01 252/101

Patented Feb. 25, 1930 1,748,494

UNITED STATES PATENT OFFICE

PAUL I. MURRILL, OF SOUTH NORWALK, CONNECTICUT, ASSIGNOR TO R. T. VANDERBILT COMPANY, INCORPORATED, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK

PICKLING AND CLEANING OF METALS

No Drawing. Application filed May 2, 1929. Serial No. 360,003.

This invention relates to the cleaning and pickling of metals. It includes both a new cleaning and pickling bath and the method of employing the same in cleaning and pickling metals. The invention is for more or less general application in the cleaning and pickling of metals, for example iron, steel, alloy steels, and nonferrous metals and alloys, for example nickel and Monel metal.

The pickling or cleaning of iron or steel is commonly effected by means of acid pickling or cleaning baths which remove the scale or oxide from the metal. The pickling baths commonly employed are acid baths, e. g. sulfuric or hydrochloric acid baths, which often attack the metal as well as the scale. This action on the metal is undersirable and objectionable, involving not only excessive consumption of acids, but also corrosion or dissolving of the metal and tending to give a rough or pitted surface.

Many of the operations for the pickling and cleaning of non-ferrous metals and alloys and of certain alloy steels, (for example nickel, Monel metal, nickel steel, chrome steel, etc.) involve the use of acid baths containing nitric acid as one of its constituents. So far as I am aware, the inhibitors heretofore used in pickling baths for ferrous metals are useless in the presence of nitric acid for the reason that they are either oxidized, nitrated, or otherwise changed so that their inhibiting action is destroyed and the inhibiting material thus rendered useless.

The present invention provides inhibitors which are not appreciably oxidized or nitrated by acid cleaning and pickling baths comprising nitric acid of the concentration ordinarily used in such baths. These inhibitors may be used to advantage in such baths and in baths comprising both nitric and sulfuric acids without being rendered inert and useless.

According to this invention, an inhibitor is employed in the acid cleaning or pickling bath. The inhibitor employed is an alkylene dibasic compound, each of the two basic nuclei of the compound of which is a nitrogenous heterocyclic nucleus joined to the alkylene chain thru the nitrogen atom of said nucleus.

The inhibitor may be a base, or the halide or another salt thereof. Where a halide or other salt is employed, the halogen or other acid ion in the salt is almost negligible in quantity and when dissolved in the acid bath is probably replaced by the salt of the acid present. Where for example a chloride of an alkylene dipyridonium compound is employed in a sulfuric acid bath the inhibitor will probably be present in the final bath as a sulfate, due to the action of the sulfuric acid of the bath on the chloride. Results so far indicate that the inhibiting effect is the same whether a free base or a salt is employed as the inhibitor. Whatever the reaction which may occur when the inhibitor is added to the acid bath I do not desire to be limited in any way by the theory here set forth.

The agents which may be added to the cleaning or picking bath, according to this invention, include various alkylene dipyridonium compounds, their homologues and derivatives. They may be the bases or halides or other salts of these bases. The halide derivatives may be made by combining a heterocyclic base such as pyridine with an alkylene di-halide such as ethylene dichloride. The resulting compound is believed to be a bis-quarternary-ammonium salt which may be represented by the following formula:

$$\begin{matrix} RN-C_nH_{2n}-NR \\ | \quad\quad | \\ X \quad\quad X \end{matrix}$$

In this formula R N represents a heterocyclic base and X represents a halide or other acid radical. In this manner, ethylene dipyridonium dichloride may be formed from ethylene dichloride and pyridine; ethylene diquinoline dichloride may be formed from ethylene dichloride and quinoline; and ethylene diquinoline dibromide may be formed from ethylene dibromide and quinoline. The base may be employed instead of the salt indicated by this formula.

The compounds produced by reacting the heterocyclic base with the alkylene dihalide may be purified by crystallization or may be

101

added directly to the pickling bath without previous purification. They are freely soluble in water and in acids and since they are used in relatively small quantities, they may be conveniently prepared as aqueous solutions of standard concentration which may be readily added to the pickling or cleaning bath in the amount desired.

The amount of inhibitor added to the bath may be varied. In general only a small amount of an alkylene dipyridonium compound is required, for example 1% or less. The following examples are illustrative of the invention, but it is to be understood that the invention is not limited thereto.

A bath of 10% sulfuric acid with or without a small amount of an alkylene dipyridonium compound may be used to remove scale and oxide from steel. If immersed in 10% sulfuric acid at 70° C., cold rolled steel, for example, becomes pitted by the acid. There is a relatively brisk action. Both ethylene dipyridonium dichloride and ethylene diquinoline dichloride were added to separate acid baths in the proportion of about eight pounds to each 1000 gallons of the dilute acid; no evidence of pitting of such steel was observed in either bath after thirty minutes.

Stainless steel can be pickled or cleaned in sulfuric acid or nitric acid with or without a small amount of an alkylene pyridonium compound as an inhibitor. The addition of eight pounds of ethylene dipyridonium dichloride per 1000 cc. of acid to a 10% sulfuric bath or 1% nitric bath at 85° C. produced a marked decrease in the loss of hot rolled and annealed stainless steel (0.10% carbon, 12–14% chromium).

A mixture of sulfuric acid and nitric acid is used for cleaning Monel metal. In treating Monel metal (70% nickel, 30% copper) rolled and hydrogen-annealed in an acid bath comprising 4% sulfuric acid, 1.68% sodium nitrate and 0.85% sodium chloride, the addition of eight pounds of ethylene dipyridonium dichloride, ethylene, diquinoline dichloride or ethylene diquinoline dibromide per 1000 cc. to the dilute acid mixture was found to greatly reduce the action of the acid on the Monel metal without producing any marked effect on the removal of scale and oxide from the metal. In a bath of boiling acid, Monel metal treated for one hour showed no roughening of the surface in baths to which each of these inhibitors had been added, whereas in a bath containing no inhibitor, surface roughening resulted.

Alkylene dipyridonium compounds inhibit the action of nitric acid baths on nickel. Rolled sheet nickel (99% nickel) can be effectively cleaned in a bath of 20% nitric acid to which eight pounds of ethylene dipyridonium dichloride has been added per 1000 cc. of the dilute acid. Treating nickel in such a bath at 80° C. for thirty minutes substantially no pitting of the metal resulted, whereas metal treated in a 20% nitric acid bath to which no inhibitor had been added showed much pitting at the end of this time.

Rolled sheet nickel (99%) hydrogen-annealed can be freed from scale in a bath containing 1.5% sulfuric acid and 12% nitric acid to which eight pounds of ethylene diquinoline dibromide per 1000 cc. of acid has been added. When treated in a bath of this composition for thirty minutes at 80° C. such nickel gave off very little gas and no odor compared to treatment in a sulfuric and nitric acid bath to which no inhibitor had been added.

Tests run in each of the cases above set forth show that the presence of a small amount of an alkylene dipyridonium compound as an inhibitor reduces to a marked degree the extent to which each of the metals is attacked by acids of the composition and at the temperatures stated. The loss of metal by solution in the acid was greatly reduced by the presence of the inhibitors.

The pickling or cleaning can be carried out continuously by passing the material to be pickled, such as wire or sheets, thru a number of baths in a regulated manner or by immersing the article to be pickled in the pickling bath for a suitable period of time. The temperature of the bath can be varied as conditions require. The pickling bath may be replenished by the addition of further amounts of acid until the iron sulfate or other salt formed reaches too great a concentration to allow further use of the solution.

The addition of the inhibitors of this invention to a cleaning or pickling bath prevents or retards or inhibits the action of the bath on the metal without interfering with the removal of scale or oxide or other foreign matter. The formation of hydrogen by the action of the acid bath on the metal is also reduced and the production of acid mist also greatly reduced. There is also a saving in the acid as well as protection of the metal. The reduced amount of action of the acid on the metal and the reduction in amount of hydrogen produced correspondingly reduces the amount of hydrogen absorbed by the metal.

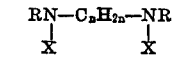
The employment of the inhibitors of this application in the pickling or cleaning operation, according to the present invention, involves but small additional expense as the compounds employed as inhibitors are relatively cheap, and results in advantages in operation, economy of acid, protection of the metal from attack, etc., which materially improve the pickling and cleaning operation.

In the claims, "a nitric acid bath" and "a sulfuric acid bath" mean a bath comprising nitric acid and sulfuric acid, respectively.

I claim:

1. A cleaning or pickling bath prepared

by adding to a suitable acid solution a small amount of a compound having the general formula



in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

2. A nitric acid cleaning or pickling bath comprising a small amount of an alkylene dipyridonium compound.

3. A cleaning or pickling bath comprising nitric acid, sulfuric acid and a small amount of an alkylene dipyridonium compound.

4. A cleaning or pickling bath comprising an acid and a small amount of an organic chemical containing two pyridine rings, the nitrogen atoms of which are connected by an alkylene chain.

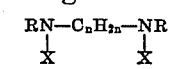
5. An acid cleaning or pickling bath comprising up to 1% of an alkylene dipyridonium compound.

6. An acid cleaning or pickling bath comprising up to 1% of an ethylene dipyridonium salt.

7. An acid cleaning or pickling bath comprising up to 1% of an alkylene diquinoline compound.

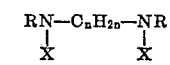
8. An acid cleaning or pickling bath comprising up to 1% of an ethylene diquinoline salt.

9. The method of cleaning or pickling metals, which comprises subjecting the same to an acid pickling or cleaning bath to which has been added a small amount of a compound having the general formula



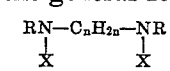
in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

10. The method of cleaning or pickling metals, which comprises subjecting the same to a nitric acid cleaning or pickling bath comprising a small amount of a compound having the general formula



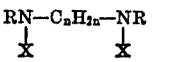
in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

11. The method of cleaning or pickling iron or steel, which comprises subjecting the same to a sulfuric acid pickling or cleaning bath comprising a small amount of a compound having the general formula



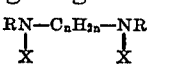
in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

12. The method of cleaning or pickling metals, which comprises subjecting the same to a cleaning or pickling bath comprising sulfuric acid, nitric acid, and a small amount of a compound having the general formula



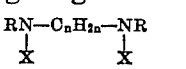
in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

13. The method of cleaning or pickling non-ferrous metals which comprises subjecting the same to a nitric acid pickling of cleaning bath comprising a small amount of a compound having the general formula



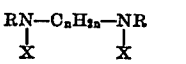
in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

14. The method of cleaning or pickling nickeliferous metals which comprises subjecting the same to a nitric acid pickling or cleaning bath comprising a small amount of a compound having the general formula



in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

15. The method of cleaning or pickling nickeliferous metals, which comprises subjecting the same to an acid bath comprising a small amount of a compound having the general formula



in which X is an acid radical and R N indicates a nitrogenous heterocyclic base or derivative thereof.

16. The method of cleaning or pickling metals, which comprises subjecting the same to an acid pickling or cleaning bath comprising up to 1% of an alkylene dipyridonium compound.

17. The method of cleaning or pickling metals, which comprises subjecting the same to an acid pickling or cleaning bath comprising up to 1% of an ethylene dipyridonium salt.

18. The method of cleaning or pickling metals, which comprises subjecting the same to an acid pickling or cleaning bath comprising up to 1% of an alkylene diquinoline compound.

19. The method of cleaning or pickling metals which comprises subjecting the same to an acid pickling or cleaning bath comprising up to 1% of an ethylene diquinoline compound.

In testimony whereof I affix my signature.

PAUL I. MURRILL.