed and kept in a closed box for a year prior to the assumption) separate weights were taken for the outer treated zones and inner untreated cores after they had been separated with a sharp knife. Oven-dry weights for each were calculated, using the ratio between zone weights to divide the total for the entire wafer.

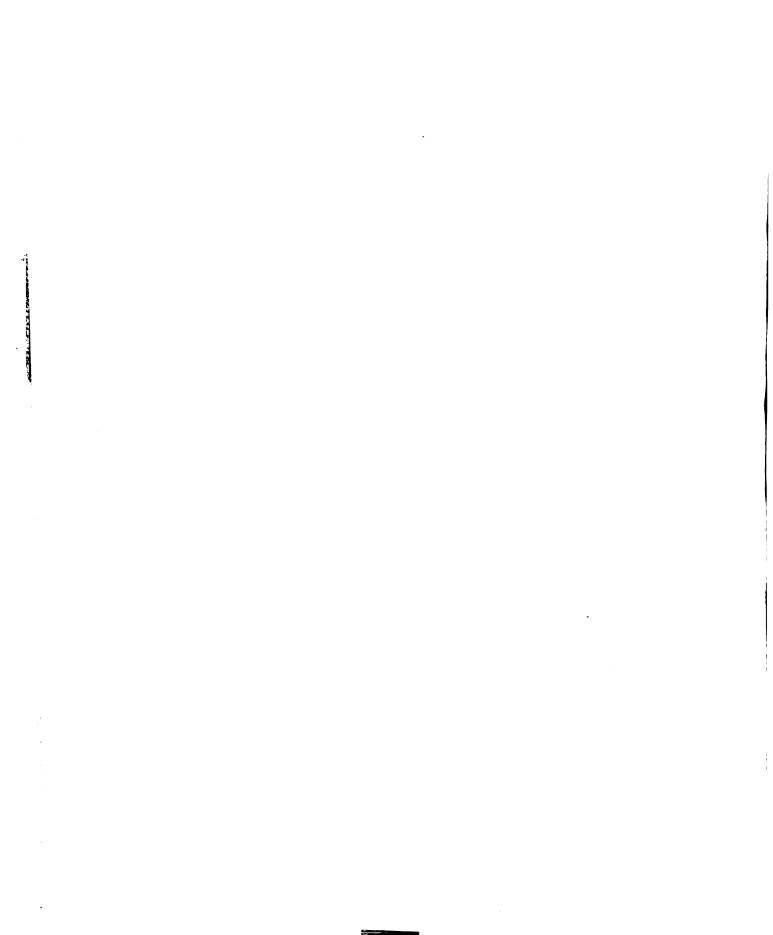
Loss in oven-dry weight was calculated after the experiment, and recorded for each zone of each wafer. No quantitative data, of course, could be taken for the several stain fungi and mold fungi which do not destroy the basic wood structure.

When each culture was judged to have worked upon the wood for a sufficient length of time to produce an appreciable loss in oven-dry weight, or an appreciable stain, the culture flask was opened and the wafers, or parts of them, were removed carefully. Adhering mycelium was gently scraped off to allow a thorough inspection of each specimen.

Several of the earlier cultures were sterilized in an autoclave before opening, but the heat had melted the agar and browned the adhering hyphae so that inspection of the specimens was unsatisfactory. All subsequent cultures were opened unsterilized.

After inspection, the specimens were allowed to air dry for about two days in individual half sealed letter envelopes marked with key numbers. Oven drying followed at a temperature of 100°C, until the

weight became constant. It was necessary to handle the decayed specimens very carefully to prevent loss of fragments or mixing of them; the envelopes proved a convenient aid.



RESULTS

"A" SERIES EXPLANATION

The "A" series represents water-like cross sections of a two-by-four scantling of white fir, commercially treated with coppermeta-arsenite. The preservative treatment was only partially effective, so that the center portion of the scantling remained untreated. Annual rings averaged eight per inch.

Specimens A-2 to A-21, inclusive, were tested in one piece, and only one weight computation was made on each.

Specimens A-22 to A-34, inclusive, were cut to separate the visible penetration zones from the uncolored central portions. Each part of each specimen was weighed separately, and tested under identical conditions.

Five specimens were oven dried to determine the average moisture content of the series, which equalled 7.75% (-.06 to +.08%). From the average moisture content and the air-dry weights of each wafer, oven-dry weights were computed. These weights have been shown singly from A-2 to A-21, and doubly from A-22 to A-34. In the latter case, the top number indicates the weight of the center portion, while the lower number indicates the weight of the outer, treated portion.

Actual oven-dry weights were taken for the respective parts after the elapse of the test periods, and the theoretical losses in oven-dry weights are shown in per cent of the computed values. Percentages less than 0.05% have been dropped as insignificant.

NO.	TEST ORGANISM	DAYS IN	COMPUTED O.D. WT.	ACTUAL O.D.WT.	%SSOI	REMARKS
A-1	SAMPLE OVEN DRIED TO DETERMINE	MOISTURE	CONTENT OF PA	PACKET		7.77% Actual M.C.
A- 2	Graphium rigidum	270	6.133 grams	6.130 gr	0	Badly spotted in center
A- 3	Trametes serialis	#	" ?!!4.6	6.180 #	3.7	Lightly attacked
4−₽	Ceratostomella pilifera	99	₩. 69 6*9	6.570 "	-0.1	Lightly stained in center
A- 5	Ceratostomella pluriannulata	н	7.022 H	7.020 "	0	Badly stained
9-V	Madison No. 517	270	6.310 "	5.880 #	6.8	Slight attack in center
A-7	Lenzites trabea	ff	7.025 "	6.345 "	9.7	Center badly decayed
A-8	Poria incrassata	95	u 054.9	6.140 "	μ.5	Contaminated; moldy
4 -9	Lentims lepideus	270	5.993 n	5.880 "	1.9	Decayed in center
A-1 0	SAMPLE OVEN DRIED TO DETERMIN	MOISTURE C	CONTENT OF PA	PACKET	1	7.83% Actual M.C.
A-11	Porta incrassata	280	1, 408.e	4.345 "	25.1	Badly decayed
A-1 2	Lenzites trabea	14	6.102 #	4.687 [#]	23.2	Badly decayed
A-13	Lentinus lepideus	ft.	5.632 "	5.515 "	2.1	Unaffected
A-1 ¹⁴	Madison No. 517	11	1°25,756 "	5.456 "	5.2	Slight attack in center
A-15	Trametes serialis	Н	o48.6	5.845 "	-0.1	Spotted
A- 16	Ceratostomella pluriannulata	911	STAIN T	TEST ONLY	1	Stained in center
A-17	Ceratostomella pilifera	H	L NIVIS	TEST ONLY	1	Unaffected

* Negative values indicate slight gains.

Poris incressata	NO.	TEST ORGANISM	DAYS IN	COMPUTED O.D.WT.	ACTUAL O.D.WT.	Noss%	REMARKS
Tenzites trabea	1-18	Porta	154		3.770	31.0	Badly rotted; shrunken
## 6.240 6.555 11.3 epideus	A-19	Lenzi tes	н		280	0.5	Contaminated and wet.
Continue Lepideus	1-20	Madison No.	н		535	11.3	Decayed in center
Trametes serialis	1-51	Lentinus	=			2.3	Slightly attacked
SAMPLE OVEN DRIED TO DETERMINE MOISTURE SAMPLE OVEN DRIED TO DETERMINE MOISTURE SAMPLE USED TO TEST EFFICACY OF STERILIZATION TECHNIQUE Cyathus stercoreus 145 2.239 " 3.195 " -0.1" 3.195 " -0.1" Madison No. 517 159 3.274 " 3.250 " 0.7 SAMPLE USED TO TEST EFFICACY OF STERILIZATION TECHNIQUE 0.7 Chaetomium sp. 45 2.930 " 2.825 " 0.5 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET 0.5 Cyathus stercoreus 83 2.543 " 2.554 " 2.564 " 2.0 Ceratostomella pluriannulata 90 2.570 " 2.555 " 0.2 Madison No. 517 159 2.516 " 2.559 " 0.2 Madison No. 517 159 2.516 " 2.590 " 0.2 2.556 2.557 " 2.555 " 0.2 0.2 2.567 " 2.557 " 2.555 " 0.2 0.2 2.560 " 2.557 " 2.555 " 0.2 0.2 3.100 " 3.105 " 2.557 " 2.555 " 0.2 3.370 " 3.350 " 2.557 " 0.2 3.370 " 3.350 " 2.555 " 0.2 3.370 " 3.350 " 2.557 " 0.2 3.350 " 3.350	-22	Trametes	83			11.9	Weakened (center) Slightly stained (outside)
Cyathus stercoreus 145 2.239 " 3.191 " 3.195 " -0.1* SAMPLE USED TO TEST EFFICACT OF STERILIZATION TECHNIQUE 3.250 " 0.7 Madison No. 517 159 3.274 " 3.250 " 0.7 SAMPLE USED TO TEST EFFICACT OF STERILIZATION TECHNIQUE 0.7 Chaetomium sp. 45 2.935 " 3.557 " 3.520 " 0.5 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET 2.547 " 2.564 " 2.0 Ceratostomella plurianniata 90 2.537 " 2.557 " 2.557 " 0.2 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET 0.2 Madison No. 517 159 2.515 " 2.557 " 0.2 Madison No. 517 159 2.515 " 2.540 " 0.2	1-23	SAMPLE OVEN DRIED TO DETERMIN		OF	ACKET		7.69% ACTUAL M.C.
SAMPLE USED TO TEST EFFICACY OF STERILIZATION TECHNIQUE SAMPLE USED TO TEST EFFICACY OF STERILIZATION TECHNIQUE Chaetomium sp. Chaetomium sp. Chaetomium sp. Lenzites trabea Cyathus stercoreus Ceratostomella pluriannulata SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Coratostomella pluriannulata SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Ceratostomella pluriannulata SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Madison No. 517 159 2.516 2.537 3.105 3.326 3.326 5.40 6.2.637 8.325 8.504 8.504 8.602	1-24	Cyathus	145				Weakened (center) Slightly attacked (outside)
Madison No. 517 Madiso	1-25	SAMPLE USED TO TEST RFFICACY			DOE:		
Chaetomium sp. 45 2.930 " 3.537 " 3.520 " 0.5 Chaetomium sp. 45 2.930 " 3.520 " 0.5 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET 2.935 " 0.5 Lenzites trabea 83 2.543 " 2.564 " 2.6 Cyathus stercoreus 83 2.516 " 2.564 " 2.0 Cyathus stercoreus 112 2.520 " 3.105 " 0.2 Ceratostomella plurianniata 90 2.637 " 3.105 " 0.2 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET 3.325 " 0.2 Madison No. 517 159 2.516 " 2.5640" 0.2	1-26	Madison No.	159			0.7	Small spot attacked (center) Unaffected (outside)
Chaetomium sp. SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Lenzites trabea Cyathus stercoreus Cyathus stercoreus Ceratostomella pluriannulata SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Ceratostomella pluriannulata SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Madison No. 517 159 2.516 3.350	1-27	USED TO TEST EFFICACY			TOE		
SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Lenzites trabea 83 2.543 " 1.860 " 26.9 Cyathus stercoreus 112 2.520 " 2.195 " 2.054 " 2.05* Ceratostomella pluriannulata 90 2.637 " 2.635 " 0.2 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET 0.2 Madison No. 517 159 2.516 " 2.530 " 5.0	1-28	Chaetomium	45			0.2	Badly molded (center) Unaffected (outside)
Lenzites trabea 83 2.543 " 1.860 " 26.9 Cyathus stercoreus 112 2.516 " 2.195 " 2.0 Ceratostomella pluriannulata 90 2.637 " 3.105 " 0.2 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Madison No. 517 159 2.516 " 2.390 " 5.0 Lenzites trabea 150 2.516 " 2.590 " 5.0	1-29	SAMPLE OVEN DRIED TO		OF	ACKET		7.72% ACTUAL M.C.
Ceratos tomella pluriannulata 90 2.637 " 2.635" 0.2 ** SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Madison No. 517 12.590 " 5.04" 5.0 ** L59 2.516 " 2.390 " 5.0 ** Addison No. 517 159 2.515 " 2.540 " 5.0 **	1-30	Lenzites	83			26.9	Badly attacked (center) Slightly attacked(outside)
Ceratostomella pluriannulata 90 2.637 " 3.325 " 0.2 SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Madison No. 517 159 2.516 " 2.530 " 5.0	1-31	Cyathus	112			5.4	Weakened (center) Stained (outside)
SAMPLE OVEN DRIED TO DETERMINE MOISTURE CONTENT OF PACKET Madison No. 517 159 2.516 " 2.390 " 5.0 2.635 " 2.640 " -0.2*	1-32	Ceratostomella pluriannul	90			0,2	Stained (center) Stained (outside)
Madison No. 517 159 2.516 " 2.390 " 5.0	4-33	SAMPLE OVEN DRIED		OE	ACKET		7.74% ACTUAL M.C.
	1-34	Madison No.	159	2.516 " 2.635 "	2.390 "	5.0	Attacked on one end(center) Unaffected (outside)

* Negative values indicate slight gains.

"B" SERIES EXPLANATION

The "B" series represents wafer-like cross sections of a two-byfour scantling of white fir, commercially treated with copper-metaarsenite. The preservative treatment was only partially effective, so
that the center portion of the scantling remained untreated. Annual
rings averaged six per inch.

Specimens B-3 to B-10, inclusive, and specimen B-19 were tested in one piece, and only one weight computation was made on each.

The remainder of the series was divided with a knife to separate the outer, treated zone from the uncolored central portion. Each part was weighed separately to obtain comparative resistances of the treated and untreated parts of the same specimen, tested under identical conditions.

Six specimens were oven dried to determine the average moisture content of the series, which equalled 7.78% (-.07 to +.05%). From the average moisture content and the air-dry weights of the parts of each wafer, even-dry weights were computed. These weights have been shown singly for B-3 to B-10, and for B-19. For the remainder, the weights are recorded doubly, the top number indicating weight of the center, untreated portion, and the bottom number indicating weight of the outer, treated portion.

Actual oven-dry weights were taken for the respective parts after the elapse of the test periods, and the theoretical losses in oven-dry weights shown in per cent of the computed values. Percentages less than 0.05% have been dropped as insignificant.

REMARKS		7.78% ACTUAL M.C.	Badly attacked.	Attacked in center	Spotted in center	Few spots in center	Unaffected		7.83% ACTUAL M.C.	Conter attacked	Attacked (Center) Unaffected (outside)	Molded all over.	Molded in center.			7.73% ACTUAL M.C.	
LOSS%		1	. 25.9	10.5	0	0.1	3.0		1	L.4	9.4 0.2	1	1			1	
ACTUAL O.D.WT.	31	PACKET	4.963 gm	6.001 "	6.820 "	6.455 "	6.995 "		PACKET	7.380 "	3,625 " 3,654 "	ONLY	ONLY			PACKET	
COMPUTED 0.D. WT.	TION TECHNIOL	CONTENT OF PA	6.697 grams	# 4o1.9	6.822 "	# 09ħ°9	7.213 "		CONTENT OF PA	<u> </u>	4.000 " 3.661 "	N TEST	STAIN TEST			CONTENT OF PA	
DAYS IN CULTURE	F STERILIZATION	MOISTURE O	270	156	55	8	270		MOISTURE C	270	90	£	E			MOISTURE C	
TEST ORGANISM	SAMPLE USED TO TEST EFFICACY OF	SAMPLE OVEN DRIED TO DETERMINE	Poria incrassata	Lenzites trabea	Ceratostomella pilifera	Graphium rigidum	Lentinus lepideus		SAMPLE OVEN DRIED TO DETERMINE	Lenzites trabea	Madison No. 517	Penicillium sp.	Aspergillus sp.			SAMPLE OVEN DRIED TO DETERMINE	
NO.	B-1	B- 2	B-3	η-g	B-5	B-6	B-7	B-8	B-9	B-10	B-11	B-12	B-13	B-14	B-15	B-16	B-17

MO.	TEST ORGANISM	DAYS IN CULTURE	COMPUTED 0.D. WT.	ACTUAL 0.D.WT.	%sso1	REMARKS
B-18	SAMPLE OVEN DRIED TO DETERMIN	MOISTURE (dontent of PA	PACKET	1	7.80% ACTUAL M.C.
в-19	Lentinus lepideus	159	5.735 grams	5.540 gm	η•£	Lightly spotted.
B- 20						
B-21	SAMPLE USED TO THST EFFICACY	OF STERILIZATION	TION TECHNIQUE	2		
B- 22	Ceratos tomella pluriannulata	36	STAIN TE	TEST ONLY		Center badly stained Outside unaffected
B-23						
मेट-ब	Cyathus stercoreus	132	3.207 Grams	2.983 gm 3.329 "	7.0	Center heavily attacked Outside also attacked
B-25	Cyathus stercoreus	06	2.864 " 3.005 "	2.780 #	2.9	celtu
B-26	SAMPLE OVEN DRIED TO DETERMINE	MOISTURE	TENT OF		1	
B-27	Trametes serialis	132	3.432 "	3.310 "	3.6	Center lightly attacked Outside 11 ohtly attacked
B-28	Lenzites trabea	21	2.766 " 3.402 "	2.780 H 3.421 H	-0.5 *	Attacked all over Contaminated with mold
B- 29						
B-30	Lenzites trabea	136	2.333 " 2.545 "	2.535 "	1.6 2.6	Center badly attacked Outside unaffected.
B-31	Madison No. 517	132	2.338 # 3.023 #	2,075 " 2,998 "	11.2 0.8	Center badly attacked Outside stained
B- 32	Graphium rigidum	30	STAIN TE	TEST ONLY		Center lightly stained Outside unaffected
B-33	SAMPLE OVEN DRIED TO DETERMINE	MOISTURE	CONTENT OF PA	PACKET		7.71% ACTUAL M.C.
η Σ- Ω	Lenzites trabes	132	2.775 " 2.771 "	2.515 " 2.770 "	4. 6	Center badly attacked Outside spotted
	A Company of the second	4.4.				

* Negative values indicate slight gains.

"C" SERIES EXPLANATION

The "C" series represents wafer-like cross sections of a two-by-four scantling of white fir, commercially treated with coppermeta-arsenite. The preservative treatment was only partially effective, so that the center portion of the scantling remained untreated. Annual rings averaged twelve per inch.

Specimens C-4, C-5, C-9 and C-26 were tested in one piece, and only one weight computation was made on each.

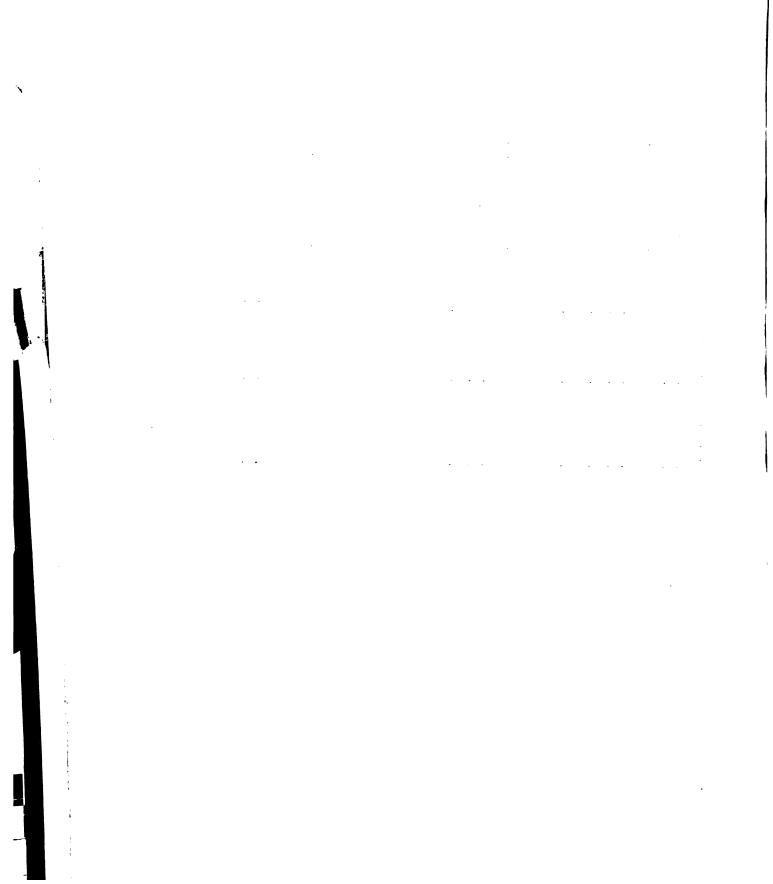
The remainder of the series was cut up to separate the visibly penetrated zones from the central, untreated portions. Each part of each specimen was weighed individually and tested under identical conditions.

Six specimens were oven dried to determine the average moisture content of the series, which equalled 7.75% (-.06 to +.06%). From the average moisture content and the air-dry weights of the parts of each wafer, oven-dry weights were computed. These weights have been shown singly for C-4. C-5, C-9 and C-26. For the remainder, the weights are recorded doubly; the top figure indicates the weight of the center portion, and the bottom figure indicates the weight of the outer, treated portion.

Actual oven-dry weights were taken for the respective parts after the elapse of the test periods, and the theoretical losses in oven-dry weights are shown in percent of computed values. Percentage less than 0.05% have been dropped as insignificant.

	<u> </u>		т	ι —	T	т—	1	1	-	т	1			Т	1	_		7
REMARKS	Wet; no attack	7.81% ACTUAL N.C.	Center appears weakened Outside lightly attacked	Badly attacked in center	Lightly spotted in center		7.73% ACTUAL N.C.	Stained, but not decayed.	All stained slightly					7.71% Actual M. C.		Center lightly attacked Outside lightly attacked		
LOSS%	00	1	4.9	25.5	0.1				-0.1 *					1		12.2		
ACTUAL O.D.WT.	3.074 8	PACKET	2.502 gm 2.705 "	3.898 "	5.498 "		PACKET	2.955 " 3.615 "	6.170 "					PACKET		3.102 "		
COMPUTED O.D.WT.	3.075 grams	e S	2.632 grams 2.710 "	2	5.501 "		CONTENT OF PA	2.962 # 3.616 #	2					CONTENT OF PA		3,534 "		
DAYS IN CULTURE	105	MOISTURE	105	270	32		MOISTURE	66	111					MOISTURE		8		
TEST ORGANISM	Cyathus stercoreus (contam.)	SAMPLE OVEN DRIED TO DETERMINE	Cyathus stercoreus	Lenzites trabea	Graphium rigidum		SAMPLE OVEN DRIED TO DETERMINE	Armillarea mellea	Ceratostomella plurianmiata					SAMPLE OVEN DRIED TO DETERTINE		Trametes serialis		
MO.	G-1	2-5	c-3	t-2	6-5	9-0	2-0	2-8	6-0	0-10	C-11	C-12	C-13	C-14	2-15	91-2	21-0	

*Negative values indicate slight gains.



NO.	TEST ORGANISM	DAYS IN CULTURE	COMPUTED O.D.WT.	ACTUAL O.D.WT.	%sso1	REMARKS
C-18	Mucor sp.	50	STAIN	TEST ONLY	1	Molded all over surface
62						
c -20	O LOVOLLE LSEL OL CESO ETAINVS	OF STERILIZATION	ECOINHOEL NOIL	21.0	-	
c- 21	d lovoille user of cesu ethivs	OF STERILIZATION	ECOINHOEL NOIL	3 L	8	
G- 22	enimeteo of ceiro nevo ethnes	MOISTURE	CONTENT OF PA	PACKET	,	7.69% ACTUAL M.C.
c- 23						
C-24						
c- 25	Trametes serialis	101	3.035 grams 2.335 "	2.760 gm 2.265 "	9.1	Badly attacked in center Slightly attacked outside
92-2	Ceratostomella pluriannulata	66	3.236 "	n 482.8	0	Lightly stained in center
c-27	Madison No. 157	06	3.104 " 3.072 "	3.075 3.065	9.3	No apparent damage in center No apparent damage outside.
C- 28	Sample oven dried to deteriine	MOISTURE	O	PACKET	1	7.76% ACTUAL N.C.
c- 29						
c-3 0						
0-31						
c-35						
0-33	SAMPLE OVEN DRIED TO DETERMINE	MOISTURE	CONTENT OF PA	PACKET	i	7.77% ACTUAL M.C.
0-34						

- :

"D" SERIES EXPLANATION

The "D" series represents wafer-like cross sections of an untreated one-by-four strip of white fir sapwood. Annual rings averaged eight per inch.

The "D" series was used as a control for twenty tests, with matched treated and untreated specimens exposed to decay fungi and stain fungi. Some of the specimens were used for independent tests in Petri dish cultures.

Four specimens were oven dried to determine the average moisture content of the series, which equalled 7.76% (-.06 to +.07%). From the average moisture content and the air-dry weights of the wafers, oven-dry weights were computed.

Actual oven-dry weights were taken for each wafer after the elapse of the test periods, and the theoretical losses in oven-dry weights are shown in percent of the computed values. Percentages less than 0.05% have been dropped as insignificant.

NO.	TEST ORGANISM	DAYS IN CULTURE	COMPUTED O.D. WI.	ACTUAL O.D.WT.	Loss%	REMARKS
D-1	SAMPLE OVEN DRIED TO DETERMINE	MOISTURE	F	PACKET		7.83% ACTUAL M.C.
D- 2	Graphium rigidum	970	3.762 grams	3.770 gm	-0.2 *	Stained over entire surface
D-3	Trametes serialis	ěš.	3.7co n	3.236 #	12.5	Slightly attacked
ከ-ወ	Ceratostomella pilifera	95	" <i>L</i> ηο•η	# 540°t	1	Lightly stained
D-5	Ceratostomella pluriannulata	u	3.010 #	# 100°E	0.1	Heavily stained on one end
9 - a	Madison No. 517	270	1. 172.5	2.883 H	ή*6ι	Badly attacked; shrunken
2-a	Lenzites trabes	ы	3.354 #	2.596 "	22.6	Almost completely destroyed
D-8	Porta incrassata	95	3.950 "	3.869 "	2.0	Contaminated; moldy
р-6	Lentimus lepideus	270	3.541 "	3.223 #	8.9	Lightly attacked
D-10	SAMPLE OVEN DRIED TO DETERMINE	MOISTURE	CONTENT OF PA	PACKET	8	7.70% ACTUAL N.C.
D-11	Porta incrassata	280	3.354 "	2.0 ⁴ 1 "	39.1	Almost completely destroyed
21 - 0	Lenzites trabea	S.	3.801 "	2.758 "	t,.72	Almost completely destroyed
D-13	Lentims lepideus	ĮĮ.	3.575 "	3.140 "	12.2	Lightly attacked
D-14	Madison No. 517	2	3,264 "	2.923 H	η•01	Lightly attacked
D-15	Trametes serialis	¥	3.338 "	3.119 #	9*9	Lightly attacked
9 1- a	Ceratostomella pluriannulata	911	STAIN TEST	T ONLY	1	Spotted irregularly
D-17	Ceratostomella pilifera	=	STAIN TEST	T ONLY		Unaffected

* Negative values indicate slight gains.

NO.	TEST ORGANISM	DAYS IN CULTURE	COMPUTED 0.D. WT.	ACTUAL O.D. WT.	LOSSE	RIMARKS
D-18	SAMPLE USED TO TEST EFFICACY	OF STERILIZATION	ATION TECHNIQUE	aut.	1	
D-19	Lentinus lepideus	159	3.576 gm	3°1103 ga	в •ћ	Lightly attacked
D- 20	SAMPLE OVEN DRIED TO DETERMINE	E MOISTURE	CONTENT OF P	PACKET	1	7.72% ACTUAL M.C.
D-21	Lenzites trabea	156	3.364 "	₩ 918°Z	14.5	Heavily attacked
D- 22	Ceratostomella pilifera	<u> </u>	μ 9ηη • ε	u tht.s	0.1	Stained badly
D-23	SANPLE USED TO TEST EFFICACY	OF STERILIZATION	Tocimes moley	a nt	1	
D– 24	SAMPLE USED TO TEST EFFICACY	OF STERILIZATION	ATION TECHNIQUE	3 000	ŧ 1	
D- 25	Cyathus stercoreus	112	3.422 "	3.273 #	9*4	Weakened
D-26	Graphium rigidum	55	3.102 "	3.108 #	-0-2 *	Spotted over surface
D-27	Penicillium sp.	90	STAIN TEST	T ONLY	1	Heavily molded
D-28	Aspergillus sp.	E	STAIN TEST	T ONLY	1	Heavily molded
D-29	Ceratostomella pluriannulata	36	STAIN TEST	T ONLY	1	Badly stained
D-30	Graphium rigidum	30	STAIN TEST	T ONLY	•	Lightly stained
D-31	Madison No. 517	132	3.517 "	2,872 "	18.3	Attacked; shrunken
D-32	SAMPLE OVEN DRIED TO DETERMINE	E MOISTURE	CONTENT OF F	FACKET		7.80% ACTUAL M.C.
D-33	SAMPLE USED TO TEST EFFICACY	OF STERILIZATION	ATION TECHNIQUE	503		
ո-34	SAMPLE USED TO TEST EFFICACY	OF STERILIZATION	ATION TECHNIQUE	and:	1	

* Negative values indicate slight gains.

PLATE I
RESULTS OF TESTS ON THE EFFICACY OF WATER STERILIZATION

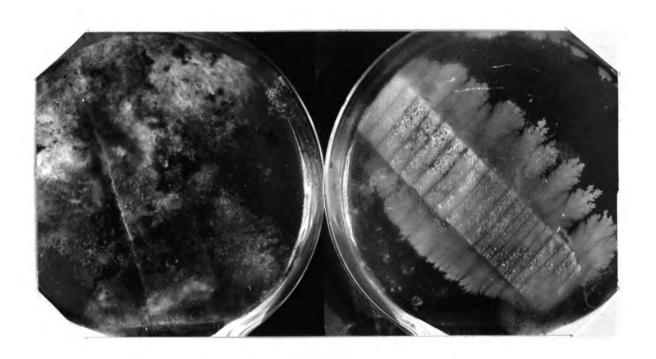


FIG.1 FIG.2

Fig. 1. Unsterilized wood wafer on agar, showing fungi and bacteria.

Fig. 2. Partially sterilized wood on agar, showing only bacteria.

PLATE II

EXTREME VARIATIONS IN CHEMOTROPIC RESISTANCE OF COPPER-META-ARSENITE



Fig. 1

Fig. 2

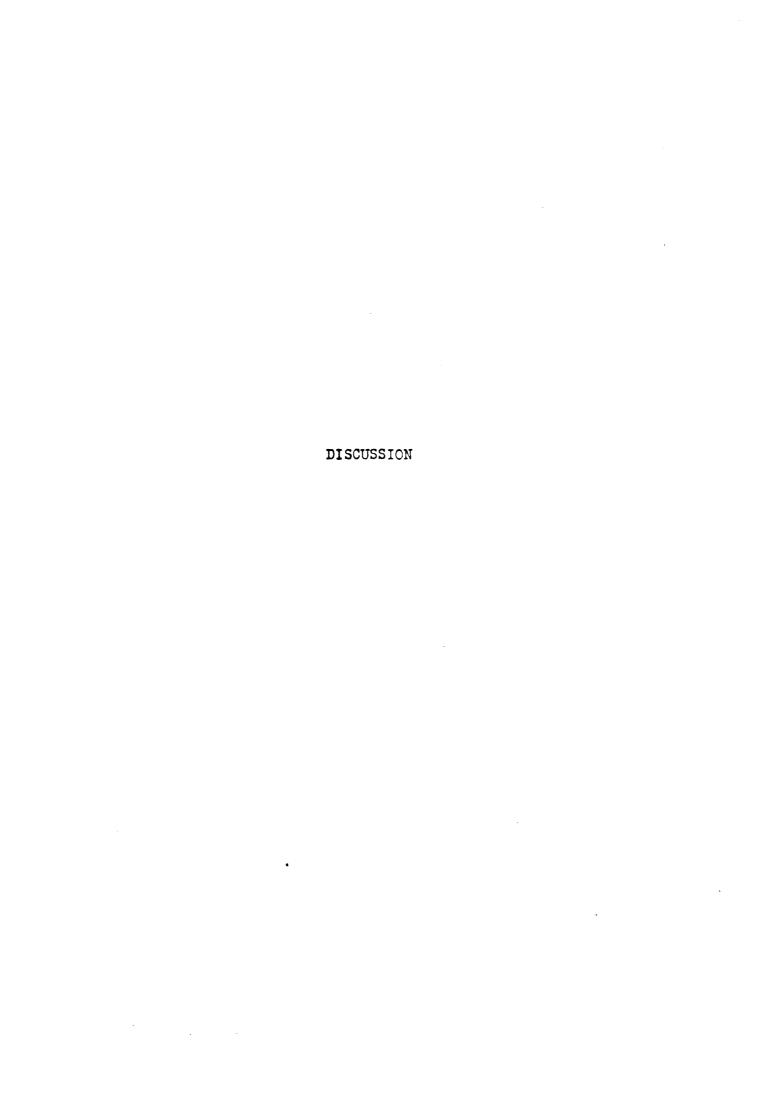
- Fig. 1. Madison No. 517 rapidly attacking untreated white fir (right) while mycelium is repulsed by treated white fir (left).
- Fig. 2. Poria incressate growing luxuriantly on both treated (right) and untreated (left) white fir.

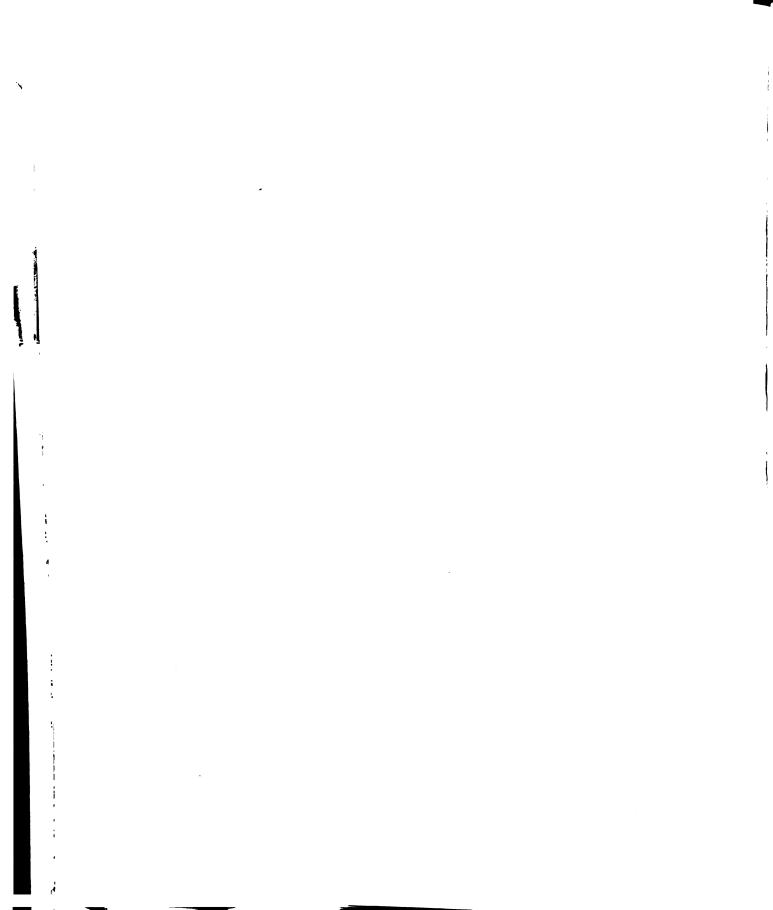
EXPLANATION OF PLATE III

Plate III is nearly self explanatory; it shows graphically the extremes of damage that were observed on copper-meta-arsenite treated white fir, especially in the center, unpenetrated portions.

Decay actually extended into the treated zones, usually where the color was lighter. In the case of <u>Poria incrassata</u>, however, even heavily treated portions were finally attacked, after the decay had developed to an advanced stage on the untreated portions.







DISCUSSION

The data gathered in this experiment do not readily lend themselves to more than cursory statistical analysis.

Variables have crept into the work despite previous efforts to anticipate them. One of the most significant variables was that of moisture content of the wood under actual test. While some specimens became water soaked in the culture chambers, others remained below the point at which decay is inhibited. Several investigators have cautioned against the use of Kolle flasks for that very reason, but it appears that the trouble could largely be overcome by raising the specimens above the agar on glass rods or blocks. The moisture absorption is facilitated by contact between the wood and agar, or thin mycelial mat.

On the other hand, raising the wood specimens above the mycelium will necessarily result in a lengthened time until the inception of actual fungus attack. The writer is striving toward a goal of standardized technique, in which speed of testing is one of the major objectives.

Industry demands it, and if we are to save our markets from the competition of durable foreign woods (71)(130), we must give industry a good rapid method of determining relative durability of new species or of treated familiar species. Absolute accuracy would not be necessary in such work, but results should be reasonably dependable.

The experimental data do, however, point to certain significant trends which should be emphasized.

A comparison of results from matched treated and untreated specimens, exposed to identical fungi and conditions, shows a trend which is unmistakable. Unfortunately, the data do not tell the story as graphically as would photographs, but the trend is clearly evident: (the following wood wafers have been tested intact.)

Concise comparison of treated and untreated white fir, exposed to fungi:

Average loss in percent of oven-dry weight for treated wood - 8.4% Average loss in percent of oven-dry weight for untreated wood - 16.0%

There is shown a striking uniformity of greater loss in the untreated wood. Visual inspection bore out the factual evidence; the visibly treated zones in the A and B series definitely resisted the action of wood-destroying fungi, while the central, untreated portions of the same pieces appear to be as badly attacked as the matched untreated white fir.

But even more striking is the following compilation, since it eliminates one variable by comparing parts of the same pieces of wood:

^{*}Negative values indicate slight gains.

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In this compilation the average loss of oven-dry weight averaged over 7.7% for the uncolored central portions, and less than 0.5% for the outer, treated portions. The difference was consistent throughout the tests, showing, furthermore, that the treated zones were highly resistant to wood-rot fungi if the copper-meta-arsenite were sufficiently concentrated to color the wood.

Noteworthy was the variation in moisture content between specimens used in each series to determine the average. The variation may well account for some of the discrepancies in computed losses in oven-dry weights. Series A and C averaged 7.7% M.C., series D averaged 7.7% and series B averaged 7.7%. The twenty-one test specimens ranged from 7.6% to 7.83% M.C., being distributed rather equally about the general averages. Taking the extreme possibility of a true 7.6% M.C. in a 3.500 gram specimen: if the averaged used as a base were taken at 7.78%, then the error due to the use of the average would equal almost 0.1% or .003 grams.

It is entirely possible, however, that an error as large or larger might enter because of physical changes if sterilization were accomplished by the oven method, affording true oven-dry weights as a basis.

If any of the preservative were volatile, oven drying before testing would be especially inadvisable.

The stain tests were not so conclusive as the decay resistance tests, although the visual evidence most certainly pointed to a definite stain resistance on the part of treated portions of white fir.

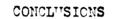
It is difficult to judge the degree of staining on pieces of wood in a flask, particularly when tests were carried on over a period of two years as this test was, but the results are presented as they were noted:

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STAIN TESTS ON COPPER-META-ARSENITE TREATED LUMBER:

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A-2 - G. rigidum - 270 days - treated - badly spotted in center
D-2 - " - untreated - stained over all surface
A-4 - C. pilifera - 56 days - treated - lightly stained in center D-4 - " - untreated - lightly stained all over
A-5 - C. pluriannulata- 56 days - treated - badly stained
D-5 - " - untreated - heavily stained, one end
A-16 - C. pluriennulata- 46 days - treated - stained in center
D-16 - " - untreated - spotted irregularly
A-17 - C. pilifera - 46 days - treated - unaffected - unaffected - unaffected
B-5 - C. pilifera - 55 days - treated - few spots in center - untreated - spotted all over
B-6 - G. rigidum - 55 days - treated - spotted in center
D-26 - " - untreated - lightly stained all over
B-12 - Penicillium sp. - 90 days - treated - molded all over
                                        - untreated - heavily molded
B-13 - Aspersillus sp. - 90 days - treated - molded in center D-28 - " - untreated - heavily molded
B-22 - C. pluriannulata- 36 days - treated - center badly stained D-29 - untreated - badly stained all over
                                " - untreated - badly stained all over
B-32 - G. rigidum - 30 days - treated - center lightly stained - untreated - lightly stained
A-28 - Cheetomium sp. - 45 days - treated - center molded
C-5 - G. rigidum - 32 days - treated - spotted in center
C-9 - C. pluriannulata- 111 days - treated - stained lightly
                               20 days - treated - molded heavily in center
C-18 - Mucor sp.
C-26 - C. pluriannulata- 99 days - treated - lightly stained in center
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More work is desirable on the subject of stain resistance alone, with as many stain producing fungi as are available.



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CONCLUSIONS

The writer does not intend to present this thesis as conclusive and definite proof of the facts which seem to be borne out by the data collected in the experiment. Rather, the spirit is one of pointing out apparent trends which the measure data seem to indicate:

- 1. Copper-meta-arsenite is a generally effective preservative in the zone where its penetration is so concentrated that it is clearly visible to the naked eye.
- 2. Other factors may inhibit wood decay to as great an extent as copper-meta-arsenite or any other preservative. These factors include: excessive moisture, insufficient moisture, and either high or low temperatures. The data gathered in this experiment have no bearing on these actual points, but specimens of preserved wood seen in the field have borne out the facts. Memberature and moisture deficiencies and excesses must be continuous, however, to be effective.
- 3. Some mold fungi will grow on the surface of copper-meta-arsenite treated wood, even when the concentration of preservative in the wood is sufficient to protect it from decay fungi.
- 4. The fungus, <u>Poria incrassata</u>, attacks even copper-meta-arsenite treated wood under favorable conditions, except where the salt concentration is very high.
- 5. Lumber or other timber products should be thoroughly air dried before treating with copper-meta-arsenite in order that the salt concentration may be high in the central portion.
- 6. It is recommended that no surfacing be done on copper-metaarsenite treated lumber after the treatment, except possibly a very light planing to smooth raised grain. Surfacing removes the most decay-

resistant part of the lumber. The public should be taught to demand heavily treated lumber, showing as much color as possible.

- 7. Decay resistance of treated or untreated lumber can be predicted by laboratory tests with about a much relative accuracy as that of commercial moisture-content indicators in the hands of untrained users (2)(12)(32)(66)(118)(144)(146).
- 8. It is highly desirable that further study be made on coppermeta-arsenite to determine its fire retardant qualities; its quantitative solubility; its possible danger to health through the release of poisonous gases when attacked by certain mold fungi or fire (56)(154); and its effect on rodents which gnaw wood.



PREFACE TO LITERATURE CITED

The following list of citations is presented with the knowledge that it does no more than touch upon the available literature covering the field of wood preservation.

Citations included herein represent only a small part of pertinent publications in the English language, and none but a very few translated examples of the excellent material available in the German, French, Swedish and Russian languages. The sole basis for selection and inclusion herein was that the articles and books must have been examined and have been of some value in the preparation of this graduate thesis. In only exceptional instances has the above objective been disregarded: when a few citations from very old writers were lifted bodily from the bibliographies to guide future researchers to valuable source material. In all such cases, full acknowledgment has been accorded to the writer whose bibliography furnished the unavailable reference.

Although the candidate is enrolled in the Department of Forestry, in which branch the library is not well stocked, this thesis is centered on a branch of botany and of chemistry in which the library resources are unusually rich. In addition, various personal collection have been made available, including the libraries of Dean Ernst A. Bessey and Professors Forrest C. Strong, Alexis J. Panshin and Paul A. Herbert. The combination of the main library resources with the private libraries mentioned has resulted in a very good foundation of source material, particularly since a large portion of the list of citations lies within the field of applied mycology.

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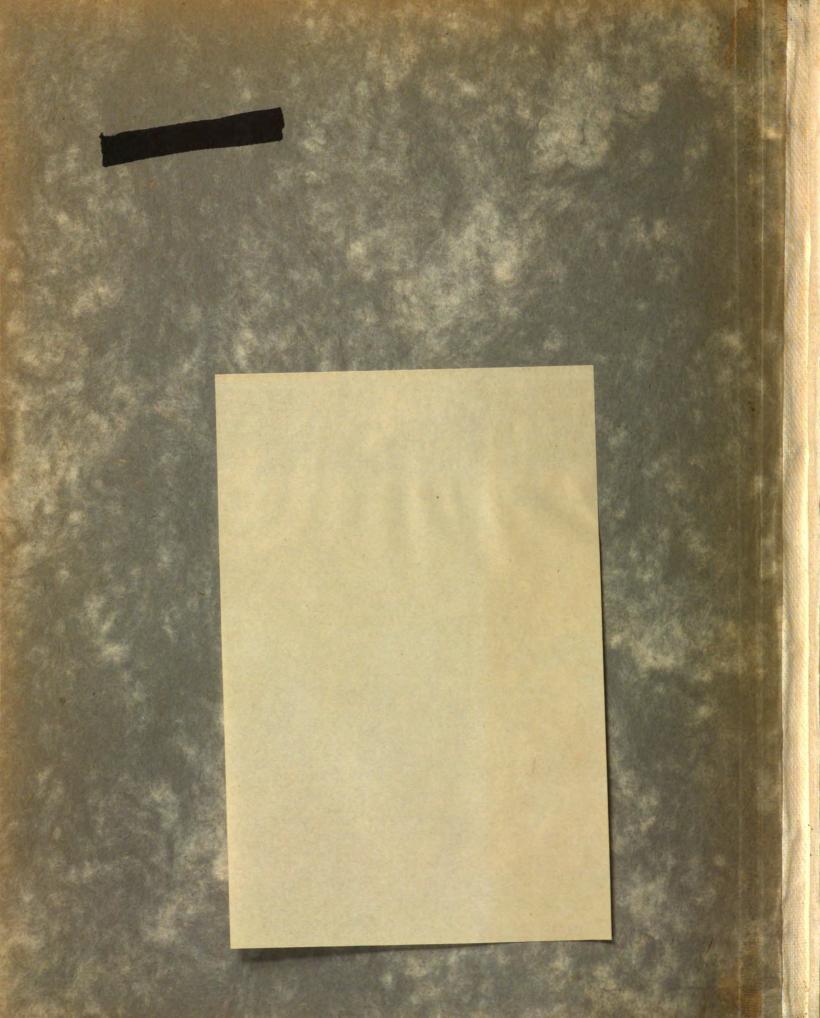
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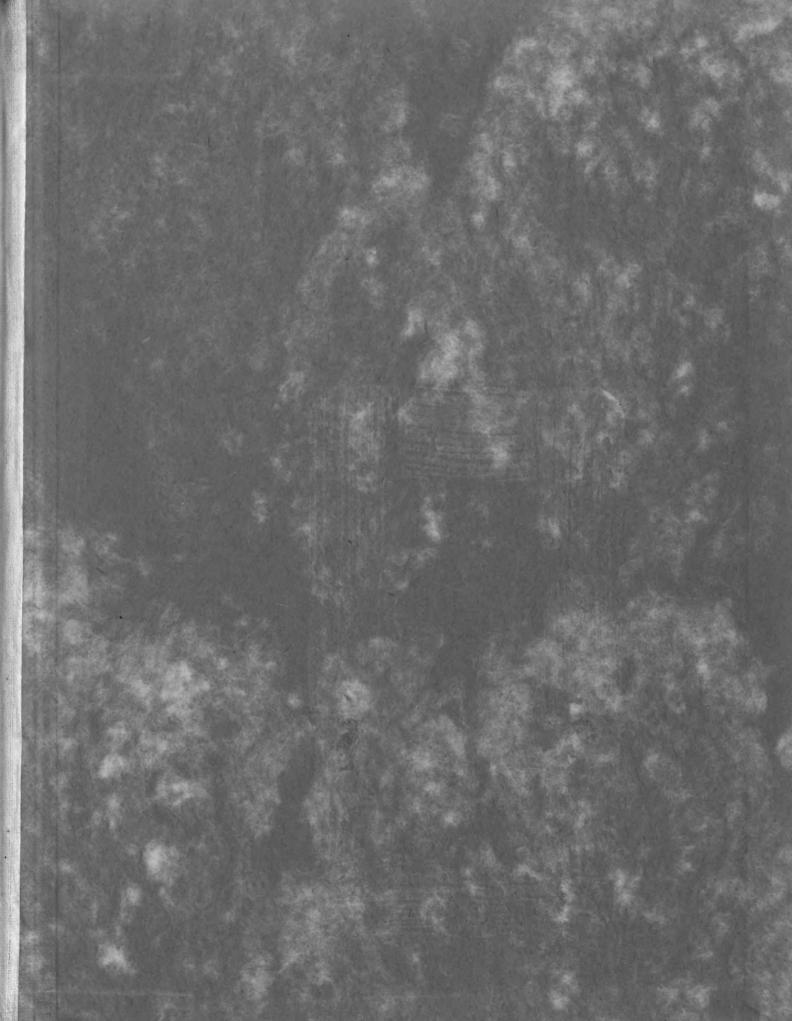
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