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COMPOSITION AND PROCESS FOR CLEANING AND PICKLING FERROUS METALS

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8 Claims. (Cl. 252—150)

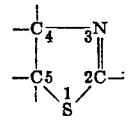
This invention relates to the modification of the action of acids on metals, and is particularly directed to processes and compositions which employ a thiazoline in conjunction with an acid.

Pickling and metal cleaning operations often involve the use of a bath of dilute non-oxidizing acids, such as sulfuric, hydrochloric, acetic, formic, aqueous solutions of acid sulfate, 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 this invention to acid pickling and acid metal cleaning operations involves no change in the customary baths and processes except for the addition of a small amount of a thiazoline inhibitor of this invention. In quantities as small as about one thousandth of one per cent, thiazoline inhibitors will check the attack of acid on metal. It is usually preferred to employ between about two thousandths of one per cent and one tenth of one per cent of a thiazoline, but more or less may be used if desired.

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

The thiazolines are a well recognized class of compounds having a heterocyclic ring structure which may be represented as follows:



In the structural formula the numbers are given to the members of the ring for reference and to permit the correct naming of the substituted thiazolines. In the simplest thiazoline, namely 4:5 thiazoline the unsatisfied valences of the carbon atoms in the above formula are taken up by hydrogen atoms. Substituted thiazolines, in which one or more of the unsatisfied valences of the carbon atoms in the above formula are taken up by groups other than hydrogen atoms, have been found to be excellent inhibitors according to this invention. Such groups may be saturated or unsaturated hydrocarbon groups such as alkyl, alkylene, aryl, alkaryl, aralkyl, or cycloaliphatic groups, or they may be groups containing such elements as sulfur or nitrogen, such as mercapto or amino groups. Thiazolines, for instance, having an organic sulfide group on the number two carbon atom have been found to be extremely effective inhibitors. For convenience in terminology, such compounds may be referred to as thiazolinyl sulfides.

As compared with conventional inhibitors heretofore available, thiazolines exhibit an effective controlling action on the corrosion of metals in acids, even when such thiazolines are present in extremely small amounts. This action is relatively independant of the metal being pickled, so that, for instance, both high carbon and low carbon steels and alloy steels may advantageously be pickled in an acid inhibited with a thiazoline, according to the invention. Furthermore, because the thiazolines are definite chemical compounds of controlled composition, it is relatively easy to control the amount of the thiazoline present in the pickling bath so that neither excesses nor deficiencies in the amount of inhibitor occur.

Metals which have been pickled in solutions containing a thiazoline inhibitor according to this invention are characterized by exceptional brightness and freedom from stain. In metal finishing operations this advantage is of great importance. For instance, the metals coming from the plating bath can be directly finished by such methods as painting or plating without laborious intermediate cleaning procedures, such as are required with metals pickled in many of the pickling solutions heretofore available.

In order that this invention may be more fully understood, reference should be had to the following illustrative examples:

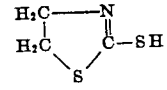
Example I

A pickling bath was made up by adding .005% by weight of a thiazoline, namely 2-dodecylamino-5-methyl-thiazoline, to a 5% aqueous solution of

sulfuric acid. The bath was used for pickling scaled sheets of SAE–1020 hot rolled steel. It was found that the scale was rapidly and completely removed and after such removal the inhibitor reduced the rate of corrosion of the bath on the clean steel by 98%.

Example II

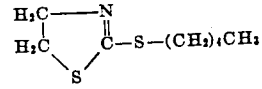
A pickling bath was made up as in Example I, except that the thiazoline inhibitor used was 2-mercaptothiazoline, which was used at a concentration by weight of 0.025%. 2-mercaptothiazoline has the structural formula:



Following the removal of the scale, the inhibitor reduced the rate of corrosion of the bath on the steel by 91%.

Example III

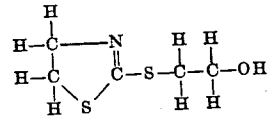
A pickling bath was made up and used as in Example I, except that the thiazoline used as the inhibitor was n-amyl 2-thiazolinyl sulfide, the concentration of the inhibitor being .0025% by weight. N-amyl 2-thiazolinyl sulfide has the structural formula:



Following the removal of the scale the inhibitor reduced the rate of corrosion of the bath on the steel plate by 98%.

Example IV

A pickling bath of this invention was made up and used as in Example I, except that the thiazoline employed was beta-hydroxyethyl 2-thiazolinyl sulfide, having the structural formula:



Used in the amount of .00375% by weight, this inhibitor reduced the rate of corrosion of the steel after scale removal by 98%.

Example V

A metal cleaning and pickling bath of this invention was made up as in Example I, except that the thiazoline inhibitor used was 1,2-ethylene di-(2-thiazolinyl sulfide). Used in a concentration of .0025% by weight, this inhibitor reduced the rate of corrosion of the steel by the acid, after scale removal, by 97%.

While in the foregoing examples there have been disclosed particular thiazolines as inhibitors, it will be understood that other thiazolines may also be used to advantage. Excellent results may be obtained, for instance, by using such thiazolines as benzyl 2-thiazolinyl sulfide, beta-naphthylaminomethyl 2-thiazolinyl sulfide, beta-phenoxyethyl 2-thiazolinyl sulfide, n-butyl 2-thiazolinyl sulfide, beta-hydroxypentyl 2-thiazolinyl sulfide, and lauryl 2-thiazolinyl sulfide. Other hydrocarbon-substituted thiazolines which may be used are, for instance, 2-methyl-thiazoline and 2-phenylthiazoline.

Certain of the thiazolines may be associated with odoriferous impurities formed as by-products in their manufacture. If such odoriferous constituents are found objectionable they can in some instances be removed by blowing air through a body of the thiazoline under alkaline conditions that is, at a pH above about 7. It should be understood, however, that the removal of odors by such alkaline blowing is optional and that the presence of such odoriferous constituents does not ordinarily interfere with the inhibitive action of the thiazolines.

If desired, there may be used in conjunction with thiazoline inhibitors such additional materials as foaming agents, dispersing agents, and wetting agents. A thiazoline may be used alone or in combination with another thiazoline or another material having inhibitive action.

While in the foregoing description of this invention there have been shown certain metal cleaning and pickling baths and certain processes using thiazolines as inhibitors, it will be understood that without departing from the spirit of this invention one skilled in the art may employ other baths and processes.

We claim:

1. A process for cleaning and pickling ferrous metals comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of a thiazolinyl sulfide as an inhibitor, for controlling the corrosion of the metal by the acid.

2. A process for cleaning and pickling ferrous metals comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of beta-hydroxyethyl 2-thiazolinyl sulfide as an inhibitor, for controlling the corrosion of the metal by the acid.

3. A process for cleaning and pickling ferrous metals comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of 1,2-ethylene di(2-thiazolinyl sulfide) as an inhibitor, for controlling the corrosion of the metal by the acid.

4. A process for cleaning and pickling ferrous metals comprising subjecting the metal to the action of a dilute non-oxidizing acid in the presence of a small amount of lauryl 2-thiazolinyl sulfide as an inhibitor, for controlling the corrosion of the metal by the acid.

5. A pickling and cleaning composition for ferrous metals, comprising a non-oxidizing acid and a thiazolinyl sulfide as an inhibitor, for controlling the corrosion of said ferrous metals by the acid.

6. A pickling and cleaning composition for ferrous metals, comprising a non-oxidizing acid and a beta-hydroxyethyl 2-thiazolinyl sulfide as an inhibitor, for controlling the corrosion of said ferrous metals by the acid.

7. A pickling and cleaning composition for ferrous metals, comprising a non-oxidizing acid and a 1,2-ethylene di(2-thiazolinyl sulfide) as an inhibitor, for controlling the corrosion of said ferrous metals by the acid.

8. A pickling and cleaning composition for ferrous metals, comprising a non-oxidizing acid and a lauryl 2-thiazolinyl sulfide as an inhibitor, for controlling the corrosion of said ferrous metals by the acid.

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