Examiner

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UNITED STATES PATENT OFFICE

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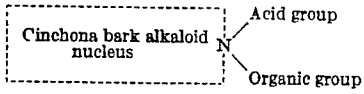
INHIBITOR

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16 Claims. (Cl. 148—8)

This invention relates to the modification of the action of acids upon metals, and is particularly directed to processes and compositions which employ, in conjunction with an acid, an inhibitor represented herein by the following:

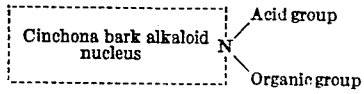


Pickling and metal cleaning operations frequently involve the use of a bath of dilute non-oxidizing acids such as sulfuric, hydrochloric, acetic, formic, aqueous solutions of acid sulfates, and the like. Such baths are used for numerous purposes, a typical example of which is the pickling of iron or steel articles such as wire, sheet, and other manufactures. The composition, concentration, temperature of operation, and other factors vary with different baths, but in every instance the primary function of a bath is the removal of undesirable incrustations. As soon as the base metal becomes exposed, it is, in the absence of an inhibitor, attacked by the bath with consequent damage to the article and with an unnecessary consumption of acid.

The application of my invention to acid pickling and acid metal cleaning operations invalves no change in the customary baths and processes, except for the addition of a small amount of an inhibitor of this invention. In quantities as small as about one-hundredth of one per cent, my novel inhibitors will check the attack of acid on metal. I usually prefer to employ between about two-hundredths of one per cent and one-tenth of one per cent of one of my inhibitors, but more or less may be used if desired.

While the inhibitors of this application are primarily adapted for use in metal pickling and cleaning processes, they may, of course, be used in numerous other relations as are the inhibitors already known to the art.

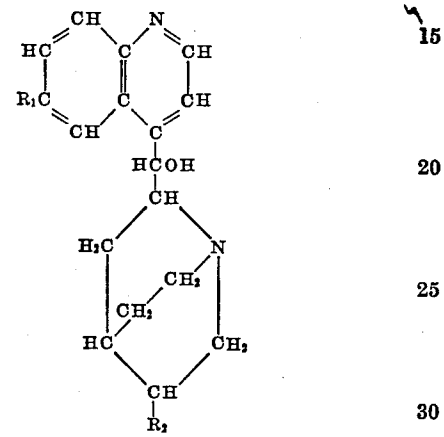
The inhibitors of this invention are derivatives of cinchona bark alkaloids of the formula:



My preferred inhibitors are prepared, generally speaking, by reacting a cinchona bark alkaloid with a hydrocarbon, a hydrogen of which is substituted by an acid group.

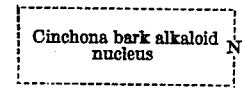
Typical of the cinchona bark alkaloids are quinine, quinidine, and cinchonine. Quinoidine, the by-product of the extraction of the medicinal alkaloids from the cinchona bark, is particularly suitable for my purposes.

The cinchona bark alkaloids, sometimes termed quinine alkaloids, are very complicated in their chemical character, and their exact molecular configuration is not well understood. It is generally believed that the compounds making up the cinchona bark alkaloids are characterized by the presence of two ternary nitrogen atoms one of which is bonded to two carbon atoms, and the other of which is bonded to three different carbon atoms. The formula ordinarily ascribed to the cinchona bark alkaloids is as follows:



In the above formula, R_1 is OCH_3 and R_2 is—$CH{:}CH_2$ in quinine. In cinchonine R_1 is H, and R_2 is—$CH{:}CH_2$.

For the purposes of this application, this complex generic formula which represents a cinchona bark alkaloid nucleus will be written as follows:



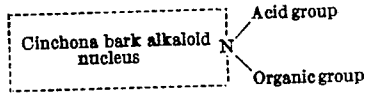
It will be observed that in this formula nitrogen is represented because it is believed that the compounds of this invention are prepared by the reaction with one or more of the nitrogens in the nucleus.

When the cinchona bark alkaloid nucleus is reacted with a hydrocarbon having an acid radical substituted for one hydrogen, I believe that the acid radical adds on to a nitrogen, and the organic group also adds on, thus producing a quaternary compound. The addition may take place at either nitrogen, or, as there are two nitrogen atoms, two molecules of alkyl halide or the like may react with one molecule of cinchona

bark alkaloid. While the organic group is preferably a hydrocarbon group, as above explained, it may be another alkyl or alkoxy group or it may be an aralkyl or aryl group.

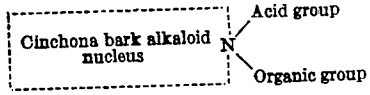
The preferred inhibitors of this invention are derived from quinoidine. Quinoidine, it is believed, is a mixture of a number of compounds which are characterized by the presence of two nitrogen atoms in a configuration like that above shown for the cinchona bark alkaloids generally. When a nitrogen of quinoidine has added thereto an acid group and an organic group, the resulting compound is a quaternary ammonium compound. That is to say, it may be regarded as a derivative of NH_4OH wherein the OH group and the four hydrogens have all been replaced. Such a compound, by analogy with pyridinium compounds, may be termed a quinoidinium compound.

Inhibitors of the formula:



are preferably made by reacting a cinchona bark alkaloid with a hydrocarbon, a hydrogen of which is substituted by an acid radical. The cinchona bark alkaloids may be reacted, for instance, with benzyl chloride, benzyl bromide, benzyl thiocyanate, and the like. As further examples of materials to react with cinchona bark alkaloids to produce the inhibitors of this invention, there may be mentioned chlorides produced from higher aliphatic alcohols. Crude octyl chloride, for instance, may be produced admixed with other chlorides from a commercial mixture of aliphatic alcohols containing from six to ten carbon atoms, octyl alcohol being present in major proportions, and a similar halide, crude dodecyl chloride, may be prepared from crude dodecyl alcohol, the crude material containing alcohols ranging from eight to fourteen carbon atoms.

Inhibitors of the formula:



may also be prepared by reacting a cinchona bark alkaloid with such compounds as benzoyl chloride, benzoyl thiocyanate, dichloro-diethyl ether, dialkyl sulfates such as dimethyl sulfate, alkyl sulfonates such as lauryl para-toluene sulfonate, dihalogen alkyl compounds such as ethylene dichloride, and the like. Other acid radicals than those listed above may, of course, be used if desired.

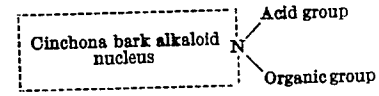
The cinchona bark alkaloid nucleus may be modified in various ways providing that the molecular configuration remains substantially unchanged. That is, the modification should not alter the carbon-nitrogen ring structure. For instance, the cinchona bark alkaloids may be sulfurized before their treatment with chlorides and the like. Such modification of the nucleus may also be made after the reaction of the cinchona bark alkaloids with chlorides and the like.

It will be understood that the exact molecular configurations of the cinchona bark alkaloids and their derivatives are not known, and I do not intend to be in any way limited by the theory and terminology herein adopted for purposes of illustration and definition.

In order that my invention may be more fully understood, reference should be had to the following examples.

Example I

An inhibitor of the formula:



was prepared by refluxing equimolecular proportions of quinoidine and crude octyl chloride for three hours. For purposes of determining the proportions of reactants, quinoidine was considered as having the same molecular weight as quinine. Specifically, there was used 32.4 parts of quinoidine and 14.9 parts of octyl chloride by weight. The quinoidinium chloride thus prepared was a red-brown brittle solid.

The octyl quinoidinium salt inhibitor of this example was used at a concentration of 0.005% based on the weight of a 5% sulfuric acid pickling bath. The inhibitor reduced the rate of corrosion of the bath on a steel plate about 98.7%.

Example II

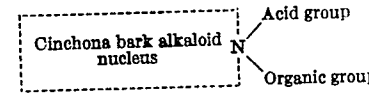
Benzyl quinoidinium chloride was prepared according to the procedure of Example I by reacting 32.4 parts of quinoidine with 12.7 parts of benzyl chloride by weight. The product was a red-brown brittle solid. A pickling bath containing 5% sulfuric acid and 0.005% of benzyl quinoidinium chloride was tested, and it was found that the inhibitor of this example reduced the rate of corrosion about 99%.

Example III

Benzyl quinoidinium bromide was prepared following the procedure of Example I by reacting 32.4 parts of quinoidine and 17.1 parts of benzyl bromide by weight. The product was a black, brittle solid which, when used at a concentration of 0.005% by weight reduced the rate of attack of a 5% sulfuric acid pickling bath by about 98.3%.

Example IV

An inhibitor of the formula:



was prepared by adding 16 parts by weight of benzoyl chloride to 20 parts by weight of finely ground sulfurized quinoidine. After the benzoyl chloride soaked through the sulfurized quinoidine, the mixture was heated gently until it became plastic and began to bubble. The mixture was allowed to cool and the product was a hard, brittle, black vitreous mass with a glistening fracture. After a few days the product became slightly softer.

To a pickling bath containing 5% H_2SO_4 there was added 0.005% by weight of the inhibitor of this example. The inhibitor was not readily soluble, but it reduced the rate of corrosion about 93.6%. To aid solution of the inhibitor, it was again tried in the same amount in a pickling bath, but before adding it to the bath it was dissolved in hot 60° H_2SO_4. After thus dissolving the inhibitor, it reduced the rate of corrosion about 96.5%.

Example V

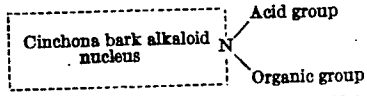
The novel compounds of this invention may be prepared in numerous ways. A composition similar to that of Example I was prepared by mixing 64.8 parts of quinoidine with 45.7 parts of crude dodecyl chloride and stirring the mixture for six

hours at 140–150° C. The alkyl quinoidinium chloride thus prepared was a dark-colored solid soluble in ethyl alcohol.

Proceeding in a somewhat different manner and using a solvent, 64.7 parts of quinoidine, 45.7 parts of crude dodecyl chloride, and 100 parts of methyl alcohol were refluxed for seventy-two hours. After removal of the alcohol by evaporation, a dark-colored solid was obtained.

Conducting the reaction under pressure to shorten the time and following a still different procedure, 64.8 parts of quinoidine, 21.9 parts of crude dodecyl chloride, and 100 parts of methyl alcohol were heated in a closed vessel for eight hours at 150° C. After evaporation of the alcohol, a compound similar to those above was obtained.

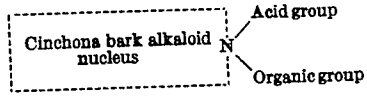
While I have shown a number of specific compositions and procedures in the foregoing, it will be understood that I do not intend to be limited thereby as one skilled in the art may readily produce a number of compounds of the type herein designated by the formula:



without departing from the spirit of this invention, and may use them in various baths and in widely varying amounts.

I claim:

1. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an inhibitor of the formula:



2. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an inhibitor comprising a reaction product of a cinchona bark alkaloid with a hydrocarbon, one hydrogen of which is substituted by an acid group.

3. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an inhibitor comprising a reaction product of quinoidine with a hydrocarbon, one hydrogen of which is substituted by an acid group.

4. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an alkyl quinoidinium salt.

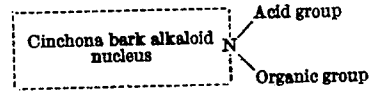
5. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an aralkyl quinoidinium salt.

6. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an inhibitor comprising an alkyl quinoidinium chloride.

7. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an inhibitor comprising an aralkyl quinoidinium chloride.

8. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of an inhibitor comprising a reaction product of sulfurized quinoidine with a hydrocarbon, one hydrogen of which is substituted by an acid group.

9. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor of the formula:



10. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor comprising a reaction product of a cinchona bark alkaloid with a hydrocarbon, one hydrogen of which is substituted by an acid group.

11. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor comprising the reaction product of quinoidine with a hydrocarbon, one hydrogen of which is substituted by an acid group.

12. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor composition comprising an alkyl quinoidinium salt.

13. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor composition comprising an aralkyl quinoidinium salt.

14. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor composition comprising an alkyl quinoidinium chloride.

15. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor composition comprising an aralkyl quinoidinium chloride.

16. A pickling and cleaning composition for metals comprising a non-oxidizing acid and an inhibitor comprising the reaction product of sulfurized quinoidine and a hydrocarbon, one hydrogen of which is substituted by an acid group.

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