Microbiological Process Report

Newer Preservative Treatments for Wood[1]

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A number of chemical treatments in which the effect is other than toxic have been and are being explored. Perhaps the most promising are those in which a reaction with the cellulose molecule takes place. Resistance to decay has been produced by treatments with phenol-formaldehyde mixtures, formaldehyde, acetic anhydride, and acrylonitrile.

In the evolution of wood preservation, as in so many other industrial processes, art preceded science. The gradual deterioration of wood exposed to damp conditions, in contrast to its tendency to remain sound when dry, was probably among man's first observations. The ancient theorists no doubt explained this phenomenon as a softening effect of water. In line with this perception, the earliest recorded attempts of wood users to prevent decay consisted of applying oily or tarry materials in order to exclude moisture. While their confidence in such measures may have been misplaced, one cannot quarrel with their desire to keep the wood dry; this still is recognized as good practice whenever it is feasible.

The protection of wood from the depredations of visible living organisms followed somewhat different lines. The use of poisonous chemicals for this purpose is mentioned in some old scientific writings. The settlers of the New World naturally followed European practices, and so we find that, in 1540, solutions of "arsenite and sublimate" were being used in the West Indies to protect wood from "wood lice."

Modern wood preservation as an industry may be said to have started with Bethel's invention of the pressure process in 1838. Bethel used coal-tar creosote, and, although his choice was made before the true nature of decay was understood, creosote remains the leading wood preservative.

The role played by living organisms in causing decay was first demonstrated by Hartig in 1874. Since then, research aimed toward the development of new wood preservatives has been confined largely to the search for new and improved toxicants. It has been recognized that the protection of wood might be achieved by some means other than impregnation with toxic materials, which is the only approach that has been commercially successful so far. It seems to be accepted by investigators, however, that this line of research has not yet reached the point of diminishing returns.

The list of requirements that must be met by a new wood preservative are practically identical in nature with the requirements that must be met by preservatives for other materials. Whether the experimenter has in view the protection of wood, textiles, cordage, paper, paint, or leather, a satisfactory preservative first of all must prevent the growth of attacking organisms. It must have satisfactory permanence. It must be relatively free from harmful effects on the material being protected, on finishes to be applied to the material, and on processing equipment. It must be free from any health hazard that cannot be controlled satisfactorily. It must be available in adequate amounts and at a reasonable cost. The relative importance of these individual requirements varies from one material to another, as does the difficulty of meeting them.

In the search for new preservatives to protect wood against decay and termites, interest lies chiefly in compounds that will leave the wood clean, paintable, and odorless. The preservatives already in use are considered quite satisfactory for products that do not have these requirements.

To begin with, the wood-preserving industry passed through an era of arbitrary trial of cheap industrial by-products. A more orderly approach has been followed during the past several decades. Relations between chemical constitution and toxicity have been studied by means of agar tests and soil-block tests. Some progress has been made toward an understanding of the loss of preservatives from wood.

This work in wood preservation has had some effect on the application of fungicides to other products. For example, fundamental investigations in relations between chemical constitution and toxicity toward wood destroying fungi led to the development of pentachlorophenol, which has grown not only to considerable stature in wood preservation, but is being used to prevent fungus attack in materials other than wood. Wood preservation in turn has borrowed from related fields. Present-day research in wood preservation is being in-

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fluenced by the findings of those who are striving to find better ways of preventing the deterioration of other organic materials.

In the development of new wood preservatives, it is assumed generally that they will be applied by conventional processes. An exception lies in the study of double-diffusion treatments being conducted at the U. S. Forest Products Laboratory. In double-diffusion treatments, green wood is soaked in separate solutions of two or more chemicals that diffuse into the wood and then react to deposit toxic precipitates. The term diffusion is used in its broader sense; that is, to denote spontaneous spreading. If wood were waterlogged, the ingress of chemical would be due entirely to the diffusion of the solute from the surrounding solution into water present in the wood. Green wood, however, contains voids filled with air, and it is accepted that some liquid movement of the solution plays a part in the movement of chemical into and through the wood.

For use in these treatments, the starting chemicals must be capable of reacting to form toxic compounds that are resistant to leaching. In addition to this, they must be capable of diffusing into wood at rates that make it possible to obtain adequate absorptions and distribution by practical treating schedules.

A number of well-known methods of applying the chemicals have been considered and several of them have been tried. Posts and lumber have been treated by complete immersion in solutions of varied concentration for varied periods of time. This appears to be a practical procedure for small-scale commercial operations where the wood is handled mechanically. The treatment of round peeled posts by standing them upright in barrels has been explored quite thoroughly. Because of the low cost of the equipment, this procedure offers promise for the on-the-farm treatment of posts. Treatments of lumber have been made by sprinkling dry chemicals, and also pastes, on the surface of green boards, which were close piled to retard drying. This might be a useful procedure in remote areas where tanks large enough to hold the lumber are not available. The treatment of veneer and thin lumber by slow passage through long shallow tanks has been visualized.

A number of combinations of chemicals are being evaluated in test plots, with treated pine posts being the principal test material. The first field tests were started in 1941 on posts treated by complete immersion, first in copper sulfate solution and then in sodium arsenate solution. Only one of the original 100 posts has failed to date. The second series of tests, started in 1942, was made with pine stakes 2 by 4 by 18 inches in size. Several time schedules were used in applying two combinations of chemicals: copper sulfate followed by sodium arsenate and copper sulfate followed by sodium chromate. One failure has occurred in the 40 stakes protected by copper chromate, and none have occurred in the 30 stakes protected by copper arsenate.

This double-diffusion project was discontinued during World War II. When it was resumed, attention was first devoted to the standing-in-barrel treatment of posts. A number of chemical combinations have been used to treat test posts by this modification of double diffusion. Variations in treating schedule and handling also have been studied in these tests.

Of the combinations of chemicals that might be used, copper sulfate followed by sodium arsenate is not considered suitable for on-the-farm treatment. The sodium arsenate solution would present a hazard to the less careful operators, and also to livestock, which is attracted by this chemical.

Copper sulfate followed by sodium chromate appears to be reasonably safe for the barrel-type treatment. If the posts are given a butt treatment only with this combination, a poor distribution of chromate is obtained. The top part of a typical post contains unchanged copper sulfate, and, since this could be expected to accelerate the corrosion of staples, it seems advisable to invert the post during part of the time in the sodium chromate solution.

Treatments have been made in which the first solution consisted of a mixture of copper sulfate and arsenic acid (in a ratio of approximately 5 to 1), with sodium chromate being used for the second stage. In this way, arsenic, with its high toxicity to termites and to certain species of fungi, may be introduced into the post without using a solution that is attractive to livestock. There is little reason to doubt the effectiveness of this treatment when properly conducted. The chief disadvantages stem from the corrosiveness of copper sulfate; it necessitates the extra handling involved in inverting the post during the second stage and also requires the use of a wooden barrel for the first solution.

A treatment similar to that described in the preceding paragraph has been made in which zinc sulfate was substituted for copper sulfate. The principal advantage of this treatment is the low corrosiveness of zinc sulfate, which permits the replacement of the wooden barrel with the more readily obtainable oil drum. Furthermore, since the excess zinc sulfate in the upper part of a post would have little corrosive effect on staples, the inversion of the post in the sodium chromate solution appears unnecessary from the standpoint of corrosion hazards.

The combination of copper sulfate and sodium fluoride appears promising on the basis of chemical analyses of treated posts and limited service tests. Either copper sulfate or zinc sulfate followed by a borax-boric acid solution (borax alone in cold water does not yield a solution of desired concentration) has possibilities and is under test. Several other combinations might be mentioned.

As would be expected, the results obtained with any given combination of chemicals vary with the thoroughness of the treatment. With posts treated by a schedule of 1 day in each of 2 solutions of 4 per cent concentration or less, the results have been fair at best. Good results appear to be attainable when the posts are stood for 2 or more days in solutions of the more effective chemicals. Concentrations of 5 per cent or above seem advisable. The field tests in progress must be continued further before the most practical combination of chemicals can be selected and its effectiveness compared with that of older preservatives.

By complete immersion of green pine posts in strong solutions, it is possible to obtain total absorptions of approximately 1 pound of chemical per cubic foot of wood by a schedule of 1 day in each solution. The analyses of sections show fairly good penetration.

Increasing the solution temperature accelerates the rate of diffusion. It also makes possible the use of stronger solutions, which further increases the rate of diffusion. Thus the use of heated solutions, which would be feasible in commercial operations, decreases the tank time required to obtain a desired absorption of chemical.

As an example of the results that are possible under favorable conditions, some 1-inch pine lumber soaked for 3 hours in 20 per cent solutions of copper sulfate and sodium chromate at temperatures of approximately 50 C showed complete penetration after it was seasoned.

A limited number of experiments have shown marked differences in the treatability of various hardwood species by this method. In general, the results have been less favorable than on pine.

Two small commercial plants now are using double diffusion in the production of posts for local use. By far the most important application of double diffusion so far has been in the treatment of cooling towers. Most towers are made of a naturally durable species, redwood, but continuous exposure to running water causes a loss of protective extractives. In a period of 5 to 8 years, decay may progress to the point where costly shutdowns and repairs are necessary. In 1952, a tower at an oil refinery was given a double-diffusion treatment with copper sulfate and sodium chromate. The copper sulfate solution first was recirculated over the tower for 3 days. After a rest period of 3 days to permit diffusion, sodium chromate solution was recirculated in a similar manner. Some time later a second tower was treated by a power company, and a different method of application was used. The solutions were sprayed over the internal surfaces by means of an orchard-type sprayer. As compared with the circulation method used in the first treatment, the spraying technique requires smaller volumes of solutions. It has been used in subsequent treatments of towers.

Reports have been received on the treatment of 58 towers containing 12,600,000 board feet of lumber. Approximately 1,578,000 pounds of chemicals have been used. The rate at which towers are being treated is shown by the fact that 2 towers were treated during 1952, 6 in 1954, 30 in 1955, and 19 will be treated during the first 5 months of 1956.

Analyses of samples from treated towers have shown that the absorption of chemicals generally falls within a range of ½ to ¾ pound total chemical per cubic foot of wood. This is within the range of absorptions used in commercial treatments of lumber. While similar absorptions of these chemicals are giving good protection to wood exposed to the soil, the differences in exposure conditions and in the species of fungi found in towers call for reservations in predicting the service life of treated towers.

In wood preservation, it is unusual for a treatment to be used to an appreciable extent without fairly conclusive evidence of its effectiveness under specific use conditions. This particular exception may be explained by the lack of any other treatment that appears as promising as double diffusion for this purpose, the extreme difficulty of treating a large structure by any other method, and also by the high value of a cooling tower in relation to the cost of the treatment.

It has been mentioned that all commercial treatments up to the present have consisted of applying toxic materials to the wood. This statement may need some qualification. The increase in the service life that results from creosoting a crosstie is not due entirely to the prevention of fungal growth. The water-shedding effect is beneficial in producing a reduction in splitting and checking, with an accompanying increase in mechanical life. The greasy surface imparted to piling by creosote or creosote coal-tar solutions is probably an important factor in preventing attack by *Limnoria.*

Efforts to preserve wood by some approach other than the application of toxicants have followed several lines. The most promising leads have come from treatments that modify the composition of the cell wall.

When wood is treated with a water-soluble phenol-formaldehyde resinoid, resistance to decay is obtained. This cannot be cited as a clear-cut example of decay resistance obtained by modification of the cell wall, because other factors may be contributing to the end result. The same is true of treatments with formaldehyde gas in the presence of an acid catalyst.

Heating wood under conditions that just avoid charring imparts resistance to fungi. The effect is believed to be due to decreased hygroscopicity that results from the formation of ether cross linkages by the elimination of water from two adjacent hydroxyl groups. The loss in mechanical strength is a serious drawback to this treatment.

The acetylation of veneer not only decreases its tendency to shrink and swell but also decreases its vulnerability to decay and termite attack. The treatment is rather costly and has not yet been utilized commercially.

Recent experiments in the cyanoethylation of wood have been very encouraging. Pine blocks treated with ammoniacal solutions of acrylonitrile have shown complete resistance to three commonly used test fungi in the soil-block test.

Other treatments that do not rely on the toxicity of chemicals are possible and merit investigation. There is a real need in many instances for rot-proof and termite-proof wood that is free from impregnants that are likely to contaminate other materials. Further developments in this type of treatment, therefore, can be anticipated.

Summary

Preservative treatments of wood up to the present have been based almost entirely on the application of materials that are toxic to wood-destroying organisms. While the older preservatives still account for a high percentage of the total volume, there has been a decided increase in the use of several of the newer preservatives. The search for effective preservatives continues, especially for chemicals that may be used to produce a clean, odorless, paintable wood product.

A two-stage diffusion process called double diffusion was developed at the Forest Products Laboratory, and is giving promising results in field tests. The process consists of soaking green wood in two separate solutions of chemicals that diffuse into the wood and then react within the wood to deposit a toxic precipitate. An interesting application is in the treatment of cooling towers that have begun to decay.

Fermentation Studies with *Streptomyces niveus*

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Novobiocin[1] (streptonivicin) is a new antibiotic discovered in the laboratories of The Upjohn Company. The announcement of the antibiotic (Smith *et al.*, 1956), chemical properties (Hoeksema *et al.*, 1956), structure (Hinman *et al.*, 1956; Hoeksema *et al.*, 1955), therapeutic activities (Wilkins *et al.*, 1956), tissue assay method (Taylor *et al.*, 1956a), pharmacologic properties (Taylor *et al.*, 1956b and Larson *et al.*, 1956), and clinical studies (Lin *et al.*, 1956 and Martin *et al.*, 1955) have been reported previously. This publication describes fermentation studies with *Streptomyces niveus*.

Materials and Methods

Streptomyces niveus was maintained on maltose-tryptone agar slants prepared from soil or freeze-dried stocks as described previously (Smith *et al.*, 1956). All fermentations were carried out in 500-ml Erlenmeyer flasks containing 100 ml of medium. The flasks were sterilized at 120 C for 20 minutes and incubated on a Gump shaker rotating at 250 rpm with a 2-inch throw. Vegetative seed was prepared by inoculating a medium containing glucose monohydrate, 25 g per L, and cottonseed meal, 40 g per L, with a loopful of spores. One hundred ml of the seed medium was incubated in a 500-ml Erlenmeyer flask as described above. The fermentation samples were prepared for assay by diluting the fermentation broth in 0.1 M phosphate buffer of pH 7.85 after removing the solids by centrifugation. The disc plate assay procedure for novobiocin using *Klebsiella pneumoniae* as test organism was described in a previous publication (Smith *et al.*, 1956). The standard error of the assay was about 20 per cent.

Cell dry weight was determined by washing the cells three times with distilled water and drying the residue at 110 C for 24 hours. Nitrogen was determined by a modified Kjeldahl procedure. Carbohydrate was determined with the anthrone reagent (Morris, 1948). Two ml of the sugar solution plus 4 ml of anthrone reagent (2 g per L in 95 per cent H_2SO_4) were heated on a steam bath for 10 minutes to develop the color, which was determined at a wave length of 620 mμ in a Bausch and Lomb "Spectronic 20" photocolorimeter. Protein nitrogen in the cells was determined on the trichloracetic acid precipitate obtained by suspending the centrifuged cells, previously washed twice with water, in 12 per cent trichloracetic acid. The precipitated cell protein was washed three times with trichloracetic acid solution prior to analysis to remove TCA soluble peptides and amino acids. Total cellular nitrogen was determined on the intact cells after washing three times with water.

Results and Discussion

The effect of composition of the medium on antibiotic production. Early media studies were reported in a

[1] The trademark of The Upjohn Company for novobiocin is Albamycin.