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COOLING WATER TREATMENT AND COMPOSITIONS USEFUL THEREIN

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The instant invention is generally concerned with corrosion compositions and their use in the treatments of cooling water systems. More specifically, the present invention relates to cooling water compositions having dual activity in both preventing corrosion of metal surfaces in contact with cooling waters, and in inhibiting fouling or build-up of deposits upon those same surfaces.

Two primary problems exist with respect to cooling water systems. First is gradual deterioration of metals in contact with the corrosive cooling water media. Second is gradual build-up of voluminous deposits upon the metal surfaces, particularly on heat transfer surfaces, until a point is reached whereby water flow is impeded through the heat exchangers and a severe reduction of heat transfer coefficient occurs.

It is generally accepted that no single chemical compound can obviate both just discussed problems by additive treatment. Combinations of various chemicals must be employed which will overcome both conditions of corrosion and fouling so as to allow proper equipment utilization and long-term equipment use.

However, certain problems arise with respect to the use of some chemical combinations in treatment of cooling water systems. First, in some instances the anti-corrosion activity attributed to one chemical is decreased in some manner via use of the second chemical designed to overcome fouling. The converse situation may also occur. Thus, a chemical successful in reducing corrosion when used as a sole treating agent may be partially or wholly inactivated by combination with a chemical tailored to prevent fouling. Likewise, an antifouling chemical may have its activity debilitated when employed in concert with a corrosion inhibitor.

Other problems may also occur in combination treatments. For example, if a single composition is desired, comprising a mixture of corrosion inhibiting and fouling reducing reagents, oftentimes chemical reaction between the two may occur, destroying effectiveness of one or both. Again, it is sometimes impossible to prepare a single composition comprising two or more useful chemicals which can exist in a single solid or liquid phase. Related problems of formulation may also occur.

It would therefore be a benefit to the art if a composition could be devised which had excellent activity in both inhibiting corrosion and reducing fouling tendencies of the metal surfaces in contact with cooling water systems. A further advantage would accure if this composition could be fed in dry form such as in form of balls or pellets, or else could be applied with equal success as a liquid concentrate.

It therefore becomes an object of the invention to provide a composition having usefulness in both preventing metal corrosion and inhibiting build-up of deposits upon metal surfaces in contact with cooling waters.

A special object of the invention is to provide a combination of compounds in a single composition of liquid or solid form which will protect metal surfaces in the presence of cooling waters from corrosion over long periods of time at relatively low dosages as well as concurrently keeping the metal surfaces free of unwanted deposits.

Other objects will appear hereinafter.

In accordance with the invention, a composition useful in inhibiting corrosion and fouling tendencies of metal surfaces in contact with industrial cooling waters has been discovered. Broadly speaking this composition comprises two components; one useful in preventing and inhibiting corrosion, and the other having excellent activity in preventing deposit build-up of various impurities in coolng waters upon metal surfaces. The corrosion inhibitor which comprises 10–90% by weight of the composition is a water-soluble chromate salt, and may include either chromate or dichromate salts or both. The other component making up 5–70% by weight of the composition is a water-dispersible tannin. This particular composition is quite specific in its chemcal definition. From among the broad genus of tannin substances, it, has been found that a particular group of water-dispersible tannins has surprisingly excellent fouling control in comparison to other tannin type materials. Specifically, this water-dispersible tannin is one wherein a natural tannin has 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, an alkali metal thiocyanate, nitric acid and sulfuric acid. Presence of both the above two constituents making up the overall composition is an essential in order to effect both corrosion control and proper inhibition of deposition upon the metal surfaces of the cooling tower. Omission of one or the other of the two ingredients does not give the proper dual protection.

The specific compounds making up the sum total corrosion inhibiting and antifouling composition may be added to a cooling water separately, or they may be combined into a single product, either liquid or granular in 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.

With more specific reference to the water-dispersible tannins forming a part of the subject matter of the invention, these materials are reaction products of tannins having been modified by a variety of synthetic methods. Natural tannins are reacted with various chemical reagents to produce the tannin antifoulants. 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% of 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 functonal 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. Patent 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 relative non-methoxylated. The disclosure of U.S. Patent 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. Patent 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 this 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 one 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 a partially polymerized ethyl silicate (about 5 mer units) and 1 ml. of distilled water. The chestnut tannin had previously been passed through an ion exchange resin to remove cations.

Twenty-five (25) ml. of a 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 (25) 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 about 11 with caustic. Again, the solution as diluted could be directly employed or active solid material could be 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 that 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. Patent 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. Patent 2,831,022. The preferred tannins, however, are the mangrove and/or quebracho tannins.

As mentioned above, the just described modified tannins have excellent activity in minimizing deposition of various solids carried in suspension in the cooling water, on metal surfaces such as heat exchange surfaces. The water-dispersible tannins are particularly useful in preventing deposition of alumina floc upon the metal surfaces of the cooling tower unit. This alumina floc is carried in the water along with other solids as carryover from various clarification operations used to pretreat the cooling water. Though the total concentration of alumina floc in solids in cooling waters may be only a few parts per million due to circulation in the system, they tend to agglomerate into larger particles and stick on surfaces of the cooling system such as cooling tower decks, and especially on heat transfer surfaces. Other suspended matter such as microbiological growths, corrosion products, silt and the like also have a tendency to be occluded upon the metal surfaces of the cooling tower. Over a period of time the suspended solids in the recirculating cooling water build up a voluminous, flocculant deposit which can severely reduce heat transfer coefficients and impede water flow through heat exchangers. This deposit, though light in density, adheres tightly to hot metal surfaces and is not readily removed by simply increasing the water velocity through heat exchanger tubes during normal operations. While the chromate portion of the compositions of the invention has excellent activity in preventing corrosion, this component has little or no ability to prevent the just discussed deposition. The above described water-dispersible natural tannins having been modified by any number of processes, have excellent activity in preventing formation of deposits upon metal surfaces of the cooling system and/or in cleaning metal surfaces already fouled.

The other essential ingredient used in making up the compositions of the invention is a water-soluble chromate salt. This chromate salt may contain either a chromate or dichromate ion. The chromates and dichromates are primarily corrosion inhibitors for ferrous metals, i.e., iron or steels. The salts particularly protect iron or steel heat exchange tubes and other ferrous metal components in the cooling tower against substantial corrosion. The most preferred chromate compositions are alkali metal chromates and dichromates such as potassium and sodium derivatives. Ammonium chromates and dichromates may also be employed. Again, mixtures of both chromates and dichromates may be used in conjunction with the water-dispersible modified natural tannins.

Other components are usefully included with the above two essential ingredients. It has been discovered that additional benefit is imparted to the chromate-tannin combination when a water-soluble lignin sulfonate is also employed as a cooling tower additive. Particularly preferred are water-soluble lignosulfonates derived as by-products in the manufacture of sulfite pulp where wood is cooked with

calcium bisulfite-magnesium bisulfite-sulfur dioxide liquor. In this process the lignin is converted to lignosulfonic acid which is thereafter converted to a solid product such as calcium lignosulfonate, ammonium lignosulfonate, potassium lignosulfonate, sodium lignosulfonate, etc. Those lignosulfonates which have only minimal amounts of reducing sugars are particularly advantageous, since reducing sugars appear to induce pitting of Admiralty metal surfaces. Thus, it is preferred to use water-soluble lignosulfonates from which the reducing sugars have been removed, as by mild oxidation with air, especially those in which the reducing sugars have been oxidized to sugar acids ranging from about 10–40% by weight of the lignosulfonate.

Another preferred class of useful water-soluble sulfonates are naphthalene sulfonates which contain one or more sulfonated naphthalene nuclei. Examples of water-soluble naphthalene sulfonates which can be used in accordance with the invention are polymethylene-bis-naphthalene sulfonate, the sodium or potassium salts thereof, and alkyl naphthalene sulfonates or the sodium or potassium salts thereof in which the alkyl group contains about 1–12 carbon atoms.

When a water-soluble lignin sulfonate is employed along with the chromate-tannin mixture, the following general ranges of proportions are preferably used to compound the composition. Composition A below sets out these ranges.

Composition A

Compound:	Percent by wt.
Chromate	10–70
Tannin	5–40
Lignin	10–70

Other chemicals may also be included with the chromate-tannin combination, used with or without lignin. As an example, it has been found that water-soluble inorganic metal salts having polyvalent cations are an aid to the chromate or dichromate corrosion protection of ferrous metals. These polyvalent metal ions are preferably selected from among zinc, nickel, cadmium, manganese, aluminum and cobalt. 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. Composition B below sets forth preferred ranges when these metal ions are used in conjunction with chromate, tannin and lignin.

Composition B

Compound:	Percent by wt.
Chromate	10–70
Tannin	5–40
Lignin	10–70
Inorganic metal salt	0.5–15

Another class of compounds which may also be used include the well-known molecularly dehydrated phosphates. These include pyrophosphates, such as tetrasodium pyrophosphate, tripolyphosphates such as sodium tripolyphosphate, any of the water-soluble polyphosphate classes of any of the alkali metals, alkaline earth metals, zinc or cadmium including those known as hexametaphosphates and glassy septaphosphates. The use of phosphates in cooling water systems is described in a patent to Fink et al., U.S. 2,358,222. Yet another preferred composition containing such phosphate is set forth below.

Composition C

Compound:	Percent by wt.
Chromate	10–70
Tannin	5–40
Lignin	10–70
Inorganic metal salt	0.5–15
Molecularly dehydrated phosphate	0.5–20

In special corrosion problems other materials may also be added to the cooling water along with the chromate-tannin combination and any one or more of the just described additional reagents. 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 atom bonded to a ring carbon atom. To the ring carbon atom is attached a non-ring sulfhydryl group. Compounds of this type are 2-mercaptothiazole, 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, and alkali metal salts of the foregoing. Particularly where heat exchange tubes are made of alloys such as Admiralty metals which are high in copper, the compositions of the invention should preferably contain one or more of the just described chemicals to protect the alloy against corrosion. Here a particularly preferred chemical is mercaptobenzothiazole or water-soluble salts thereof, e.g., the sodium, potassium and ammonium salts. This chemical has been found particularly useful in protecting Admiralty metals and brass against corrosion. Admiralty metals are a class of alloys of copper, zinc and tin, ranging from about 65–90% copper, 4–34% zinc, and 1–10% tin. Exemplary Admiralty metals are (a) 87% copper, 5% zinc and 8% tin, and (b) 70% copper, 29% zinc, and 1% tin. When the nitrogen-containing heterocyclic compound is employed, preferred ranges of this material as well as those of other corrosion control substances are set out in Composition D.

Composition D

Compound:	Percent by wt.
Chromate	10–70
Tannin	5–40
Lignin	10–70
Inorganic metal salt	0.5–15
Molecularly dehydrated phosphate	0.5–20
Nitrogen heterocycle	0.1–10

When a ball from the chromate-tannin composition with or without any one or more of the just described additional additives is desired, certain water-soluble binding agents are generally used to hold the solid particles together in a shaped article, e.g., water treating ball. For example, dextrin, sodium chloride, and soda ash may be usefully employed in this role either alone or in some combination one with the other.

The chromate and tannin constituent of the composition of the invention as well as the other discussed corrosion and fouling aids may be added separately to the cooling water, or first made up into a total composition which is then used as a sole treatment agent. The latter method is preferred, particularly since there is no interference of chromate with the antifoulant activity of the tannin nor interference of the corrosion properties of the chromate by inclusion with tannin substance.

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

In order to determine the effectiveness of the subject chromate-modified tannin compositions, a series of tests were devised using steel heat transfer tubes as test materials. A particular aim of these tests was to demonstrate effectiveness of the modified tannin substituent as an antifoulant. This material not only gave excellent deposition

control, but also did not destroy in any way the anti-corrosion effectiveness of the chromate component.

The effectiveness of the modified tannin component was especially noticeable in comparing its antifoulant activity to that of another similar organic material, namely, a sodium lignosulfonate. The modified tannin was surprisingly more effective than this organic substance in preventing unwanted deposition upon the metal surfaces of steel heat transfer tubes.

The tests themselves were run at a pH of 6.0 to 6.5 and at a temperature of 120° F. The flow rates in all the tests were 2.0 g.p.m. (gallons per minute). A complete description of the test procedures is set forth in Materials Protection, volume I, pages 23–30, October 1962.

In the experiments the following test water was used:

	P.p.m.
Total hardness	138 as $CaCO_3$.
Bicarbonate alkalinity	50
Calcium hardness	97 as $CaCl_2$.
Magnesium hardness	41 as NaCl.
Chloride	300 as NaCl.
Sulfate	400 as Na_2SO_4.
Silica	20 as SiO_2.
Fluoride	4 as F.
Iron	0.5 as Fe.
Copper	0.8 as Cu.
Aluminum	10 as Al_2O_3.

The heat transfer tubes were assembled in a number of apparatus corresponding to the number of tests to be run. Heated water having the just discussed amounts of corrosive ingredients was circulated around the heat transfer tube for a total of 14 days. The heat transfer tubes which had been previously weighed were then dried and reweighed and deposition and corrosion rates determined.

The formulations used in the tests include the following:

Formulation No. 1—	P.p.m. added
Component:	
Sodium chromate as CrO_4	10
"Rayflo" (a modified tannin produced by the method disclosed in U.S. Patent 2,831,022)	8
Sodium lignosulfonate	12
Molecularly dehydrated phosphate	3.5
Zinc sulfate monohydrate as Zn	1
2-mercaptobenzotiazole	1.5

Formulation No. 2—	P.p.m. added
Component:	
Sodium chromate as CrO_4	10
Sodium lignosulfonate	12
Molecularly dehydrated phosphate	3.5
Zinc sulfate monohydrate as Zn	1
2-mercaptobenzothiazole	1.5

Formulation No. 3—	P.p.m. added
Component:	
Sodium chromate as CrO_4	10
"Rayflo" (a modified tannin produced by the method disclosed in U.S. Patent 2,831,022)	12
Molecularly dehydrated phosphate	3.5
Zinc sulfate monohydrate as Zn	1.0
2-mercaptobenzothiazole	1.5

Formulation No. 4—	P.p.m. added
Component:	
Sodium chromate as CrO_4	10
Sodium lignosulfonate	20
Molecularly dehydrated phosphate	3.5
Zinc sulfate monohydrate as Zn	1
2-mercaptobenzothiazole	1.5

Formulation No. 5—	P.p.m. added
Component:	
Sodium chromate as CrO_4	10
"Rayflo" (a modified tannin produced by the method disclosed in U.S. Patent 2,831,022)	20
Molecularly dehydrated phosphate	3.5
Zinc sulfate monohydrate as Zn	1
2-mercaptobenzothiazole	1.5

The results obtained using the subject formulations are set forth in the following table:

TABLE I

Formulation No.	Heat Transfer Tube	
	Corrosion, MPY	Deposit, Total Mg.
1	0.8	276
2	0.8	501
3	0.9	348
4	1.0	545
5	0.9	248

As is apparent from the above table, Formulations 1, 3, and 5 which contain the "Rayflo" modified tannin constitutent have superior activity in reducting the total amount of deposit on the heat transfer tubes. Generally, deposition is highest on heat transfer tubes and obviation of this problem in cooling tower systems is particularly arduous. Moreover, the addition of the "Rayflo" material did not in any way effect the anticorrosive ability imparted by the sodium chromate component. Reliance on sodium lignosulfonate as an organic antifoulant proved to be unsuccessful and resulted in a good deal more deposit being formed upon the heat transfer tube.

Thus, it is evident that use of a combination of chromates and modified tannins provides highly advantageous results in both inhibiting corrosion and fouling of metal surfaces coming in contact with the cooling waters. Only by inclusion of both types of materials it is possible to receive the wanted dual benefits of anti-corrosion and antifoulant activity.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

This invention is hereby claimed as follows:

1. A treated industrial cooling water which comprises a major portion of an industrial cooling water having a tendency to corrode and foul metal surfaces in contact therewith, and a minor portion of a composition present in an amount sufficient to inhibit said tendency, said composition consisting essentially of 10–90% by weight of a water-soluble chromate salt selected from the group consisting of chromate and dichromate salts, and 5–70% by weight of a water-dispersible 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 halobutryrate, ammonium cyanide, an alkali metal cyanide, ammonium thiocyanate, alkali metal thiocyanate, nitric acid and sulfuric acid.

2. A treated industrial cooling water which comprises a major portion of an industrial cooling water having a tendency to corrode and foul metal surfaces in contact therewith, and a minor portion of a composition present in an amount sufficient to inhibit said tendency, said composition consisting essentially of 10–90% by weight of a water-soluble chromate compound selected from the group consisting of chromate and dichromate salts, 5–40% by weight of water-dispersible 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 bisulfite, ammonium sulfite, an 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, and 10–70% by weight of a water-soluble sulfonate compound selected from the group consisting of lignosulfonates and naphthalene sulfonate.

3. A treated industrial cooling water which comprises a major portion of an industrial cooling water having a tendency to corrode and foul metal surfaces in contact therewith, and a minor portion of a composition present in an amount sufficient to inhibit said tendency, said composition consisting essentially of 10–90% by weight of a water-soluble chromate compound selected from the group consisting of chromate and dichromate salts, 5–40% by weight of water-dispersible 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 cynide, an alkali metal cyanide, ammonium thiocyanate, alkali metal thiocyanate, nitric acid and sulfuric acid, 10–70% by weight of a water-soluble sulfonate selected from the group consisting of lignosulfonates and naphthalene sulfonate and 0.5–15% by weight of a water-soluble inorganic metal salt having a polyvalent cation.

4. A treated industrial cooling water which comprises a major portion of an industrial cooling water having a tendency to corrode and foul metal surfaces in contact therewith, and a minor portion of a composition present in an amount sufficient to inhibit said tendency, said composition consisting essentially of 10–90% by weight of a water-soluble chromate selected from the group consisting of chromate and dichromate salts, 5–40% by weight of a water-dispersible 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 alkili metal cyanide, ammonium thiocyanate, alkali metal thiocyanate, nitric acid and sulfuric acid, 10–70% by weight of a water-soluble sulfonate selected from the group consisting of lignosulfonate and naphthalene sulfonate, 0.5–15% by weight of a water-soluble inorganic metal salt having a polyvalent cation, and 0.5–20% by weight of a molecularly dehydrated phosphate compound.

5. A treated industrial cooling water which comprises a major portion of an industrial cooling water having a tendency to corrode and foul metal surfaces in contact therewith, and a minor portion of a composition present in an amount sufficient to inhibit said tendency, said composition consisting essentially of 10–90% by weight of a water-soluble chromate compound selected from the group consisting of chromate and dichromate salts, 5–40% by weight of a water-dispersible natural tannin having been modified by reaction with a material selected from a 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 cynide, an alkali metal cyanide, ammonium thiocyanate, an alkali metal thiocyanate, nitric and sulfuric acid, 10–70% by weight of a water-soluble sulfonate selected from the group consisting of lignosulfonate and water-soluble naphthalene sulfonates, 0.5–15% by weight of a water-soluble inorganic metal salt having a polyvalent cation, 0.5–20% by weight of a molecularly dehydrated phosphate, and 0.1–10% by weight of a nitrogen-containing heterocyclic compound characterized by a ring nitrogen bonded to a ring carbon to which is attached a sulfhydryl group.

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