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PREVENTING CORROSION OF FERROUS METAL SURFACES IN CONTACT WITH WATER

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This invention relates to novel water soluble corrosion inhibitors and to the use therefor in preventing corrosion of metallic surfaces in contact with water.

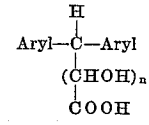
Corrosion of metallic surfaces, particularly iron and steel, in contact with fresh or salt water or various aqueous solutions, results in a serious economic loss. There is an urgent need for, and the present invention provides, improved water soluble corrosion inhibitors which will retard and/or prevent such corrosion.

While the novel inhibitors of the present invention may be used in any system wherein water or aqueous solutions contact metallic surfaces, the following specific examples are set forth as illustrative but not limiting, instances in which the inhibitors of the present invention are useful. Storage tanks, pipe lines, and the like containing petroleum oils and/or other organic compounds generally contain water which causes corrosion of the metallic surfaces. For example, in oil storage tanks the water settles to the bottom and causes corrosion of the internal surface of the storage tank. The water soluble corrosion inhibitors of the present invention will dissolve in the water phase and will serve to retard and/or prevent such corrosion. Another example is in the stamping, rolling, or other working of metal in which a water stream is sprayed thereon or otherwise used as a coolant. Because these operations are effected at high temperatures, the cooling water often causes extensive corrosion. Such corrosion is avoided by incorporating the corrosion inhibitor of the present invention into the water spray. Still another application is in the salt-ice water solutions used as refrigerants, for example, in railroad cars, trucks, etc. When used in railroad cars, the salt solution not only effects corrosion of the railroad cars but also drips onto the rails and causes corrosion thereof. It is readily seen that such corrosion is a serious economic problem because it requires frequent replacement of rails, with concurrent expense both in manpower and in material cost. Still other applications include boiler water, acid solutions such as pickling solutions, etc.

The novel corrosion inhibitors of the present invention are alkali metal salts of aryl-1-desoxy-alduronic acids. The aryl-1-desoxy-alduronic acid utilized in preparing the salt is selected so that the inhibitor molecule as a whole is at least partially water soluble. This will be described further in detail hereinafter in the specification. While not intended to be limited thereby, one explanation of the manner in which the present inhibitors function is that the relatively polar salt linkage serves to attract the inhibitor to the metal surface where the hydrocarbon substituent of the alduronic acid covers the surface and exerts a protective action by keeping water

soluble corrodents away from the metal. The hydroxy groups of the aryl-1-desoxy-alduronic acid render the inhibitor compound at least partially water soluble so that it will penetrate the water film or layer covering the metallic surfaces and thereby will cover and protect the metallic surfaces in the manner hereinbefore set forth.

Any suitable aryl-1-desoxy-alduronic acid may be used in preparing the alkali metal salts thereof and these may comprise the monoaryl-desoxy-alduronic acids, the di-aryl-1-desoxy-alduronic acids, or mixtures thereof. In the preferred embodiment of the invention, these aryl-1-desoxy-alduronic acids are di-aryl-1-desoxy-alduronic acids having the following formula:



in which n is an integer from 1 to about 5 or more. The aryl groups may be unsubstituted or may be substituted by various hydrocarbon radicals such as alkyl, cycloalkyl, aryl, alkaryl, etc.

Illustrative preferred aryl-1-desoxy-alduronic acids for use in preparing the alkali metal salt thereof for use as hereinbefore set forth include the following specific compounds:

1-phenyl-1-desoxy-lyxuronic acid
1,1-di-phenyl-1-desoxy-lyxuronic acid
1-phenyl-1-desoxy-xyluronic acid
1,1-di-phenyl-1-desoxy-xyluronic acid
1-phenyl-1-desoxy-arabinuronic acid
1,1-di-phenyl-1-desoxy-arabinuronic acid
1-phenyl-1-desoxy-riburonic acid
1,1-di-phenyl-1-desoxy-riburonic acid
1-phenyl-1-desoxy-taluronic acid
1,1-di-phenyl-1-desoxy-taluronic acid
1-phenyl-1-desoxy-galacturonic acid
1,1-di-phenyl-1-desoxy-galacturonic acid
1-phenyl-1-desoxy-iduronic acid
1,1-di-phenyl-1-desoxy-iduronic acid
1-phenyl-1-desoxy-guluronic acid
1,1-di-phenyl-1-desoxy-guluronic acid
1-phenyl-1-desoxy-mannuronic acid
1,1-di-phenyl-1-desoxy-mannuronic acid
1-phenyl-1-desoxy-glucuronic acid
1,1-di-phenyl-1-desoxy-glucuronic acid
1-phenyl-1-desoxy-altruronic acid
1,1-di-phenyl-1-desoxy-altruronic acid
1-phenyl-1-desoxy-alluronic acid
1,1-di-phenyl-1-desoxy-alluronic acid
1-p-tolyl-1-desoxy-lyxuronic acid
1,1-di-(p-tolyl)-1-desoxy-lyxuronic acid
1-p-tolyl-1-desoxy-xyluronic acid
1,1-di-(p-tolyl)-1-desoxy-xyluronic acid
1-p-tolyl-1-desoxy-arabinuronic acid
1,1-di-(p-tolyl)-1-desoxy-arabinuronic acid
1-p-tolyl-1-desoxy-riburonic acid
1,1-di-(p-tolyl)-1-desoxy-riburonic acid
1-p-tolyl-1-desoxy-taluronic acid
1,1-di-(p-tolyl)-1-desoxy-taluronic acid
1-p-tolyl-1-desoxy-galacturonic acid
1,1-di-(p-tolyl)-1-desoxy-galacturonic acid
1-p-tolyl-1-desoxy-iduronic acid
1,1-di-(p-tolyl)-1-desoxy-iduronic acid
1-p-tolyl-1-desoxy-guluronic acid

1,1-di-(p-tolyl)-1-desoxy-guluronic acid
1-p-tolyl-1-desoxy-mannuronic acid
1,1-di-(p-tolyl)-1-desoxy-mannuronic acid
1-p-tolyl-1-desoxy-glucuronic acid
1,1-di-(p-tolyl)-1-desoxy-glucuronic acid
1-p-tolyl-1-desoxy-altruronic acid
1,1-di-(p-tolyl)-1-desoxy-altruronic acid
1-p-tolyl-1-desoxy-alluronic acid
1,1-di-(p-tolyl)-1-desoxy-alluronic acid
1-(3,4-dimethylphenyl)-1-desoxy-lyxuronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-lyxuronic acid
1-(3,4-di-methylphenyl)-1-desoxy-xyluronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-xyluronic acid
1-(3,4-dimethylphenyl)-1-desoxy-arabinuronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-arabinuronic acid
1-(3,4-dimethylphenyl)-1-desoxy-riburonic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-riburonic acid
1-(3,4-dimethylphenyl)-1-desoxy-taluronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-taluronic acid
1-(3,4-dimethylphenyl)-1-desoxy-galacturonic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-galacturonic acid
1-(3,4-dimethylphenyl)-1-desoxy-iduronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-iduronic acid
1-(3,4-dimethylphenyl)-1-desoxy-guluronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-guluronic acid
1-(3,4-dimethylphenyl)-1-desoxy-mannuronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-mannuronic acid
1-(3,4-dimethylphenyl)-1-desoxy-glucuronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-glucuronic acid
1-(3,4-dimethylphenyl)-1-desoxy-altruronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-altruronic acid
1-(3,4-dimethylphenyl)-1-desoxy-alluronic acid
1,1-di-(3,4-dimethylphenyl)-1-desoxy-alluronic acid
1p-ethylphenyl-1-desoxy-lyxuronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-lyxuronic acid
1-p-ethylphenyl-1-desoxy-xyluronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-xyluronic acid
1-p-ethylphenyl-1-desoxy-arabinuronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-arabinuronic acid
1-p-ethylphenyl-1-desoxy-riburonic acid
1,1-di-(p-ethylphenyl)-1-desoxy-riburonic acid
1-p-ethylphenyl-1-desoxy-taluronic acid
1,1-di-(p-ethyphenyl)-1-desoxy-taluronic acid
1-p-ethylphenyl-1-desoxy-galacturonic acid
1,1-di-(p-ethylphenyl)-1-desoxy-galacturonic acid
1-p-ethyphenyl-1-desoxy-iduronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-iduronic acid
1-p-ethylphenyl-1-desoxy-guluronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-guluronic acid
1-p-ethylphenyl-1-desoxy-mannuronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-mannuronic acid
1-p-ethylphenyl-1-desoxy-glucuronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-glucuronic acid
1-p-ethylphenyl-1-desoxy-altruronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-altruronic acid
1-p-ethylphenyl-1-desoxy-alluronic acid
1,1-di-(p-ethylphenyl)-1-desoxy-alluronic acid.

It is understood that mixtures of aryl- and diaryl-1-desoxy-alduronic acids may be employed.

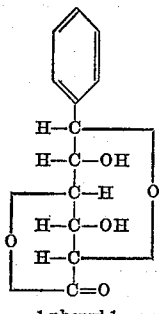
These aryl-1-desoxy-alduronic acids are formed by reacting uronic acids and lactones thereof with aromatic hydrocarbons in the presence of Friedel-Crafts metal halide catalysts, and particularly in the presence of aluminum chloride. These condensation reactions are carried out conveniently in ordinary glass alkylation equipment using temperatures of from about —20° C. to about 150° C., and preferably at temperatures of from about 20° C. to about 100° C. While many of the condensation reactions are carried out at substantially atmospheric pressure, it may be desirable in certain instances and with certain reactants to carry out the reaction in metal autoclaves at pressures up to 100 atmospheres or more. It is convenient in most instances to operate the equipment utilized at the pressure generated by the reaction mixture and catalyst contained therein at the temperature utilized.

Aromatic hydrocarbons suitable for use in preparing aryl-1-desoxy-alduronic acids include compounds containing only carbon and hydrogen and in which there is retained at least one hydrogen atom attached to a carbon atom of the aromatic nucleus. Thus compounds such as hexamethylbenzene cannot be utilized since such compounds are inoperative in preparing aryl-desoxy-alduronic acids. Aromatic hydrocarbons which may be utilized include those substituted with alkyl, aralkyl, aryl, alkaryl, cycloalkyl, alkylcycloalkyl, etc., radicals containing only carbon and hydrogen. Some utilizable aromatic hydrocarbons may contain olefinic unsaturates or double bonds in the side chains or substituent groups containing only carbon and hydrogen, and while such compounds in general may be utilized, they are, however, not preferred. Thus, the preferred aromatic hydrocarbons are unsubstituted aromatic hydrocarbons, and aromatic hydrocarbons containing saturated or aromatic substituents containing only carbon and hydrogen. Utilizable aromatic hydrocarbons include benzene, toluene, ortho-xylene, meta-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenze, penta-methylbenzene, ethylbenzene, ortho-ethyltoluene, meta-ethyltoluene, para-ethyltoluene, n-propylbenzene, isopropylbenzene, n-butylbenzene, isobutylbenzene, sec-butylbenzene, tert-butylbenzene, amylbenzenes, para-cymene, and higher molecular weight alkyl-aromatic hydrocarbons. Also, alkyl-aromatic hydrocarbons with long chain alkyl groups may be utilized. Such compounds are produced by the alkylation of aromatic hydrocarbons with olefin polymers to yield such materials as hexylbenzenes, hexyltoluenes, nonylbenzenes, nonyltoluenes, dodecylbenzenes, dodecyltoluenes, etc. Other aromatic hydrocarbons suitable for use in the preparation of aryl-1-desoxy-alduronic acids include those with two or more aryl groups such as diphenyl, diphenyl methane, triphenyl methane, etc. Examples of suitable utilizable aromatic hydrocarbons which contain condensed benzene rings include naphthalene, alpha-methylnaphthalene, beta-methylnaphthalene, phenanthrene, anthracene, naphthacene, pyrene, chrysene, rubrene, etc. Examples of other aromatic hydrocarbons include indan, fluorene, cyclopentylbenzene, methylcyclopentylbenzene, cyclohexylbenzene, etc.

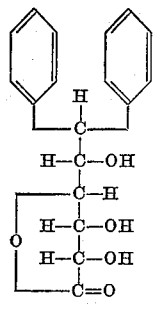
Alduronic acids and lactones thereof which are reacted with the above-mentioned aromatic hydrocarbons in the presence of a Friedel-Crafts metal halide catalyst to produce aryl-1-desoxy-alduronic acids include the alpha and beta forms of riburonic acid, arabinuronic acid, xyluronic acid, lyxuronic acid, alluronic acid, altruronic acid, glucuronic acid, mannuronic acid, guluronic acid, iduronic acid, galacturonic acid, taluronic acid, etc. The alduronic acids are a group of compounds which are obtainable by oxidation of the terminal alcohol groups of aldoses. Suitable lactones of alduronic acids include riburonolactone, arabinuronolactone, xyluronolactone, lyxuronolactone, alluronolactone, altruonolactone, glucuronolactone, mannuronolactone, guluronolactone, iduronolactone, galacturonolactone, taluronolactone, etc. These lactones of alduronic acids are spontaneously formed upon heating suitable alduronic acids in which formation of a 1–4 or gamma-lactone structure is possible, or in which formation of a 1–5 or delta-lactone structure is possible. Since the alduronic acids must contain at least 5 carbon atoms to be able to form gamma-lactones, the sugar acid lactones which may be utilized in preparing aryl-1-desoxy-alduronic acids will contain at least 5 carbon atoms. Sugar acid lactones containing 6 carbon atoms or more may also be utilized. When these uronic acids or lactones thereof react with aromatic hydrocarbons, they do so by reaction at the number 1 carbon atom.

As an example of such a preparation, glucuronolactone

may be reacted with an equimolecular proportion or less of benzene to give 1-phenyl-1-desoxy-glucuronolactone or with more than an equimolecular proportion of benzene to give 1,1-diphenyl-1-desoxy-glucuronolactone. The structures of these lactone reaction products are represented as follows:

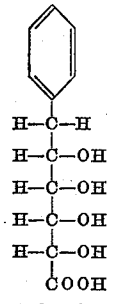


1-phenyl-1-desoxy-glucuronolactone

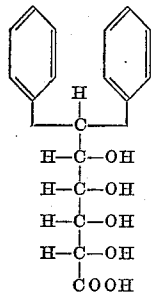


1,1-diphenyl-1-desoxy-glucuronolactone

Hydrolysis of these lactones results in the formation of the respective glucuronic acids of the following structures:



1-phenyl-1-desoxy-glucuronic acid



1,1-diphenyl-1-desoxy-glucuronic acid

This hydrolysis can be carried out in either acidic or basic solutions of the respective lactones.

The reaction of an aromatic hydrocarbon with an alduronic acid or lactone thereof may be carried out, as set forth hereinabove, in the presence of a Friedel-Crafts metal halide catalyst. Friedel-Crafts metal halide catalysts which may be employed are used in substantially anhydrous form or modified by means of an alcohol, an ether, an ester, a nitroparaffin, etc., to give a catalyst of controlled activity, if so desired. The preferred Friedel-Crafts metal halide catalyst is substantially anhydrous aluminum chloride. Other Friedel-Crafts metal halide catalysts which may be utilized but not necessarily with equivalent results are aluminum bromide, ferric chloride, ferric bromide, zinc chloride, beryllium chloride, gallium chloride, titanium tetrachloride, zirconium chloride, stannic chloride, etc.

This reaction may be carried out by slowly adding a Friedel-Crafts metal halide catalyst such as aluminum chloride to a stirred mixture of an aromatic hydrocarbon and an alduronic acid or lactone thereof while maintaining the reaction temperature at from about —20° C. to about 150° C. and preferably at from about 20° C. to about 100° C. After the reaction has reached the desired degree of completion, the entire reaction mixture and catalyst may be mixed with water or may be added to ice in order to quench the activity of the catalyst and to permit separation of the organic reaction product and unreacted starting materials.

As hereinbefore set forth, the alkali metal salts of aryl-1-desoxy-alduronic acids are prepared and utilized in the present invention. Suitable alkali metal salts include those selected from lithium, sodium, potassium, rubidium, and cesium. Of these alkali metal salts, the sodium salts are preferred. Typical sodium salts include the following: the sodium salt of 1-phenyl-1-desoxy-lyxuronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-lyxuronic acid, the sodium salt of 1-phenyl-1-desoxy-xyluronic acid, the

sodium salt of 1,1-di-phenyl-1-desoxy-xyluronic acid, the sodium salt of 1-phenyl-1-desoxy-arabinuronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-arabinuronic acid, the sodium salt of 1-phenyl-1-desoxy-riburonic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-riburonic acid, the sodium salt of 1-phenyl-1-desoxy-taluronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-taluronic acid, the sodium salt of 1-phenyl-1-desoxy-galacturonic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-galacturonic acid, the sodium salt of 1-phenyl-1-desoxy-iduronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-iduronic acid, the sodium salt of 1-phenyl-1-desoxy-guluronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-guluronic acid, the sodium salt of 1-phenyl-1-desoxy-mannuronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-mannuronic acid, the sodium salt of 1-phenyl-1-desoxy-glucuronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-glucuronic acid, the sodium salt of 1-phenyl-1-desoxy-altruronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-altruronic acid, the sodium salt of 1-phenyl-1-desoxy-alluronic acid, the sodium salt of 1,1-di-phenyl-1-desoxy-alluronic acid, the sodium salt of 1-p-tolyl-1-desoxy-lyxuronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-lyxuronic acid, the sodium salt of 1-p-tolyl-1-desoxy-xyluronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-xyluronic acid, the sodium salt of 1-p-tolyl-1-desoxy-arabinuronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-arabinuronic acid, the sodium salt of 1-p-tolyl-1-desoxy-riburonic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-riburonic acid, the sodium salt of 1-p-tolyl-1-desoxy-taluronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-taluronic acid, the sodium salt of 1-p-tolyl-1-desoxy-galacturonic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-galacturonic acid, the sodium salt of 1-p-tolyl-1-desoxy-iduronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-iduronic acid, the sodium salt of 1-p-tolyl-1-desoxy-guluronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-guluronic acid, the sodium salt of 1-p-tolyl-1-desoxy-mannuronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-mannuronic acid, the sodium salt of 1-p-tolyl-1-desoxyglucuronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-glucuronic acid, the sodium salt of 1-p-tolyl-1-desoxy-altruronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-altruronic acid, the sodium salt of 1-p-tolyl-1-desoxy-alluronic acid, the sodium salt of 1,1-di-(p-tolyl)-1-desoxy-alluronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-lyxuronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-lyxuronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-xyluronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-xyluronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-arabinuronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-arabinuronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-riburonic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-riburonic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-taluronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-taluronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-galacturonic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-galacturonic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-iduronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-iduronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-guluronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-guluronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-mannuronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-mannuronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-glucuronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-glucuronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-altruronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-altruronic acid, the sodium salt of 1-(3,4-dimethylphenyl)-1-desoxy-alluronic acid, the sodium salt of 1,1-di-(3,4-dimethylphenyl)-1-desoxy-alluronic acid, the sodium salt of 1-p-

ethylphenyl-1-desoxy-lyxuronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-lyxuronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-xyluronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-xyluronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-arabinuronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-arabinuronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-riburonic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-riburonic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-taluronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-taluronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-galacturonic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-galacturonic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-iduronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-iduronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-guluronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-guluronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-mannuronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-mannuronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-glucuronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-glucuronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-altruronic acid, the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-altruronic acid, the sodium salt of 1-p-ethylphenyl-1-desoxy-alluronic acid, and the sodium salt of 1,1-di-(p-ethylphenyl)-1-desoxy-alluronic acid.

The salt may be prepared in any suitable manner and, in general, is prepared by mixing the aryl-1-desoxy-alduronic acid or lactone thereof and an alcoholic solution of sodium hydroxide or a sodium alcoholate at ambient temperature, preferably with vigorous stiring. The salt is readily prepared at room temperature, although slightly elevated temperatures may be preferred to speed up the reaction, which temperatures will generally not exceed about 100° C. Excessive temperatures should be avoided as the temperature should be kept below that at which dehydration of the alduronic acid occurs and decomposition of the salt occurs. In general, it is preferred to utilize a solvent, either in forming a more fluid mixture of the acid and caustic before mixing or during the mixing thereof, and to absorb the exothermic heat of reaction. Any suitable solvent may be employed. Ethanol and isopropanol are preferred alcohol solvents, although other alcohols including methanol, n-propanol, butanols, pentanols, etc. may be utilized.

As hereinbefore set forth, the salts prepared in the above manner are utilized as water soluble corrosion inhibitors. The salt is incorporated in water, aqueous solutions, or substrates containing water in a sufficient concentration to effectively retard corrosion of metallic surfaces. Generally it will be utilized in a concentration of below about 1 percent by weight of the water, aqueous solution, or substrate containing water, and usually in a concentration within the range of from about 0.001 percent to about 1 percent or more, particularly from about 0.01 percent to about 0.5 percent by weight thereof, although higher concentrations may be utilized when excessive corrosion is encountered. It is understood that the corrosion inhibitor may be used in conjunction with other additives which are incorporated in the substrate for various reasons.

The following examples are introduced to illustrate further the novelty and utility of the present invention but with no intention of unduly limiting the same.

EXAMPLE I

In a one-liter alkylation flask with a mercury sealed stirrer and reflux condenser, the following were contacted 4 hours at 70–80° C.:

Glucuronolactone	grams	25
$AlCl_3$	do	93
Benzene	cc	300

During the contacting, 29 grams of HCl were evolved. The flask contents were decomposed with ice and the following recovery noted exclusive of unreacted benzene:

	Grams
Hydrocarbon soluble oil	4.2
Water washed, cold water insoluble solid (A)	54

Segment (A) was boiled with caustic solution, the insoluble part filtered off; the filtrate acidified, throwing down precipitate (B); the filtrate from (B) was ether extracted to give solid (C).

Pure compounds isolated

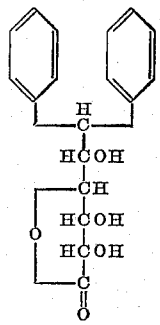
(1) $C_{18}H_{18}O_5$

Segment (B) contained 12 grams of a component, (1), insoluble in cold water and crystallizing from hot water in needles forming star clusters. Dried on a filter paper, these crystals showed a slight yellow sheen, and melted at 178–180° C. These crystals dissolved immediately in NaOH solution but in concentrated solution separated immediately as a sodium salt in the form of short needles melting at 205–210° C. with decomposition. The sodium salt dissolved when diluted with water; when this solution was acidified, no immediate precipitation occurred, but in 2 to 3 days, needles came out melting at 179–180° C., identical to the original. The compound burned with difficulty and difficulty was observed in carbon and hydrogen analysis in obtaining complete combustion.

Elementary analysis of (1)

	Percent C	Percent H
Found	68.00 68.21	5.95 5.93
Calc. for $C_{18}H_{18}O_5$	68.78	5.77

Thus, elementary analysis and chemical behavior of product (1) are in accord with 1,1-di-phenyl-1-desoxy-glucuronolactone:



(1)

1,1-diphenyl-1-desoxy-hexuronolactone

Glucuronolactone does not exist as the free acid, and the lactone structure apparently went through the reaction and subsequent water recrystallizations unchanged.

(2) $C_{18}H_{20}O_6$

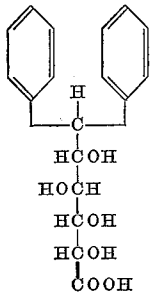
Segment (C) crystallized from ether to crystals, designated (2), of melting point 138–139° C. This product had a fatty acid odor and gave a foamy solution in water. Like compound (1), it burned with difficulty.

Analysis

	Percent C	Percent H
Found for (2)	64.25	6.01
Calc. for $C_{18}H_{20}O_6$	65.05	6.06

The yield of compound (2) could not be evaluated from the data available; its yield, however, was substan-

tially less than that of (1). On the basis of analysis, chemical behavior, and fatty acid odor, (2) corresponds to the free acid of which (1) is the lactone.



(2)

1,1-di-phenyl-1-desoxy-hexuronic acid

EXAMPLE II

The sodium salt of compound 1, as described in Example I, was prepared by reaction of 1,1-di-phenyl-1-desoxy-glucuronolactone with an ethanolic solution of sodium hydroxide. The sodium salt is a solid and was recovered by filtration. This sodium salt was tested as a corrosion inhibitor in 300 cc. of a 5% sodium chloride solution. The concentration of this sodium salt of 1,1-di-phenyl-1-desoxy-glucuronic acid utilized was 0.05 weight percent in the sodium chloride solution.

The corrosion inhibitor was evaluated by adding the 300 cc. of 5% sodium chloride solution containing 0.05% of the inhibitor into a 600 cc. beaker which was stirred at 250 r.p.m. and air bubbled therethrough at a rate of 5.6 liters per hour. On the bottom of the beaker in contact with the brine solution was a mild steel strip one end of which was elevated by a glass rod. Stirring and air introduction was continued for 6 hours' time. At the same time a duplicate experiment was carried out with no added corrosion inhibitor in the brine solution. The iron strip in the blank or control experiment lost 22 milligrams in weight during the run in comparison to a weight loss of 7.5 milligrams for the iron strip in contact with the brine solution and the sodium salt of 1,1-di-phenyl-1-desoxy-glucuronic acid.

These experiments show that 1,1-di-phenyl-1-desoxy-glucuronic acid in the form of its sodium salt is equivalent to or slightly better than sodium nitrite, a well known corrosion inhibitor. The addition of the same concentration of sodium nitrite to a brine solution results in a weight loss of 8 milligrams in a comparable corrosion test. Water soluble corrosion inhibitors for brine solutions are particularly important for use by railroads since brine which drips from refrigerator cars causes serious corrosion of railroad tracks. Also, water soluble corrosion inhibitors are important in other diverse uses such as in boiler water, etc.

We claim as our invention:

1. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising an alkali metal salt of an aryl-1-desoxy-alduronic acid.

2. A method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising an alkali metal salt of a monoaryl-1-desoxy-alduronic acid.

3. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising an alkali metal salt of a diaryl-1-desoxy-alduronic acid.

4. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the sodium salt of a monoaryl-1-desoxy-alduronic acid.

5. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the sodium salt of a diaryl-1-desoxy-alduronic acid.

6. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the sodium salt of a monoaryl-1-desoxy-glucuronic acid.

7. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the sodium salt of a diaryl-1-desoxy-glucuronic acid.

8. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the sodium salt of 1-phenyl-1-desoxy-glucuronic acid.

9. The method of retarding corrosion of a ferrous metal upon contact with water which comprises effecting said contact in the presence of a water soluble corrosion inhibitor comprising the sodium salt of 1,1-diphenyl-1-desoxy-glucuronic acid.

References Cited in the file of this patent

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