

[54] **CORROSION INHIBITION WITH A
TANNIN, CYANOHYDRINATED
LIGNOSULFONATE, AND AN
INORGANIC METAL SALT
COMPOSITION**

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[56]

References Cited

UNITED STATES PATENTS

3,256,203 6/1966 Robertson et al. 252/387
3,352,793 11/1967 Robertson 252/389

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[57]

ABSTRACT

A corrosion-inhibiting composition and process consisting of (a) a water-dispersible tannin, (b) a cyanohydrinated lignosulfonate or naphthalene sulfonate, and (c) a polyvalent metal ion masking agent for the chelating system, e.g., zinc nitrate.

9 Claims, No Drawings

CORROSION INHIBITION WITH A TANNIN, CYANOHYDRINATED LIGNOSULFONATE, AND AN INORGANIC METAL SALT COMPOSITION

The instant invention is directed to a process of inhibiting corrosion of iron surfaces in contact with cooling waters. More specifically, the subject invention relates to compositions which inhibit corrosion of iron in presence of cooling waters by aiding in formation of a protective iron oxide film over the iron substrate.

One of the best known ways to inhibit corrosion of iron surfaces, such as carbon steel, which are in contact with corrosive cooling waters is to somehow increase the tendency of the iron surface to form a protective iron oxide film. However, in the usual situation corrosion or rusting occurs because either the type or form of the oxide produced is nonprotective or because the film-forming reaction is too slow. Thus, soluble iron species are allowed to migrate too far from the surface to be of any appreciable value in forming a surface barrier to ionic and/or molecular corrodants or corrosion products. Dissolved oxygen in the aqueous environment in contact with the iron equipment or container then diffuses to the free metal surface more rapidly and high-corrosion rates ensue.

If this diffusion could somehow be slowed down and controlled, corrosive attack would cease or be greatly reduced. Specifically, if, by some means formation of a thin, tightly bonded, uniform film of the proper type of iron oxide over the iron surface could be promoted, the iron system under attack from cooling water media would be less prone to corrode, or in many cases would be substantially noncorrosive.

In order to somehow aid formation of a protective iron oxide film, a chemical composition must not form strong complexes or chelates with soluble iron species which would increase the demand for iron in the cooling water and thereby increase corrosion rates. Yet, such a composition must be able to react with or absorb on iron or the iron oxides at the iron surface to control the crystallinelike growth and habit of the oxides. Also, a chemical treating agent when added to the cooling water system as a corrosion inhibiting substance must be able to reach the metal surface under attack or at least make a very close approach to the surface, certainly within the ionic double layer, while still in active form. In brief, a useful chemical anticorrosive material should be able to help produce an ideal oxide film in a quick and efficient manner by a facile, close approach to an iron surface to which it can attach itself or be in close proximity. The additive would then be able to absorb or react with iron species just formed through the additive's active sites, thereby enhancing filming on the iron or steel surface to be protected.

The above problem is a particularly arduous one with which prior art materials have not been dependably able to cope. In some instances, the additive reagents while tying up in some manner the iron which has escaped from the surface of the corroding metal and through the ionic double layer, are thereby rendered almost immediately ineffective. In other words, such prior art material becomes quickly exhausted after some type of reaction or absorption with the iron ions, and is no longer effective in combating corrosion by promotion of protective iron oxide film. On the other hand in some cases, substances added to cooling waters to inhibit corrosion of iron substances in contact with these liquids, are so aggressive in their reaction with iron ions by some types of complexing or chelation, that the concentration of iron ions in solution is rapidly depleted. This then has the adverse effect of shifting the equilibrium reaction at the metal surface and actually increasing the release of iron ions to the water. Metal attack is thereby increased. If, therefore, a corrosion inhibiting composition could be devised to somehow enhance formation of a protective iron oxide film on surfaces of corrodible iron metals, and obviate the just discussed problems, a substantial advance in the art would be made.

It, therefore, becomes an object of the invention to provide cooling water compositions and method for their use.

Another object is to provide cooling water compositions which will promote formation of a protective iron oxide film upon the surfaces of corrodible iron metals and thereby control the diffusion of oxygen to the free iron metal surface which is susceptible to its corrosive effects.

A special object of the invention is to provide a combination of compounds in a single composition which will protect corrodible iron surfaces in the presence of cooling water over long periods of time even at relatively low dosages, which compositions are not quickly depleted of activity by rapid reaction of their active sites with water dispersible iron species.

In accordance with the invention, a method of inhibiting corrosion of iron metal surfaces such as heat exchange surfaces in contact with cooling waters, has been discovered. Generally, corrosion as well as fouling of the iron metal surfaces can be controlled through the use of a corrosion-inhibiting composition comprising a chelating system which includes both a water-dispersible tannin and an HCN modified lignosulfonate or naphthalene sulfonate and a masking agent for the chelating system which comprises a multivalent metal ion.

The above three constituents of the corrosion-inhibiting compositions are all essential to efficient control of corrosion. Omission of any one of the three ingredients, as will be seen more clearly later, does not give the proper corrosion protection when compared to a cooling water treatment involving all three components.

The specific compounds making up the sum total corrosion-inhibiting composition may be added to a cooling water separately, or they may be combined into a single product in either liquid or granular form, or in the form of a shaped article of manufacture, e.g., a water-treating ball. The subject composition may be readily formed into compact balls which may then be conveniently added to the cooling water.

The chelating system which is added to the cooling water in order to complex or tie up water-dispersible iron species existing in the cooling water includes a water-dispersible tannin and an HCN modified lignosulfonate or naphthalene sulfonate.

A. Water-Dispersible Tannin Substituents

Greatly preferred water-dispersible tannins are those which have been modified by a variety of synthetic method by reaction of natural tannins with various chemical reagents. Mixtures of these modified tannins may also be used in preparing the subject compositions.

The tannins have been divided into two principal groups—the catechol tannins and the pyrogallol tannins. After dry distillation the catechol tannins yield catechol as a principal product of decomposition, and the pyrogallol tannins after dry distillation yield pyrogallol. Solutions containing catechol give a greenish-black precipitate with ferric salts, whereas solutions containing pyrogallol tannins give a bluish-black precipitate with ferric salts. In general, only pyrocatechol derivatives are found in catechol tannins, whereas gallic acid is always present in pyrogallol tannins. The preferred tannins for use in the subject process are the catechol tannins although pyrogallol tannins can also be used in the process.

Natural tannins can be obtained from a number of materials. One of the principal sources is the quebracho trees, the wood of which contains about 20 to 23 percent easily extractable tannin of the catechol type. Other sources include chestnut wood, redwood bark, divi-divi pods, mangrove bark cutch (one of the preferred sources along with quebracho trees), wattle bark, gallnuts, hemlock bark, sumac, and oak bark.

A discussion of tannins and tannin chemistry is set forth in the Encyclopedia of Chemical Technology, Vol. 13, pages 578-599, which article is by reference included as part of this disclosure.

In the modification step the tannins are bisulfited by reaction with sulfite, bisulfite or formaldehyde and bisulfite, or are modified by reaction with sodium or ammonium cyanides, with sodium chloroacetate, with sulfuric acid (either sulfonation or oxidation), with nitric acid (which would involve either oxidation or nitration), etc., to produce functional group changes in the natural tannin. Thereby its performance is markedly improved as an aid to its action in the subject treatment.

A preferred group of modified tannins which can be used in the subject invention is described in U.S. Pat. No. 2,831,022. In the process disclosed in this patent, water solutions of sulfurous acid salts of alkali metals or ammonia are caused to react with the insoluble portion of Western hemlock bark at increased temperatures and in the presence of an excess of sulfurous acid. The water-soluble alkali sulfonic acid salts which are produced are separated as water solutions from the reaction mixture. The water solutions can include aqueous sodium sulfite and aqueous sodium bisulfite. The produced compounds are sulfonic acid derivatives or sodium sulfonate derivatives of the tannins occurring in the bark. Such compounds have a high content of phenolic hydroxyl and are relatively nonmethoxylated. The disclosure of U.S. Pat. No. 2,831,022 is included in this specification by reference. In the instant process tannins from sources other than hemlock bark which are modified as described in U.S. Pat. No. 2,831,022 also can be used with great success.

The following examples will serve to illustrate synthetic modes of preparation of modified tannins which are usefully employed in the invention.

EXAMPLE I

This example shows one method which can be used to modify tannins. In the method, 100 grams of mangrove tannin was dissolved in 150 ml. of distilled water. A second solution was formed by dissolving 16.6 grams of sodium chloroacetate in 50 ml. of distilled water. The second solution was added slowly to the first solution as the tannin was being heated. The mixture of the two solutions was agitated for 1 hour at a temperature slightly below boiling. During the mixing 10 ml. of a sodium hydroxide solution was added to maintain the pH of the mixture above 8. The final solution could be used as one of the component inhibitors of the invention or further processed to active solid form.

EXAMPLE II

This example illustrates a second method which can be used to produce the modified tannins of the subject invention. In this method, 50 grams of chestnut tannin was mixed with 0.1 gram of V_2O_5 , 0.5 ml. of ethyl silicate "40" and 1 ml. of distilled water. The chestnut tannin had previously been passed through an ion exchange resin to remove cations.

Twenty-five ml. of concentrated sulfuric acid was added to the above mixture and the mixture was allowed to react in its own heat for 20 minutes. After 20 minutes, 275 ml. of distilled water was introduced into the reaction mixture. Initially a thick paste was formed which thinned as more water was added. Twenty-five ml. of isopropanol was added to precipitate the reaction product. The precipitate on filtration gave a black-brown cake. The cake was solubilized in water by raising its pH to above 11 with caustic. Again, the solution as diluted could be directly employed or active solid material extracted out.

The tannins can be reacted with nitric acid in a manner similar to sulfuric acid. In both cases the reaction is a nitration or sulfonation and/or oxidation reaction. Likewise, the modification can be carried out through the use of sodium, potassium or ammonium cyanide or sodium, potassium or ammonium thiocyanate in which case the modification procedure would be carried out in a manner similar to those shown above in example I in connection with sodium chloroacetate. As a substitute for sodium chloroacetate one can use any sodium or potassium haloacetate, halopropionate or halobutyrate. The

preferred halogens are chlorine, bromine and iodine. As has been indicated previously, the tannins can also be modified by the method shown in U.S. Pat. No. 2,831,022. The sulfite or bisulfite modifications shown in the patent are preferred for preparation of tannins for use in connection with this invention. In the bisulfite treatment, the reaction is carried out initially at a moderate pH (5-7) whereby the bisulfite addition takes place with the oxy ring structure being split to form additional -OH groups. The solubilizing of the product with caustic preferably is then carried out under sufficiently mild condition (pH of 8-9) so as not to cause the product to hydrolyze or to revert to its original condition. Potassium or ammonium sulfite or bisulfite can be substituted for sodium sulfite or bisulfite in the process. As was indicated above, any natural tannin may be substituted for the hemlock tannin of U.S. Pat. No. 2,831,022. The preferred tannins, however, are the mangrove and/or quebracho tannins.

B. The HCN Modified Lignosulfonate Substituent

Lignin, a waste product in the processing of wood during the manufacture of paper and other cellulosic products is converted into lignosulfonate in the so-called sulfite process designed to remove lignin as water-soluble derivatives. Modern chemical theorists believe that the reaction goes due to the replacement of phenolic hydroxyl groups by bisulfite as described, for example, in *Organic Chemistry*, Cram and Hammond, 2nd Edition, 1964, page 697. Since the basic substance, lignin, is a wood fraction which is a noncarbohydrate polymer, the soluble product obtained by digestion with alkali bisulfite known as lignosulfonate is a mixture of polymers containing various groups. In the present invention there is utilized a further modification of the solubilized lignin which comprises reacting HCN with the lignosulfonate to produce an HCN modified lignosulfonate. The term "HCN modified lignosulfonate" is defined as a modification by use of HCN or its alkali metal or ammonium salt of a lignosulfonate and its normally contained wood sugars. It is presently theorized that either in the soluble lignin mixture there are sufficient carbonyl groups for nucleophilic attack by HCN in a type of cyanohydrin reaction or a portion of the phenolic hydroxyl groups are attached. See, for example, *Organic Chemistry*, 3rd Edition, 1956, Fieser & Fieser, pages 203-204. These cyanide modified lignosulfonates may be prepared by conventional chemical techniques and optionally in catalyzed environment. The HCN modified constituent is also presently in commercial supply under the following MARATHON (American Can Company) marks and trade designations, Chelig 32, Marathon B-10-7, Marathon B-22-15 and Marathon B-40-5. Marathon B-10-7 is identified as about 25 percent cyanohydrinated.

Similar to the cyanohydrin products with aldehydes and reactive ketones, the HCN modified lignosulfonate products are extremely stable and practically irreversible, having an extremely negligible HCN release factor.

In the substitution of the HCN modification of the present invention for the sugar complex substituent described in the Robertson patent, it may additionally be necessary to add, in certain cases, a minor but effective amount of an antifoam. A preferred antifoam is described in British application No. 22,771/47, Aug. 15, 1947, and comprises an intimate mixture of an inorganic aerogel and a methyl siloxane polymer having perceptible rubbery characteristics and containing an average of from 1.75 to two carbon atoms per atom of silicon. Such a composition is commercially available under the name Dow-Corning Antifoam A, and is effective in an amount less than about 0.1 percent by weight, ordinarily at about 0.03 percent.

Additionally, it may be necessary in selected cases in the utilization of the new substituent vice previous formulations to incorporate a nonelectrolyte freezing point depressant, for example, isopropanol, ethylene glycol, glycerol and the like. At least about 0.3 oz. of the depressant composition, having reference only to the ingredients comprising the invention, is

incorporated in each gallon of liquid. The composition is ordinarily added in an amount of about 0.3–3 oz. per gallon, or about 0.225–2.25 percent by weight of the liquid based on a liquid specific gravity of 1. Preferably, at least 0.75 oz. per gallon is added, and at least 1.0 oz. per gallon is further preferred for optimum metal protection.

Alternative to the water-dispersible lignosulfonate precursors there may be utilized additionally water-soluble naphthalene sulfonates which contain one or more sulfonated naphthalene nuclei, for example, polymethylene-bis-naphthalene sulfonate in its sodium or potassium salt form, alkyl naphthalene sulfonates or the sodium or potassium salts thereof in which the alkyl group contains about one -12 carbons as described in U.S. Pat. No. 3,173,864, Freedman (Nalco). The HCN modified naphthalene sulfonates may be used in the same manner and proportions as the lignosulfonates when treated with HCN, NaCN, KCN or NH_4CN .

In conventional lignosulfonates there are contained wood sugars which when present provide the major increase in functionality by conversion of the sugars to sugar acids as for example by oxidation of the terminal carbon of the aldose to glycaric acid.

In treating copper containing surfaces, preferable starting materials for HCN modification are lignosulfonates wherein the usual appreciable quantities of reducing sugars have been previously removed or reduced as by oxidation. This is especially true in utilizing the compositions of the present invention in treating admiralty metal surfaces where such sugars induce pitting but does not appear critical where the cooling water system surfaces are ferrous or carbon steel.

C. Polyvalent Metal Ion Masking Agent.

The third component comprising the compositions of the invention is what is termed as a "masking agent." This is a material which when added with the above-described chelating system, associates with the chelating or complexing agents. This reaction or absorption upon the active sites of the chelating agents tends to retard the complexing or chelating reaction of these chemicals with soluble iron species. This allows the "masked" organics to pass through the ionic double layer in a relatively undisturbed state. At the metal surface the organics are then "demasked" by release of the metal cation, allowing more effective reaction or adsorption at the surface than otherwise obtainable. As mentioned above, rapid depletion of iron concentration near the surfaces of the walls of the corrodible metal causes either a more severe case of corrosion than would be the situation in absence of additives, or, at the very least, the additives are quickly rendered ineffective by their active sites being blocked by reacting with or adsorbing soluble iron species. The masking agents then, in effect, help to slow down the reaction of the chelating agents with iron to the proper rate whereby both chelating agents remain in an active state long enough for effective reaction at the surface. The masking agents must themselves be capable of being displaced or exchanged by iron at the metal surface as the masked complexing agents approach the surface.

It has been discovered that excellent masking agents which help to retard the complexing action of the chelating agents with soluble iron bodies are polyvalent metal ions. These ions are preferably selected from among zinc, nickel, cadmium, manganese, aluminum and cobalt. These metal ions, as mentioned above, react with the organic active sites whereby the entire corrosion inhibiting composition is allowed to make a close approach to the surface before being inactivated by iron species. Preferred sources of the above ions are water-soluble salts of these metals such as halides, acetates, nitrates, and sulfates. Most preferred are the zinc and cobalt salts in any water-soluble form.

The portion of the three constituents making up the corrosion compositions of the invention may be varied over a wide range according to the type of water under treatment and the type of iron metal being protected. Preferred though are cor-

rosion compositions which contain 10–70 parts by weight of water-dispersible tannin, 5–50 parts by weight of HCN modified lignosulfonate and 10–60 parts by weight of inorganic water-soluble metal salt. The most preferred compositions comprise 20–60 parts by weight of tannin, 20–50 parts by weight of HCN modified lignosulfonate and 20–60 parts by weight of inorganic salt. Actual plant procedure from experience gained since the filing date of Robertson U.S. Pat. No. 3,256,203 has shown that where solid or balled compositions are utilized, preferably about one-third additional HCN modified lignosulfonate is used as compared with the liquid formulations.

The compounds disclosed here are useful in protecting any type of corrodible iron such as mild or carbon steel and alloys of iron.

Again, use amounts of the corrosion-inhibiting composition may be varied according to the severity of the corrosion problem. Generally, from about 10 parts of composition per million parts of cooling water to about 500 p.p.m. should be employed. More preferably 25–300 p.p.m. are used, with the most preferred use range being from about 30 to about 100 p.p.m. One specific type of useful application involves a short term high-level initial treatment followed by continual low-level treatment. For example, a cooling water may be treated with about 300 p.p.m. of the composition of the invention for several days followed by a 30–75 p.p.m. level treatment. The pH of the water itself is preferably adjusted prior to treatment. For optimum results the pH should range from about 6.0 to about 8.0.

It has also been discovered that the corrosion compositions of the invention are useful not only in inhibiting corrosion but have a pronounced tendency to retard deposition of suspended matter upon the corrodible iron surface. Turbid waters are often used as the cooling source and generally contain suspended clay and other forms of suspended silt, calcium and iron salts, microbiological growths, alumina floc, corrosion products themselves, and other suspended solids. These contaminants are present in the natural water or are subsequently introduced by standing in presence of air or through water pretreatment processes. The compositions of the invention help to keep these solids from building up voluminous flocculant deposits upon the surfaces of the iron heat exchange tubes or other surfaces susceptible to such deposition. These deposits can severely reduce heat transfer coefficients in the feedwater flow to heat exchangers, unless controlled. Deposition may be prevented to a substantial degree by addition of the compositions of the invention to cooling water, preferably in the above-stated use ranges.

Other materials may also be added to the cooling water along with the masked chelating system in order to increase the performance of that composition under special circumstances. For example, where nickel or copper alloys as well as iron come in contact with the cooling water, sulfhydryl-containing compounds may be employed. These may be classified broadly as nitrogen-containing heterocyclic compounds, characterized by a ring nitrogen bonded to a ring carbon. To the ring carbon is attached a nonring sulfhydryl group. Compounds of this type are 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole and alkali metal salts of the foregoing. Preferably the mercaptobenzothiazole is utilized in the amount ranging from about 2.35 to about 7.8 percent by weight.

Although the direct thrust of the present invention is directed to nonphosphate, nonchromate corrosion inhibitors, of course, if commercially needed, the present corrosion inhibitors may be combined with other well-known inhibitors such as the sodium salt of a copolymer of ethylene and maleic anhydride, phosphates and chromates. For example, both ortho and polyphosphates may be used, as well as hexavalent chromium such as sodium chromate and sodium dichromate.

COMPARATIVE EXAMPLE I

Liquid Formulation According to

Example III of U.S. Pat. No. 3,256,203 Robertson

Ingredient	%
ZnO	5.60
H ₂ SO ₄	7.25
ClCH ₂ CO ₂ H	1.85
Sucrose	6.24
Rayflo C	16.95
50% NaOH	1.36
Soft H ₂ O	60.76

A Liquid Formulation According to
the Present Invention

Ingredient	%
ZnSO ₄ ·H ₂ O	12.35
Rayflo C	16.95
Marathon B-10-7	8.47
Soft H ₂ O	62.23

(Rayflo C is a bisulfited tannin produced by the method disclosed in U.S. Pat. No. 2,831,022.)

(Marathon B-10-7 is an HCN modified lignosulfonate produced by American Can Co.)

COMPARATIVE EXAMPLE II COMPARISON OF DRY
FORMULATIONS PREPARED ACCORDING TO
TEACHINGS OF U.S. PAT. NO. 3,256,203 ROBERTSON
('203) TO SOLID COMPOUNDS PREPARED
ACCORDING TO TEACHINGS OF THE PRESENT
INVENTION (HCN)

Ingredient	'203	HCN	'203	HCN
Rayflo C	41.4	43.6	39.00	42.50
Sucrose	14.9		14.90	
40% ClCH ₂ CO ₂ Na	13.7		13.70	
Marathon B-10-7		21.8		21.30
ZnSO ₄ ·H ₂ O	30.0	31.6	30.05	30.80
MBT			2.07	2.13
BZT			0.28	0.25
Soft Water		3.0		3.02
Total	100.0	100.0	100.00	100.00

It was found that a superiority margin exists for the new products as versus the liquid and dry formulations prepared according to Robertson U.S. Pat. No. 3,256,203 especially in the areas of storage stability in the liquid version of comparative example I.

Additionally, as to the dry formulations of comparative example II, extensive testing showed that the Marathon-based formulas of the present invention were superior to the formulations of Robertson U.S. Pat. No. 3,256,203 in the areas of plant balling operations, corrosion inhibition and deposit control performance. The deposit control laboratory results were especially rewarding, being uniformly in the desired area of $\leq$ 2.0 MPY (mils per year) in the standard deposit coupon test utilized. This value was substantially lower than the Robertson U.S. Pat. No. 3,256,203 results which at times appeared erratic in shifting pH media.

The embodiments of the invention in which an exclusive

property or privilege is claimed are defined as follows:

1. A corrosion-inhibiting composition useful in preventing corrosion of iron surfaces in contact with cooling water consisting essentially of a chelating system to complex water-dispersible iron species existing in said cooling water which chelating system comprises 10-70 parts by weight of a water-dispersible tannin and 5-50 parts by weight of a substance selected from cyanohydrinated lignosulfonates and cyanohydrinated naphthalene sulfonates; and 10-60 parts by weight of a masking agent to retard said complexing action of said chelating system, which comprises a water-soluble inorganic metal salt containing a multivalent metal ion selected from the group consisting of zinc, aluminum, cadmium, cobalt, nickel and manganese.

2. The composition of claim 1 wherein said water-dispersible tannin is a natural tannin having been modified by reaction with a material selected from the group consisting of an alkali metal sulfite, an alkali metal bisulfite, ammonium sulfite, ammonium bisulfite, an alkali metal haloacetate, an alkali metal halopropionate, an alkali metal halobutyrate, ammonium cyanide, an alkali metal cyanide, ammonium thiocyanate, alkali metal thiocyanate, nitric acid, and sulfuric acid.

3. The composition of claim 2 wherein said inorganic salt is zinc sulfate and said cyanohydrinated compound is cyanohydrinated lignosulfonate.

4. The composition of claim 1 which additionally contains about 2.35 to about 7.8 percent by weight of a compound selected from the group consisting of 2-mercaptobenzothiazole and its alkali metal salts.

5. A process for inhibiting corrosion of a ferrous metal surface in contact with a corrosive cooling water medium which comprises maintaining contact of said surface with said water which additionally contains a corrosion-inhibiting composition consisting essentially of a chelating system to complex water-dispersible iron species existing in said cooling water which chelating system consists essentially of 10-70 parts by weight of a water-dispersible tannin, and 5-50 parts by weight of a compound selected from the group consisting of cyanohydrinated lignosulfonates and cyanohydrinated naphthalene sulfonates, and 10-60 parts by weight of a masking agent to retard said complexing action of said chelating system which consists essentially of a water-soluble inorganic metal salt containing a multivalent metal ion selected from the group consisting of zinc, cobalt, aluminum, cadmium, manganese and nickel.

6. The process of claim 5 wherein said water-dispersible tannin is a natural tannin having been modified by reaction with a material selected from the group consisting of an alkali metal sulfite, an alkali metal bisulfite, ammonium sulfite, ammonium bisulfite, alkali metal haloacetate, an alkali metal halopropionate, an alkali metal halobutyrate, ammonium cyanide, an alkali metal cyanide, ammonium thiocyanate, an alkali metal thiocyanate, nitric acid and sulfuric acid.

7. The process of claim 6 wherein said water-soluble salt is zinc sulfate and said sulfonate compound is cyanohydrinated lignosulfonate.

8. The process of claim 5 wherein said composition additionally contains about 2.35 to about 7.8 percent by weight of a compound selected from the group consisting of 2-mercaptobenzothiazole and its alkali metal salts.

9. The process of claim 5 wherein said cooling water has a pH ranging from about 6.0 to 8.0 and said inhibitor composition is present in said cooling water in the amount of 10-500 parts per million.

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