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PICKLING COMPOUND AND METHOD OF MAKING AND USING SAME

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This invention relates to the art of pickling metals for the removal of oxides and rust and particularly to pickling baths and corrosion inhibitors, and to processes of making and using the same.

Pickling solutions for removing oxides from the surface of metals ordinarily consist very largely of a dilute solution of an inorganic acid such as sulfuric or hydrochloric acid. The acid, although it dissolves the oxides and scale, also attacks the metal to some extent so that the acid is largely consumed and a certain amount of metal is lost. It also appears that the hydrogen liberated by the action of the acid on the metal has a serious embrittling effect upon the metal being treated. For these reasons, inhibitors are commonly employed in such solutions to decrease the activity of the acid with respect to the metal without greatly affecting the solvent action of the solution with respect to the oxides.

Many different materials have been employed for this purpose. It has been suggested that crude anthracene and acid extracts of anthracene oil residues with mineral acids be employed for this purpose. It is known that certain compounds of nitrogen, such as the heterocyclic compounds, e. g. compounds contained in commercial pyridine, quinoline, and acridine, are effective as inhibitors in acid pickling baths. On the other hand, these compounds while lowering the rate of dissolution of metal by means of the acid, are known to present many disadvantages in the art. For instance, it is generally known that the rate of scale removal increases as the pickling bath temperature increases but the efficiency of pickling compounds of the above type in general use decreases rapidly as the temperature of the bath is raised.

It is an object of the present invention to overcome the disadvantages now known in the art by means of the new and improved process, inhibitor, and bath for pickling metals. A further object of this invention is to provide a means for reducing the metal losses in acid pickling to a minimum and to prepare a bath which can be used at high temperatures without the loss of the valuable properties of the corrosion inhibitor, thus effecting economies in time and savings in materials. Other objects of the invention will in part be obvious and will in part appear hereinafter.

My invention accordingly comprises a composition of matter active as a corrosion inhibitor in the acid pickling of metals, and a process for producing such a composition of matter. My invention comprises, further, an acid pickling bath comprising a corrosion inhibitor and a process of pickling metals by means of such a bath. The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the product possessing the features, properties, and the relation of constituents, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

The corrosion inhibitor of my invention comprises the product of the reaction between a compound containing a carbon nitrogen ring and an organic ester of a hydrohalic acid, said ester comprising an aromatic residue, for example, an aromatic-substituted aliphatic halide, and an organic nitrogen base containing a nucleus in which several carbon atoms are directly linked to a nitrogen atom.

The nitrogen bases employed in practicing my invention may include among others that class of nitrogen compounds known as organic nitrogen bases, particularly nitrogen heterocyclic bases, or more specifically those polyatomic-carbon heterocyclic compounds containing one or more trivalent nitrogen atoms in the heterocyclic nucleus. For example, I may use pyridines, quinolines, acridines, and derivatives of these compounds, or similar compounds or mixtures of these, or commercial materials in which such compounds are present, such as denaturing or flotation pyridines, bone oils, etc. which I denominate collectively hereinafter as pyridine bases.

For instance, I have prepared efficient inhibitors using a crude pyridine base fraction, obtained from coal tar distillates, which was characterized by the following boiling range at atmospheric pressure (100 c. c. sample):

Start:	217° C.	
5 cc.	227° C.	
20 cc.	250° C.	
40 cc.	262° C.	
60 cc.	289° C.	
80 cc.	346° C.	
82 cc.	346° C.	Decomposed

I have likewise made efficient inhibitors with bases derived from the above sample by fractional distillation under reduced pressure; of the different fractions thus obtained under 13 mm. pressure, I would prefer to use those distillates cut in the ranges of 105° to 125° C. and 185° to 240° C., but the use of other fractions or of crude materials is within the scope of my invention.

As examples of the organic esters of inorganic

acids which are effective in producing, by reaction with the nitrogen bases above referred to, a corrosion inhibitor of the desired properties, may be cited organic sulfonates and organic halides and in particular such compounds as the phenyl methyl halides, such as benzylchloride, benzalchloride, benzotrichloride, benzylbromide, etc.; phenyl ethyl halides, such as phenyl ethyl chloride, phenyl ethyl bromide, etc.; substituted phenyl alkyl halides such as orthochlorbenzyl chloride, para-nitrobenzyl bromide, etc.; benzoyl halides, such as benzoyl chloride, benzoyl bromide, m-nitrobenzoyl chloride, para nitrobenzoyl chloride, etc.; halogen substituted ketones of the aryl-alkyl series, such as chloroacetophenone ($CH_2Cl.CO.C_6H_5$). I may use compounds of the general type whose aromatic nucleus consists of one or more carbocyclic or heterocylic rings with or without substitutents such as —NH_2 or —NH—, —NO_2, —HSO_3, —Cl, —Br, —I, —CN, —OH, etc. and whose aliphatic chain contains one or more carbon atoms to which one or more halogen atoms are attached, which aliphatic chain may be partially or completely saturated with hydrogen or oxygen atoms.

As an example of the preferred modification of my invention, the inhibitor may be made in the following manner: Add about 38 grams of phenyl methyl chloride to 100 grams of high-boiling pyridine bases and heat the mixture, under a reflux condenser, to about 130° C.; the reaction will occur with evolution of heat and the temperature of the mixture will rise to about 160° to 170° C. Maintain this temperature for about one-half hour, or longer if convenient. Then allow the mixture to cool to a temperature of about 75° to 100° C., (depending on the solvent chosen), and add one of the following solvents, namely:

1. 160 cc. of denatured alcohol, or
2. 160 cc. of high-boiling pyridine bases, or
3. 145 cc. of 36% hydrochloric acid, or
4. 15 cc. of alcohol and 130 cc. of hydrochloric acid, or
5. 15 cc. of pyridine bases and 130 cc. of hydrochloric acid.

After adding the solvent, agitate the warm mixture until the reaction product is dissolved. The resulting solution constitutes one form of my new corrosion inhibitor. The last solvent listed, No. 5, (pyridine bases and hydrochloric acid) gave the best results, and is my preferred solvent.

Solutions of the reaction products above described have been found to deposit tarry matter under certain conditions in the pickling bath. Where this is likely to occur, such deposition may be obviated by diluting the inhibitor solution, made as described above, with approximately an equal volume of water, allowing the mixture to stand, and decanting the clear liquid from precipitated tarry matter. Such a solution, when added to a pickling bath deposited little or no tar.

Instead of precipitating the tarry matter by diluting the prepared solution, the solution may be prepared by employing a more dilute solvent. This method is not as advantageous as the method wherein the prepared solution is subsequently diluted, however, and such is the preferred method.

This treatment applied to inhibitor made with solvent No. 5 above, is particularly effective. In this case the diluted solution contains as the solvent a hydrochloric acid solution of about 20% concentration or less containing pyridine bases.

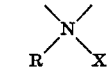
Another effective inhibitor preparation may, however, be made as follows:

The product of the example, comprising the reaction product of 38 grams benzyl chloride and 100 grams pyridine bases, is dissolved in 160 cc. of 40% sulfuric acid. 100 volumes of this solution are diluted with 75 volumes of water, and the mixture allowed to stand until the supernatant liquid, which is a solution of the inhibitor in an H_2SO_4 solution of about 26% concentration is clear. The latter is decanted and constitutes a satisfactory inhibitor.

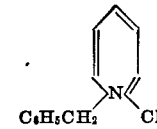
The nature of the solvent chosen to dissolve the reaction product, as the final step in the preparation of the inhibitor, has an effect on the latter's efficiency. I have found that aromatic nitrogen bases, such as crude commercial pyridines, and denatured or methyl alcohol are excellent solvents for the reaction product, also I have made inhibitors of high efficiency for certain types of steel by dissolving the reaction product in strong hydrochloric acid (about 22° Baumé). And so it will be understood that alcohol or hydrochloric acid, or so-called pyridine bases may be used, singly or in mixtures, as a solvent but that the invention is not necessarily restricted to these materials.

In the process of making the inhibitor, the procedure may be varied considerably, as different starting materials are selected for the reaction and different solvents for solution of the reaction product. I have found that the reaction may be conducted between the temperature limits of about 120° and 200° C., that the proportion of the organic ester of an inorganic acid to aromatic nitrogen base may be varied from the ratio of about one mol of the former to 3 mols of the latter to about equimolar proportions, and that the quantity of solvent chosen may vary between the limits of about 1.0 to about 5.0 times the weight of the reaction product.

While the exact constitution of the product of the above process has not been determined, I believe the composition comprises substantially an organic nitronium salt. In its preferred form the product comprises substantially an aralkyl nitronium salt in which the nitrogen is a member of a polycarbon heterocyclic nucleus and in which the aralkyl group is directly united to the nitrogen of the nucleus, i. e., all the compounds of this class contain the following general group—



in which R is an aralkyl radical and X is a halogen radical. By the term "aralkyl" as used herein is meant an alkyl group containing an aryl substituent. In the aralkyl radical the aliphatic residue may be a monotomic or polyatomic chain and the aromatic substituent may comprise a monocyclic or polycyclic radical. When benzyl-chloride and pyridine are treated in the process as described, the product of the reaction is believed to consist substantially of benzyl-pyridinium-chloride, which corresponds to the following probable formula:



Likewise by choice of suitable reagents, aralkyl

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quinolinium or acridinium halides may be produced.

As an example of the pickling baths which are suitable for pickling iron and steel, I may use a bath containing 5% of sulfuric acid in which has been dissolved about .1% of the product of the reaction of benzylchloride and pyridine. The corrosion inhibitor may be added to the bath either alone or in solution in alcohol, pyridine, or a mineral acid or in solution in a mixture of these solvents. Instead of sulfuric acid, other mineral acids capable of dissolving iron oxides may be used and instead of the product of the reaction of benzylchloride and pyridine, any one or more of the reaction products herein defined as coming under my invention may be used as the corrosion inhibitor. If iron or steel be placed in such a bath, it will be found that iron oxides, rust or those compounds collectively known as scale will be quickly and substantially completely removed from the metal and that only a very small amount of the metal will be lost by solution in the bath. Since little or no hydrogen is produced when the action of the acid on the metal is inhibited, the amount of obnoxious acid vapor carried away by escaping hydrogen will be materially decreased. Furthermore, the corrosion inhibitor prepared under my invention may be used in baths at temperatures in excess of those commonly employed in the art without a substantial loss in the efficiency of the inhibitor, thus making a great saving in time of treatment.

Since certain changes in carrying out the above process, and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

The advantages of my invention in the pickling art may be summarized as the reduction of metal losses, reduction in acid consumption per ton of metal due to action of the inhibitor, reduction in time of treatment, and prevention of formation of obnoxious acid fumes.

I claim:

1. A corrosion inhibitor comprising the product of the reaction between a pyridine compound and benzyl chloride.

2. A corrosion inhibitor comprising the product of the reaction between from 1 to 3 mols of pyridine and one mol. of benzyl chloride, and a solvent for said reaction product.

3. A corrosion inhibitor comprising benzyl pyridinium chloride and a solvent for said chloride.

4. The process of making a corrosion inhibitor which comprises mixing from 1 to 3 mols of pyridine and one mol. of benzyl chloride, heating the mixture and allowing the temperature to rise to 160° to 170° C., maintaining this temperature for a limited period of time, cooling the product of the reaction to a temperature between 75° and 100° C., and dissolving the said product in a solvent.

5. A pickling bath comprising a dilute solution of a mineral acid and a corrosion inhibitor, said inhibitor comprising the product of the reaction between from 1 to 3 mols of pyridine bases and one mol. of benzyl chloride, and a solvent for said reaction product.

6. A pickling bath comprising a dilute solution of a mineral acid and a corrosion inhibitor, said inhibitor comprising benzyl pyridinium chloride, and a solvent for said chloride.

7. The process of pickling metals which comprises subjecting the metal to the action of a bath containing a dilute solution of a mineral acid and a corrosion inhibitor, said inhibitor comprising the product of the reaction between from 1 to 3 mols. of pyridine bases and one mol. of benzyl chloride.

8. A corrosion inhibitor obtainable by reacting from 1 to 3 mols. of high boiling pyridine bases with 1 mol. of benzyl chloride, dissolving the reaction product in a solvent comprising a pyridine base and an aqueous hydrochloric acid to obtain a solution of the reaction product, the aqueous hydrochloric acid solution present comprising not substantially less than about 80 per cent water, and removing tarry matter from the solution.

9. A corrosion inhibitor obtainable by reacting from 1 to 3 mols of high boiling pyridine bases with one mol. of benzyl chloride, dissolving the reaction product in a solvent comprising a pyridine base and an aqueous hydrochloric acid of about 36 per cent concentration, diluting the solution with water, and removing from the solution precipitated tarry matter.

10. A corrosion inhibitor obtainable by reacting benzyl chloride and a pyridine base, dissolving the reaction product to obtain an aqueous sulfuric acid solution of the reaction product, the solvent containing not less than about 75 per cent water, and separating tarry matter from the solution.

11. A corrosion inhibitor obtainable by reacting benzyl chloride and a pyridine base, dissolving the reaction product in aqueous sulfuric acid of about 40 per cent concentration, diluting the solution thus formed with water, and separating precipitated matter from the solution.

12. A corrosion inhibitor comprising the product of the reaction between a pyridine base and an aralkyl ester of an inorganic acid.

13. A corrosion inhibitor comprising the product of the reaction between a pyridine base and an aralkyl halide.

14. A corrosion inhibitor comprising the reaction product of a crude high boiling distillate fraction of coal tar bases with an aralkyl halide.

15. A corrosion inhibitor comprising a coal tar base distillate fraction having a boiling range for the major portion of its constituents within the range 217° to 346° C., and an aralkyl halide.

16. The method of inhibiting corrosion of a metal in an acid bath, which comprises providing in the bath as a corrosion inhibitor the product of reaction between a pyridine base and an aralkyl halide.

17. The method of inhibiting corrosion of a metal in an acid bath, which comprises providing in the bath as a corrosion inhibitor the product of the reaction between a crude high boiling distillate fraction of coal tar bases with an aralkyl halide.

18. The process for pickling a metal, which comprises subjecting the metal to the action of a dilute inorganic acid bath containing the reaction product of a crude high boiling distillate fraction of coal tar bases with an aralkyl halide.

19. The process for pickling a metal, which comprises subjecting the metal to the action of a dilute inorganic acid bath containing as a corrosion inhibitor the reaction product of an aralkyl halide and a coal tar base distillate fraction having a boiling range for the major portion of its constituents somewhere within the range 217° to 346° C. and an aralkyl halide.

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