

Dec. 20, 1955

J. C. CHRISTENSEN ET AL

2,727,832

COMPOSITE COATED STRUCTURAL ARTICLE

Filed May 11, 1954

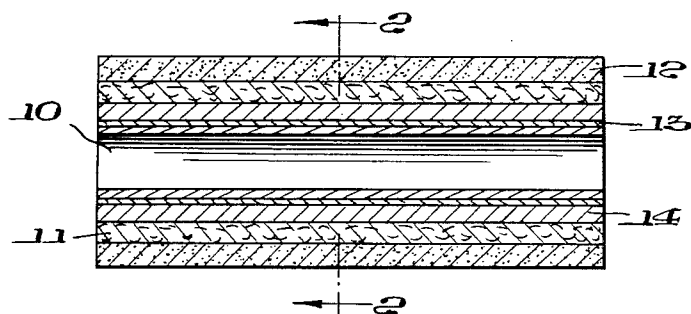


Fig. 1.

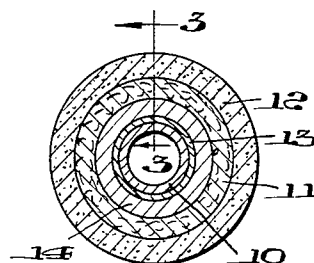


Fig. 2.

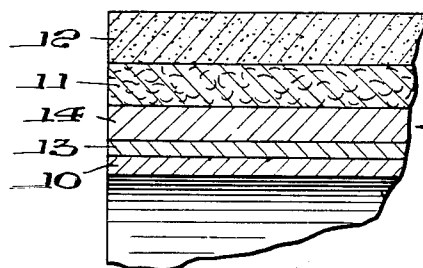


Fig. 3.

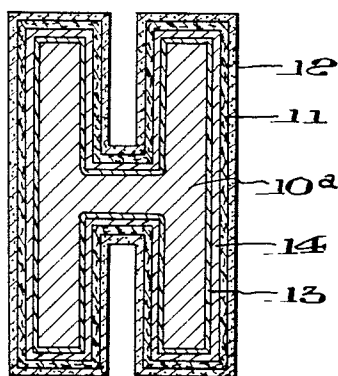


Fig. 4.

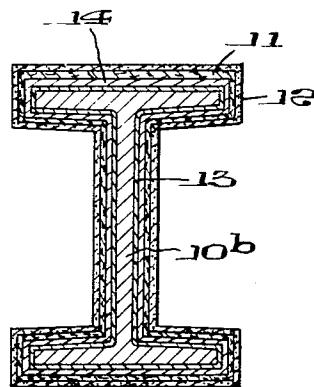


Fig. 5.

INVENTOR.

William F. Fair, Jr.
BY John C. Christensen

Walter J. Monacelli

ATTORNEY.

1

2,727,832

COMPOSITE COATED STRUCTURAL ARTICLE

John C. Christensen, Westfield, and William F. Fair, Jr.,
Cranford, N. J., assignors to Koppers Company, Inc.,
a corporation of Delaware

Application May 11, 1954, Serial No. 428,936

10 Claims. (Cl. 117—70)

This invention relates in general to composite coated structural articles. More specifically the instant invention is directed to structural articles such as pipes, piling, beams, rods and like articles made by the process of coating with a first protective coating of a coal-tar enamel, a second coating of a fibered coal-tar emulsion, and a third coating of a Portland cement-sand composition.

Heretofore some bituminous coating compositions have been formulated solely for use above ground, and others have been specifically formulated for protection of metal below ground. However, these coating compositions have not proved satisfactory when immersed in sea water for long periods of time. Asphalt enamels have been relatively quickly penetrated by marine organisms such as, for example, barnacles and teredos, which penetration results in corrosion of the metallic substrate. Hot-applied coal-tar enamels, unless specially formulated to be impenetrable by the organisms, are eventually punctured in waters heavily infested with these organisms.

In the course of installing pipe lines, rods, beams and driving piling, small portions of the coating on these structural articles are occasionally scraped off. When this occurs, it is possible for current to flow from one exposed portion of the article, the anodic area, to another exposed portion, the cathodic area, through the sea water or soil electrolytes and return to the anodic area through the metallic wall of the article. When such a current flows, metal is taken away from the bare anodic area of the pipe. Cathodic protection is an electrical method of stopping the flow of current wherein a stronger current in the opposite direction is applied to the article to neutralize the harmful current flow. This neutralizing electrical force is generally provided by passing current from a surface power source through a rectifier-sacrificial ground bed installation or through sacrificial metallic anodes composed usually of either magnesium, aluminum or zinc located at calculated intervals along the pipeline or structural article to be protected. The current from the ground beds or anodes fans out in the sea water or soil, enters the metallic pipe or article at the damaged area, and flows through the metallic pipe or article in a direction opposite to the flow of the harmful current so as to oppose and neutralize the harmful current and thus prevent corrosion. The replaceable metallic ground beds or anodes are corroded or disintegrated by this method instead of the pipe.

Cathodic protection engineers have usually recommended initial application of voltages and currents far in excess of those necessary to protect any bare spots on the coated metal with the intention of depositing calcareous deposits at bare spots from sea water electrolytes. Many coatings have been "blasted" off the article by formation of hydrogen blisters at the metal surface under the coating when such excessive currents and over-voltages are applied. The protective potential is known to be about 800 millivolts negative to a calomel half-cell in sea water to protect bare metal from corrosion in sea water.

It is therefore an object of the present invention to

2

provide, as articles of manufacture, pipes, piling, rods, beams and similar articles coated in accordance with the instant invention on which the coatings will not be substantially affected by the attack of marine organism such as, for example, barnacles, teredos and similar pestiferous marine organisms, when submerged in or contacted with water, salt water and brackish water in particular.

Another object of the present invention is to provide a process for rendering pipes, piling, rods, beams and similar structural articles substantially resistant to the attack of pestiferous marine organisms and to corrosion and rusting wherein coatings are employed that are substantially resistant to cathodic protective potentials when these articles are subjected to cathodic protective current.

Another object is to provide, as articles of manufacture, pipes, piling, beams, rods and similar structural articles coated in accordance with the instant invention on which the coatings are substantially resistant to cathodic protective potentials when these articles are being subjected to cathodic protective current.

An additional object is to provide, as articles of manufacture, pipes, piling, beams, rods and similar structural articles coated in accordance with the instant invention on which the coatings are substantially resistant to corrosion and rusting.

Ancillary and additional objects and advantages will be apparent as the invention is hereinafter described in more detail.

The term "structural article" will be employed hereinafter to designate pipes, pipelines, piling, beams, rods and similar structural articles.

It has now been found that structural articles are rendered substantially resistant to attack from barnacles, teredos and similar pestiferous marine organisms, advantageously after being cleaned and then primed with a bituminous priming solution, by being coated with a first protective coating of a plasticized coal-tar enamel, a second coating of a fibered coal-tar pitch emulsion and a third coating of a cement composition comprising from about 2 parts to about 3 parts by volume of sand and about 1 part by volume of Portland cement. The foregoing coated structural articles exhibit outstanding resistance to corrosion and rusting, even when immersed in water or buried in the earth for a period of many years.

In the drawings:

Figure 1 is a longitudinal sectional view through a composite coated pipe of the instant invention.

Figure 2 represents a transverse sectional view taken substantially on line 2—2 of Figure 1.

Figure 3 is an enlarged sectional detail view taken substantially on line 3—3 of Figure 2.

Figure 4 is a transverse sectional view through a composite coated H-beam of the instant invention.

Figure 5 is a transverse sectional view illustrating a composite coated I-beam of the instant invention.

The term "coal digestion pitch," as used herein, is applied in the tar industry to modified pitches obtained by digesting powdered bituminous coal in pitch and tar heavy oil. These modified pitches are also referred to as plasticized pitches. This mixture is fluxed with tar heavy oil if required to give the desired softening point and penetration properties.

The term "plasticized coal-tar enamel" is used herein to mean a coal-tar enamel having a coal digestion pitch or plasticized pitch as its pitch ingredient. "Unplasticized coal-tar enamel," as employed herein, designates a coal-tar enamel containing ordinary coal-tar pitch as its pitch ingredient and not a coal digestion pitch or plasticized pitch, so that the term "unplasticized," used herein, merely differentiates an ordinary or conventional coal-

tar enamel from a plasticized coal-tar enamel containing a coal digestion pitch.

The term "tar heavy oil" herein designates a tar fraction having not more than 1% distillate at 300° C. and a 25% maximum distillate at 355° C. It has a minimum specific gravity of 1.140 and contains not more than 0.5% water. This oil is not limited to being derived from a tar of any one particular source and can be obtained, for example, from coal-tar, heavy water gas tar, light water gas tar, etc.

The term "pitch" as used herein is understood in the tar industry to designate a residue of tar distillation having a consistency ranging from that of heavy tar to that of hard pitch or semi-coke. Pitch may have a softening point of about 100° to 300° F. Softening points referred to herein are determined by the A. S. T. M. ring and ball method D36-26 unless otherwise specified, and penetration values by A. S. T. M. method D5-52.

The terminology "primed," "priming," etc. is employed throughout the specification and appended claims to designate the cold application of an adhesive coal-tar composition, preferably to clean metal surfaces, so as to insure an effective bond of maximum strength between the coating compositions of the instant invention and the pipes, piling, rods, etc.

The term "fibered coal-tar pitch emulsion" is employed throughout this specification to designate a coal-tar pitch emulsion in which a predetermined quantity of mineral fibers such as, for example, asbestos fibers have been incorporated. The asbestos fibers utilized are advantageously grade 7M (Canadian Government grade) fibers. The size of this grade of asbestos fibers is determined in the following manner: 16 ounces of asbestos fibers are placed on a sieve having ½ inch openings. A sieve having ¼ inch openings is positioned directly beneath the ½ inch sieve and a sieve having ⅛ inch openings is positioned directly beneath the sieve having the ¼ inch openings. A pan is positioned directly beneath the sieve having ⅛ inch openings. With grade 7M fibers it is found that no asbestos fibers are retained on the sieve having the ½ inch openings and that no asbestos fibers are retained on the sieve having the ¼ inch openings. One to two ounces of asbestos fibers are retained on the sieve having the ⅛ inch openings, and 14 to 15 ounces of the fibers pass through the ⅛ inch-opening sieve to the pan positioned below. Other mineral fibers which can be utilized in place of the asbestos fibers, if desired, are, for example, rock wall fibers, slag wool fibers, glass fibers, etc. If such other fibers are utilized the same size is desirable as indicated for asbestos fibers.

In the preparation of coal digestion pitch or plasticized pitch, powdered bituminous coal is digested with pitch and tar heavy oil at a temperature range of from 270° to 350° C. and advantageously at about 315° C. until a homogeneous dispersion of the coal in the pitch is obtained. A suitable dispersion is obtained within a reasonable time at temperatures within this range. This dispersion is then fluxed with tar heavy oil, if required, to the desired softening point and penetration characteristics. The amount of coal used can ordinarily vary from about 15 to about 30 parts by weight; the amount of tar heavy oil utilized can range from about 30 to about 55 parts by weight, and the pitch can range from approximately 20 to approximately 45 parts by weight; the exact amounts of these materials utilized being dependent, of course, on their respective properties and the properties of the products desired. Examples of typical coal digestion pitch compositions, in which the parts are by weight unless otherwise specified, which can be utilized in bituminous enamel suitable for practice of the instant invention are those prepared as follows:

34 parts of coal-tar pitch (softening point 158° F.) and 25 parts of a powdered bituminous coal, and 41 parts of coal tar heavy oil are charged to a still or a digesting tank equipped advantageously with a mechanical agitating

device to prevent local overheating and provided with heating means. These ingredients are then heated together, advantageously with agitation or stirring, at a temperature of about 315° C. for between 2 and 4 hours. At the end of this period, the heating is discontinued. After several minutes of cooling, the product is discharged from the still and is ready for use. The product has a softening point of 208° F. and a penetration at 77° F. of 15 decimillimeters.

Another coal digestion pitch composition which can be utilized is prepared by repeating the foregoing procedure with 39 parts of a heavy water gas pitch (softening point 140° F.), 21 parts of powdered bituminous coal, and 40 parts of coke oven tar heavy oil. The product has a softening point of 228° F. and a penetration at 32° F. of 12 decimillimeters.

An additional pitch composition which can be utilized is prepared by repeating the foregoing initial procedure utilizing 40 parts of coal-tar pitch having a softening point of 130° F., 25 parts of powdered bituminous coal, and 35 parts of coal-tar heavy oil. The resulting product has a softening point of 215° F. and a penetration of 11 decimillimeters at 77° F.

In a preferred embodiment of the instant invention, a ferrous metal pipe 10 as disclosed in Figures 1 and 2 and in more detail in Figure 3, or as shown in Figure 4, a metal H-beam, or as disclosed in Figure 5, a metal I-beam, is advantageously cleaned and advantageously primed with a primer coat 13 of a bituminous priming solution. The primer coat is permitted to dry, and the article is then coated with a first protective coating 14 of the hereinafter-described plasticized coal-tar enamel.

A plasticized coal-tar enamel which is eminently adapted for utilization in this first protective coating is one containing about 70% by weight of coal digestion pitch and about 30% by weight of talc. This plasticized coal-tar enamel conforms to American Water Works Association specifications which require the following characteristics:

Softening point (R. & B.)	°F.	220-235
Penetration at 77° F.		10-20
Penetration at 115° F.		15-55
Ash by weight (by ignition)	percent	25-35
Specific gravity, 25/25° C. (A. S. T. M. Method D-71-52)		1.40-1.60

Other plasticized coal-tar enamels can be utilized in place of the foregoing plasticized enamel if desired. For example, plasticized coal-tar enamels containing from about 65 to about 80% by weight of coal digestion pitch and from about 20 to about 35% by weight of a filler such as talc may be utilized if desired. Such enamels are prepared by heating a suitable coal digestion pitch until it assumes a liquid state and thereafter admixing a filler such as talc of substantially 200 mesh fineness therein until the admixture of coal digestion pitch and talc becomes homogeneous throughout.

Coatings of plasticized coal-tar enamels are particularly advantageous when the structural article is a pile or similar marine structure inasmuch as these plasticized enamels are substantially more resistant to pile driving shocks and other shocks than are the less plasticized or the unplasticized bituminous coating compositions. However, for pipe line work where the coated pipe is to be laid in a trench or under water rather than driven as is the case with piling, a more advantageous coating composition which can be utilized, if desired, as a first protective coating 14 is one of the class of unplasticized enamels containing from about 65 to about 80 parts by weight of coal-tar pitch and from about 20 to about 35 parts by weight of a filler such as, for example, talc. Examples of unplasticized coal-tar enamels which are eminently adapted for this first protective coating, where the pipe is to be laid in a trench or under water without being subjected to shock,

5

in which the percentages are by weight unless otherwise specified, are:

UNPLASTICIZED COAL-TAR ENAMEL A

	Percent
Coal-tar pitch.....	65
Talc.....	35

UNPLASTICIZED COAL-TAR ENAMEL B

	Percent
Coal-tar pitch.....	79
Talc.....	21

UNPLASTICIZED COAL-TAR ENAMEL C

	Percent
Coal-tar pitch.....	75
Slate dust.....	25

UNPLASTICIZED COAL-TAR ENAMEL D

	Percent
Coal-tar pitch.....	68
Ground mica.....	32

The foregoing unplasticized coal-tar enamels have properties which are represented by the following range of values:

Softening point, °F.....	180 to 205
Penetration at 77° F.....	0 to 3
Penetration at 115° F.....	1 to 10
Ash by weight (by ignition).....	20 to 39
Specific gravity, 25/25° C. (A. S. T. M. Method D71-52).....	1.40 to 1.65

They are prepared by heat liquifying coal-tar pitch having softening points ranging from approximately 100° F. to 200° F. and thereafter admixing a filler such as, for example, talc therein until a homogeneous mixture of these two ingredients is produced.

It is to be noted that other fillers can be employed in the plasticized and unplasticized coal-tar coating composition in place of the talc in substantially identical quantities as talc. For example, slate dust or flour, ground mica, clay, shale, etc., can be utilized. The fillers should be powdered sufficiently to pass a 200-mesh sieve.

Covering this first protective coating 14 is a second coating 11 of the hereinbefore-described fibered coal-tar pitch emulsion. This second coating acts as a binding agent to effect a bond of excellent strength between the smooth-surfaced first protective coating 14 and the third coating 12. Specific examples of fibered coal-tar pitch emulsion compositions containing a major amount of coal-tar emulsion and a minor amount of mineral fibers and added water which can be employed as this second coating 11, in which the parts and percentages are by weight unless otherwise specified, are:

Example I

	Parts	Percent
Coal-Tar Pitch.....	24	79
Residuum Tar Pitch.....	8	
Bentonite.....	3	
Water.....	47	
Talc.....	18	6
Asbestos Fibers (grade 7M).....		
Water.....		15

Example II

	Parts	Percent
Coal-Tar Pitch.....	34	80.5
Bentonite.....	4	
Water.....	52	
Talc.....	10	
Glass Fibers.....		7.5
Water.....		12

6

Example III

	Parts	Percent
Coal-Tar Pitch.....	16	79
Residuum Tar Pitch.....	16	
Bentonite.....	3	
Water.....	47	
Talc.....	18	6
Asbestos Fibers (grade 7M).....		
Water.....		15

Example IV

	Parts	Percent
Coal-Tar Pitch.....	31	78.5
Bentonite.....	3	
Water.....	49	
Ground Mica.....	17	
Slag Wool Fibers.....		4.5
Water.....		17

Example V

	Parts	Percent
Coal-Tar Pitch.....	26	77
Bentonite.....	2	
Water.....	52	
Slate Dust.....	20	
Rock Wool Fibers.....		7.5
Water.....		15.5

The fibered coal-tar pitch emulsions of foregoing Examples I and III, Example I in particular, wherein coal-tar pitch obtained from coke oven operations and residuum tar pitch are employed as constituents of the emulsion are preferred for the practice of this invention. Similar coal-tar emulsions can be made with different proportions of coke oven tar pitch and residuum tar pitch, or the residuum tar pitch can be eliminated but the total amount of pitch utilized is advantageously within the range of from about 25 to about 36% by weight. It is apparent from the foregoing examples that the constituents of the coal-tar pitch emulsion and of the final fibered coal-tar pitch emulsion can be varied. For example, in the coal-tar pitch emulsion, the bentonite can be present in an amount ranging from about 2 to about 4% by weight, filler such as, for example, talc in an amount ranging from about 10 to about 20% by weight, and water in an amount from about 45 to about 55% by weight. Other fillers such as, for example slate dust, ground mica, shale, clay, etc., can be utilized in the emulsion in place of talc. The fillers should be powdered sufficiently to pass a 200-mesh sieve. The coal-tar pitch has a softening point within the range of about 90 to about 140° F. and advantageously from 100 to 120° F. as determined by the standard ring and ball softening point test. The composition of the fibered tar-pitch emulsion can be varied within the range of from about 77% to about 81% by weight of the coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers, and from about 11 to about 18% by weight of added water.

This fibered coal-tar pitch emulsion can be prepared by making a slurry of water, talc and bentonite with amounts of these constituents in accordance with any of the foregoing examples or within the foregoing range. Coal-tar pitch, either a coke oven tar pitch-residuum tar pitch blend or a coal tar pitch without any residuum tar pitch blended therewith (in an amount according to any of the foregoing examples or within the broad range) which has been heated to fluidity, for example a temperature of about 215° F., is then admixed with the slurry with vigorous agitation by means of any conventional stirring or agitating device. Water and mineral fibers (also in an amount according to any of the foregoing examples) are then added to this emulsion and mixed therewith with moderate agitation.

Covering this second coating 11 is a third coating 12 of a cement composition comprising from about 2 parts to about 3 parts by volume of sand and about 1 part by volume of Portland cement. A specific cement composition which is eminently adapted for utilization if the instant invention is prepared as follows:

Sand and ground Portland cement in the proportion of about 2 parts by volume of sand and about 1 part by volume of Portland cement are changed to a conventional cement mixing apparatus. These ingredients are intimately mixed by agitation for a few minutes. Sufficient water to dilute this composition to a troweling consistency is then admixed with the ingredients and agitated for several minutes. If it is desired to apply this cement composition by brushing, sufficient water is admixed with the ingredients to produce an admixture having a suitable brushing consistency. The sand and Portland cement particles are advantageously of a size to pass substantially a 200 mesh screen.

The protective coatings disclosed herein cooperate and coact together in providing the protection for the structural article. In the preferred composite coated structural article shown by Figures 1-5, the primer coat 13 acts as a bonding agent to provide a bond of maximum strength between the structural article and the first protective coating 14 of coal-tar enamel. The second coating 11 of the fibered coal-tar pitch emulsion acts as a bonding agent to provide a bond of maximum strength between the third coating 12 of the Portland cement-sand composition which is resistant to penetration by marine organisms and the smooth-surfaced first protective coating 14 of the coal-tar enamel which renders the structural article resistant to corrosion. This second coating 11 of the fibered coal-tar pitch emulsion is critical inasmuch as when this coating is omitted the coating of the Portland cement-sand composition either does not adhere to the smooth-surfaced first protective coating of coal-tar or the bond between these two coatings is so weak as to be inoperative.

The preferred composite coated structural article is advantageously primed as hereinbefore-described with a bituminous priming solution. This primer coat may be omitted, if desired, but if this is done, the first protective coating 14 of plasticized coal-tar enamel will not adhere as well to the smooth-surfaced metallic structural article as when the primer coat is employed, unless the structural article is immersed in the hot enamel for a sufficient length of time to allow the metal to approach the temperature of the hot coating before the structural article is coated therewith.

With reference to Figures 1-5 which illustrate a preferred composite coated structural article of this invention, the surface of the structural article is advantageously thoroughly cleaned prior to the application of the coating materials thereto, to remove any foreign materials present such as dirt, rust, welding scale, etc. This cleaning operation can be advantageously accomplished by sand blasting but also may be effected by means of brushing with suitable wire brushes, by subjecting the surfaces of these articles to the action of manually or mechanically operated knives, scrapers, etc., by flame cleaning, by treating the surfaces of these articles with a pickling solution, such as, for example, sulfuric or nitric acid, or by applying steam to the surface of the structural article, etc.

A primer coat 13 of a bituminous priming solution is then advantageously applied cold by brushing or spraying, advantageously immediately after the structural article has been cleaned. On new ferrous metal or steel, this priming solution is advantageously applied in a uniform thin film free of runs, drips, or missed spots at the rate of preferably 500-700 square feet per gallon. On a roughened or slightly pitted surface, the coverage can drop to 300-500 feet per gallon.

A typical priming solution suitable for the practice of the instant invention is one containing from about 50 to

about 60 and advantageously about 57.5 parts by weight of a coal digestion pitch, having a softening point of about 160-230° F. and advantageously of approximately 205-215° F. and from about 40 to about 50 and advantageously about 42.5 parts by weight of a coal-tar solvent naphtha having not more than 5% distillate at 150° C. and not less than 90% distillate at 200° C. These constituents are thoroughly admixed for several minutes at an initial pitch temperature of between about 310° and 325° F., and the temperature allowed to drop during later agitation.

Other priming solutions composed of from about 35 to about 45 parts by weight of refined coal-tar naphtha of the 150-200° C. boiling range and from about 55 to about 65 parts by weight of a coal-tar pitch having a softening point of from 150° to 190° F. can be utilized in place of the foregoing priming solution. The pitch base of each primer is advantageously selected so as to produce the best adhesion with its companion enamel.

Other volatile solvents can be utilized in whole or in part in place of the coal-tar solvent naphtha. For example, fractions of heavy water-gas tar distillates and light water-gas tar distillates, and petroleum distillates containing a preponderance of aromatics can be utilized. The boiling points of these solvents can vary from about 150° C. to about 200° C. Additionally the solvents of the above mentioned boiling range may be replaced in whole or in part, if desired, by lower boiling compatible coal-tar solvents such as solvents boiling between 80° C. and 150° C. when quicker drying bituminous coating compositions are specified.

The primer coat 13 will dry in from 12 to 24 hours, depending upon atmospheric conditions. When the weather is hot and dry, the evaporation of the solvent is accelerated. When the weather is cold and damp, a considerably longer drying period is required. The temperature of the structural article should be over 35° F. for best results. Under these conditions, the primer coat will dry in not more than 24 hours.

The primed structural article is then substantially ready for the coating operation. However, just prior to the application of the protective coatings, the primed pipe is advantageously freed of all dust, dirt, and other foreign material.

The coal-tar enamel, which is to be applied to the primed structural article as the first protective coating 14, is then liquified by means of heat. If the particular coal-tar enamel to be used for the first protective coating in the hereinbefore described plasticized coal-tar enamel, the enamel is heated at a temperature range of from approximately 450 to 490° F. and is applied to the primed structural article at a temperature within this range by non-atomized spraying, brushing, dipping or by the use of any conventional coating machine known in this art. However, if the composition of the coal-tar enamel to be applied as the first protective coating 14 is that of one of the hereinbefore-described unplasticized coal-tar enamels A, B, C or D which are characterized by containing unplasticized coal-tar pitch and not coal digestion pitch as the pitch ingredient, the enamel should be heated at a temperature range of from approximately 375°-490° F. This first protective coating 14 of coal-tar enamel is applied advantageously in a thickness of from about $\frac{3}{32}$ " to about $\frac{1}{16}$ " and preferably in a thickness of approximately $\frac{1}{16}$ ". This is true regardless of whether the first protective coating is the hereinbefore-described plasticized coal-tar enamel or one of the hereinbefore-described unplasticized coal-tar enamels A, B, C or D. The first protective coating 14 may be applied in a thickness substantially greater than $\frac{3}{32}$ ", if desired, as there is no critical upper limit as to the thickness of this first protective coating. This first protective coating 14 is permitted to cool and harden and thereafter the second coating 11 of the previously described cold applied fibered coal-tar pitch emulsion is applied in any conventional manner over the first pro-

protective coating and permitted to dry or harden, which usually takes about 2-12 hours. This second coating 14 is applied advantageously in a coverage of from about 50 to about 60 square feet per gallon. A third coating 12 of the hereinbefore described Portland cement-sand composition which is resistant to marine organism penetration is then applied over the second coating 11 by brushing, troweling, or by positioning a suitable form or mold around the structural article and thereafter pouring the Portland cement-sand composition into the space defined by the mold and the structural article. This third coating 12 is applied advantageously at a thickness of about $\frac{1}{16}$ " to about $\frac{1}{8}$ " or can be substantially thicker if desired. The third coating is then allowed to harden and set in the conventional manner.

It is to be understood that additional materials such as, for example, inhibitors, anti-oxidants, etc. can be incorporated into the plasticized and unplasticized coal-tar enamels, the fibered coal-tar pitch emulsion, and the Portland cement-sand compositions of this invention. Other dispersing agents or emulsifying agents can be utilized in the coal-tar emulsion compositions of this invention in place of the bentonite such as, for example, sodium alkyl naphthalene sulfonates, sodium alkyl benzene sulfonates, the dioctyl ester of sodium sulfosuccinic acid, etc.

Structural articles coated in accordance with the concepts of this invention have been found to be unharmed by barnacles, teredos and similar marine organisms even after 4 years' immersion. Conventional coatings were penetrated in from 3 to 6 months by these marine organisms.

The invention claimed is:

1. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and to corrosion comprising: applying to a structural article a first protective coating of a hot composition containing from about 65 to about 80 parts by weight of coal-tar pitch and from about 20 to about 35 parts by weight of filler; permitting said first protective coating to cool and harden; applying a second coating of a fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers, and from about 11% to about 18% of added water; permitting said second coating to dry; applying a third coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement over said second coating; and thereafter permitting said third coating to harden.

2. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and to corrosion comprising: applying to a structural article a first protective coating of a hot composition containing from about 65 to about 80 parts by weight of coal digestion pitch and from about 20 to about 35 parts by weight of filler; permitting said first protective coating to cool and harden; applying a second coating of fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers and from about 11% to about 18% of added water; permitting said second coating to dry; applying a third coating over said second coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement; and thereafter permitting said third coating to harden.

3. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and to corrosion comprising: applying at a temperature ranging from approximately 375-490° F. to a structural article a first protective coating of a composition containing from about 65 to about 80 parts by weight of coal-tar pitch and from about 20 to about 35 parts by weight of filler;

permitting said first protective coating to cool and harden; applying a second coating of fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers, and from about 11% to about 18% of added water; permitting said second coating to dry; applying a third coating over said second coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement; and thereafter permitting said third coating to harden.

4. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and to corrosion comprising: applying at a temperature ranging from approximately 450-490° F. to a structural article a first protective coating of a composition containing from about 65 to about 80 parts by weight of coal digestion pitch and from about 20 to about 35 parts by weight of filler; permitting said first protective coating to cool and harden; applying a second coating of fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers, and from about 11% to about 18% of added water; permitting said second coating to dry; applying a third coating over said second coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement; and thereafter permitting said third coating to harden.

5. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and corrosion comprising: applying a primer coat to a structural article of a bituminous solution containing from about 55 to about 65 parts by weight of coal-tar pitch and from about 35 to about 45 parts by weight of volatile solvent boiling within the range of from approximately 80-200° C.; permitting said primer coat to dry; applying at a temperature ranging from approximately 375-490° F. over said primer coat a first protective coating of a composition containing from about 65 to about 80 parts by weight of coal-tar pitch and from about 20 to about 35 parts by weight of filler; permitting said first protective coating to cool and harden; applying a second coating of fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers and from about 11% to about 18% of added water; permitting said second coating to dry; applying a third coating over said second coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement; and thereafter permitting said third coating to harden.

6. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and to corrosion comprising: applying a primer coat to a structural article of a bituminous solution containing from about 50 to about 60 parts by weight of a coal digestion pitch and from about 40 to about 50 parts by weight of a volatile solvent boiling within the range of from about 80-200° C.; permitting said primer coat to dry; applying at a temperature ranging from approximately 450-490° F. over said primer coat a first protective coating of a composition containing from about 65 to about 80 parts by weight of coal digestion pitch and from about 20 to about 35 parts by weight of filler; permitting said first protective coating to cool and harden; applying a second coating of fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers, and from about 11% to about 18% of added water; permitting said second coating to

11

dry; applying a third coating over said second coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement; and thereafter permitting said third coating to harden.

7. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and to corrosion comprising: cleaning the structural article; applying to the cleaned structural article a primer coat of a bituminous solution containing from about 55 to about 65 parts by weight of coal-tar pitch and from about 35 to about 45 parts by weight of volatile solvent boiling within the range of from approximately 80–200° C.; permitting said primer coat to dry; applying at a temperature ranging from approximately 375–490° F. over said primer coat a first protective coating of a composition containing from about 65 to about 80 parts by weight of coal-tar pitch and from about 20 to about 35 parts by weight of filler; permitting said first protective coating to cool and harden; applying a second coating of fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of mineral fibers, and from about 11% to about 18% of added water; permitting said second coating to dry; applying a third coating over said second coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement; and thereafter permitting said third coating to harden.

12

8. A process for rendering structural articles resistant to the attack of pestiferous marine organisms and to corrosion comprising: cleaning the structural article; applying to the cleaned structural article a primer coat of a bituminous solution containing from about 50 to about 60 parts by weight of a coal-tar pitch and from about 40 to about 50 parts by weight of a volatile solvent boiling within the range of from about 80–200° C.; permitting said primer coat to dry; applying at a temperature ranging from approximately 375–490° F. over said primer coat a first protective coating of a composition containing from about 65 to about 80 parts by weight of coal-tar pitch and from about 20 to about 35 parts by weight of filler; permitting said first protective coating to cool and harden; applying a second coating of fibered coal-tar pitch emulsion over said first protective coating, said fibered coal-tar pitch emulsion containing from about 77% to about 81% by weight of coal-tar pitch emulsion, from about 3% to about 9% by weight of grade 7M asbestos fibers, and from about 11% to about 18% of added water; permitting said second coating to dry; applying a third coating over said second coating of a composition comprising from about 2 to about 3 parts by volume of sand and about 1 part by volume of Portland cement; and thereafter permitting said third coating to harden.

9. An article of manufacture made according to the process of claim 4.

10. An article of manufacture made according to the process of claim 8.

No references cited.