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METHOD OF PROTECTING WOOD FROM MARINE ORGANISMS

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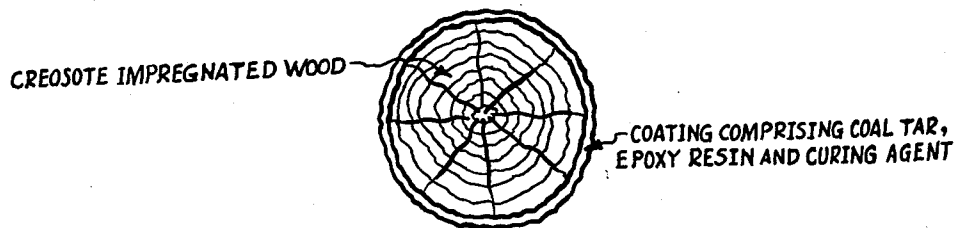


Fig. 1.

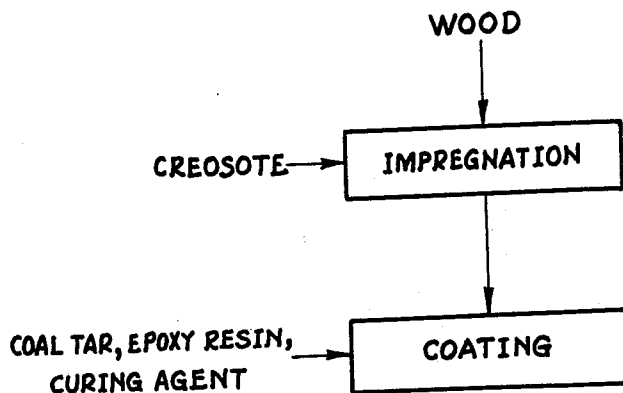


Fig. 2

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METHOD OF PROTECTING WOOD FROM MARINE ORGANISMS

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3 Claims. (Cl. 117-72)

This invention relates to members adapted for use in sea water and more particularly to members which are basically wood but which resist attack by marine organisms.

The submerged portions of wooden members such as marine piling and wharf timbers are subject to attack by marine organisms or borers of two general types: molluscan borers and crustacean borers. Tereidos, perhaps the most common of the molluscan type, can completely riddle unprotected pilings in the course of a year. The tereidos enter the wood at right angles to the grain and then begin to burrow in a longitudinal direction following an irregular course, some burrowing deeply toward the center of the wood before turning with the grain. This continuing honeycombing of the wood will so reduce the structural strength of a pile that the pile fails under stress. Impregnating the wood with creosote so that 10-15% of the weight of the piling is creosote is generally effective to protect the wood against all attack by molluscan borers, but crustacean borers, particularly the genus *Limnoria*, are not repelled until the creosote content reaches 25% and even then may not be completely repelled. The *Limnoria* move freely about the wood, eating along the periphery of the wood and seldom extend more than one-half inch below the surface of the wood, they may eat the wood so as to form a gallery that runs obliquely for an inch or more. The *Limnoria* may attack in such great numbers that the outer surface of the timber becomes thoroughly honeycombed at the points of attack; then as the mechanical action of water and floating objects break away the thin portion of wood separating the burrows, a new surface is exposed to the borers and the destruction is carried progressively deeper. The attacks are usually concentrated between the tide levels, where the rolling action of the waves and the battering of floating debris accelerates the breaking down of the honeycomb surface of the wood, so that piling tend to assume a distinctive hourglass shape between the tide levels.

To protect the timber, paints usually of asphaltic or bituminous materials have been used heretofore as coatings for the wood, but coatings of paint have always been rather fragile, soft, and therefore, are usually broken and worn away by the action of the waves or drifting objects or deteriorated by the sea water so that they have been effective only for about six months. Impregnating the wood with a 25% by weight of creosote has not been completely effective against *Limnoria*. The action of the waves and air at the surface of the wood leaches the creosote therefrom and the *Limnoria* attack this leached area, thereby opening another area for leaching and subsequent attack.

It has now been discovered that wood which is impregnated with creosote and coated with a composition comprised of coal tar, an epoxy resin, and a curing agent resists attack by marine organisms. The novel article of this invention is particularly adapted for use as pilings

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and wharf timber. Such novel pilings are readily produced by impregnating wood with creosote and then coating this creosoted wood with a composition comprised of coal tar, an epoxy resin, and a curing agent.

In the drawings:

FIGURE 1 is a cross-sectional view of the article comprising creosote impregnated wood coated with the coal tar, epoxy resin, curing agent composition;

FIGURE 2 is a flow sheet describing the process of rendering wood resistant to attack by marine organisms.

It is surprising that submergible articles made in accordance with this invention will resist penetration by marine organisms because tereidos have been known, for example, to penetrate even concrete structures. The mere fact that the wood has been creosote-treated does not deter the action of certain marine borers such as *Limnoria* because, as the wave and salt water leach the creosote from the surface of the wood, the *Limnoria* attack this surface. Also the coating of creosoted wood is usually extremely difficult; the creosote tends to bleed through the coating, thereby softening and causing an early deterioration of the coating. In accordance with this invention, the coating composition comprised of coal tar, an epoxy resin, and a curing agent adheres firmly to the creosoted wood, resists attack by marine organisms, and provides a hard, infusible, solvent-insoluble coating for the wood.

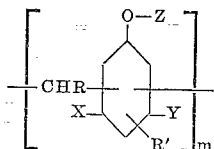
The wood for use in this invention may be impregnated with creosote in any of the well known methods. Creosote, as defined by the American Wood Preservers Association, is a distillate of coal tar produced by the high temperature carbonization of bituminous coal and consists principally of liquid and solid aromatic hydrocarbons and contains appreciable quantities of tar acids and tar bases, has a continuous boiling range of at least 125° C. beginning at about 200° C., and is heavier than water. The creosote is sometimes mixed with coal tar and such mixtures called creosote-coal tar solutions contain 20-40% of coal tar. The American Wood Preservers Association and American Railway Engineers Association have standard specifications for these materials. The impregnation of wood with creosote or creosote-coal tar solutions has been practiced for many years, and standard methods for the impregnation of wood with those compounds are recommended by the American Wood Preservers Association, "Manual of Recommended Practice," 1953. Generally, the wood is subjected to a vacuum, then at an elevated temperature and under elevated pressure is immersed in a creosote solution for a period of time, and thereafter is removed from the creosote solution and allowed to drip dry.

Wood, which has been impregnated with creosote, can by any of the well known coating methods such as dipping, spraying, brushing, etc., to be coated in accordance with this invention with a composition comprised of coal tar, an epoxy resin, and a curing agent therefor.

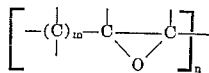
The coal tar of this composition is that residue which remains from the distillation of coal tar produced by the high temperature carbonization of coal. The coal tar, as recovered from this carbonization, normally contains light oils, coal tar acids, coal tar bases and water which are removed by distillation of the coal tar. The residue from this distillation is generically known as "pitch" and ranges from a viscous liquid at room temperature to a solid resinous product, depending upon the temperature (usual-

ly from 250–400° C.) to which the distillation is carried. These pitches may be modified by the addition of the hydrocarbons such as xylene, benzene, toluene or solvent naphtha to obtain a desired consistency or viscosity.

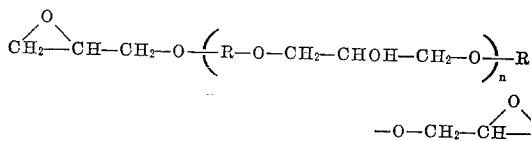
A preferred group of epoxy resins for use in the invention is prepared by reacting a novolak resin with haloepoxyalkane. Such resins and the process for the production thereof are described in U.S. Patent No. 2,658,884 by G. F. D'Alelio. The resins are represented by the following formula:



wherein R is a substituent of the class consisting of hydrogen and alkyl, alkylene, aryl, aralkyl, alkaryl, cycloalkyl and furyl groups; X and Y are substituents selected from the class consisting of hydrogen, chlorine and alkyl and hydroxyl groups; R' is chlorine or a hydrocarbon group of the class consisting of alkyl, aryl, aralkyl, and alkaryl groups; at least one of the groups X, Y and R' is chlorine; m is an integer having a value of at least three; and Z is a substituent of the class consisting of hydrogen and epoxyalkyl groups, at least one Z per polymer molecule being an epoxyalkyl group and said epoxyalkyl groups having the formula



wherein n is an integer having a value advantageously no greater than 8, and the unoccupied valences within the bracket of the formula are satisfied by substituents of the class consisting of hydrogen and alkyl groups of no more than 7 carbon atoms, the number of carbon atoms in any epoxyalkyl group totaling no more than 10 carbon atoms. Less preferable there can be used products prepared by reacting a dihydric phenol with epichlorohydrin in alkaline solution. Many of the various dihydric phenols can be used such as the mononuclear phenols exemplified by resorcinol, catechol, hydroquinone, or the polynuclear phenols such as bis-(4-hydroxyphenyl)-2,2-propane (bisphenol, 4,4'-dihydroxybenzophenone), bis-(4-hydroxyphenyl)-1,1-ethane, bis-(4-hydroxyphenyl)-1,1-isobutane, bis-(4-hydroxyphenyl)-2,2-butane, and bis-(4-hydroxy-2-methylphenyl)-2,2-propane. The product may be represented by the formula:



wherein n is an integer preferably from 1 to 7 and R represents the divalent hydrocarbon radical of the dihydric phenol.

There can also be used the epoxy-containing glycidyl ethers of polyhydric phenols such as polyglycidyl ether of ethylene glycol, the glycidyl ether of propylene glycol, the glycidyl ether of trimethylene glycol, the glycidyl ether of diethylene glycol, the glycidyl ether of triethylene glycol, glycerol, the glycidyl ether of dipropylene glycol, and the glycidyl ethers of glycol diglycerol, pentaerythritol, pentaglycerol, mannitol, ceritol, polyallyl alcohol, polyvinyl alcohol, and the like.

The curing agent is an amine having one or more active hydrogens for reaction with the epoxy group of the epoxy resin. Preferably the curing agent is a polyfunctional amine such as ethylene diamine, ethylene triamine, diethylene triamine, benzyl dimethylamine, 3-diethylamine propylamine, and other primary, secondary and polyfunctional amines.

Since the epoxy resin will cure at ambient temperatures

(10–60° C.) when the resin and the curing agent are brought together, the composition is made as two components which are mixed at the point of application. One component includes the epoxy resin, the other component includes the amine. The coal tar may be included with either component. In the final mixture the epoxy resin may constitute from 10–90% of the tar epoxy resin composition. Because of the direct reaction with epoxy resin a specific amount of a curing agent is required, advantageously one equivalent of active hydrogen from the curing agent for one equivalent of oxirane oxygen of the epoxy resin, to give a complete reaction. Too little or too much of the curing agent may yield a soft film. In general, from 0.5 to 10% of the amine is provided for the composition.

To this composition may be added various hydrocarbon solvents such as benzene, xylene, toluene, or ketones and acetates, to give a desired viscosity. Fillers and bodying agents such as clay, talc, etc. may also be added.

The composition is applied to the wood by conventional means such as painting, dipping, or by spraying, to provide a coating which may range from 10 mils to 50 mils in thickness. The ratio of volume conversion from wet coating film to cured film varies between 70 and 90%. To get thick film it is desirable that the film be applied in several applications. Since the resulting films are substantially insoluble and infusible, it is necessary that the second and subsequent films be applied within 12–24 hours of the first application to permit a good bonding of one film to the other, otherwise the possibility of delamination of the films exists.

It has been found that in some tropical waters where the attacks by Limnoria are particularly vicious, the creosoted piles have been attacked by Limnoria from the date on which the piling was placed in service. Under the same conditions the pilings when coated with a heavy coal tar enamel lasted for about six months before attack on the enamel at the tide line had completely disintegrated the coating. Under these same conditions a piling impregnated with creosote to the extent of 25% by weight and then coated with the tar epoxy resin curing agent composition has withstood attack for 2–6 years and is still satisfactory.

In general, the coated wood is immune from attack as long as the coating is continuous, but a chip or a crack in the coating no larger than a pin will tend to permit the clam teredo or Limnoria to commence attack upon the wood. In accordance with this invention, a tendency exists for the creosote to migrate in the wood so if any chipping of the coating occurs, the entire volume of the wood serves to feed this particular point and it, therefore, takes years for the creosote to bleed from or be washed from this point to a level which will permit marine borers to attack the wood. The invention will be illustrated further by the following examples.

Example I

Following the process outlined in the American Wood Preservers Association "Manual of Recommended Practice," 1953, wood was impregnated with creosote to obtain a wood containing 25% by weight of creosote. This timber was divided into three lots; one lot was coated with a composition comprised of 12 parts of coal tar, 2 parts of an epoxy resin formed by the condensation of epichlorohydrin and a novolak resin having 5 phenyl groups connected by methylene linkages made in accordance with Patent No. 2,658,884, and one part of ethylene diamine. A second lot was treated with a composition similar to that of A except that an epoxy resin made by the condensation of epichlorohydrin and a bisphenol (Shell "Epon 828") was substituted for the epoxy resin of A. The third lot was not treated. These three lots were then placed in sea water where they were subjected to the attack by marine organisms. Within six months lot C showed attack by the marine organisms, but lots B and A resisted

attack. At the end of a two-year period lot C had been substantially attacked by marine organisms and lot B showed slight evidence of attack. Lot A was resistant to attack. At the end of a three-year period lot B showed slightly more attack and lot C showed evidence of rapid destruction by marine organisms, but lot A had still resisted attack. At the end of a six-year period lot C showed marked evidence of the ravages of the marine organisms, but lot A still resisted attack. Lot B, in comparison with lot C, showed substantial immunity to the attack whereas lot C was destroyed.

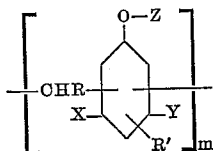
The foregoing has illustrated a novel process for the protection of wood which is submerged in sea water and subjected to attack by marine organisms.

I claim:

1. An article resistant to attack by marine organisms which comprises wood impregnated with creosote to the extent of 5-25 percent of the weight of the wood and coated to a thickness of from about 10-50 mils with a composition comprised of 10-90 weight percent coal tar, 10-90 weight percent of an epoxy resin, and 0.5-10 weight percent of a curing agent.

2. A method for the protection of the submerged portions of timbers which are subject to attack by marine organisms which comprises impregnating the wood with creosote to the extent of 5-25% of the weight of the wood and then coating the wood to a thickness of from about 10-50 mils with a composition comprised of 10-90 weight percent of coal tar, 10-90 weight percent of epoxy resin, and 0.5-10 weight percent of curing agent.

3. The process of claim 2 wherein the epoxy resin has the general formula:



wherein

R is a substituent of the class consisting of hydrogen and alkyl, alkylene, aryl, aralkyl, alkaryl, cycloalkyl and furyl groups;

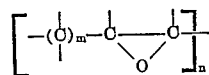
X and Y are substituents selected from the class consisting of hydrogen, chlorine and alkyl and hydroxyl groups;

R' is chlorine or a hydrocarbon group of the class consisting of alkyl, aryl, aralkyl, and alkaryl groups;

at least one of the groups X, Y and R' is chlorine;

m is an integer having a value of at least three; and

Z is a substituent of the class consisting of hydrogen and epoxyalkyl groups, at least one Z per polymer molecule being an epoxyalkyl group and said epoxyalkyl groups having the formula



wherein n is an integer having a value advantageously no greater than 8, and the unoccupied valences within the bracket of the formula are satisfied by substituents of the class consisting of hydrogen and alkyl groups of no more than 7 carbon atoms, the number of carbon atoms in any epoxyalkyl group totaling no more than 10 carbon atoms.

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