The present invention relates to new inhibiting compositions for metal pickling by means of acid solutions. The invention also relates to solutions prepared from these inhibiting compositions and to pickling processes wherein such compositions are used.

Numerous substances have been proposed as pickling and corrosion inhibitors. The inhibiting power of these substances is determined by the degree to which the attacks on the metal in the presence and in the absence of an inhibiting agent, all other operating conditions remaining the same.

If $P$ is the weight loss of a metal by action of an acid and $P'$ the weight loss of the same metal under the same conditions but the acid contains an inhibiting agent, the inhibiting power $I$ is calculated from the formula:

$$ I = 100 \frac{P - P'}{P} $$

It is obvious that for the sake of completeness the amount of inhibitor which has been added should be taken into account.

Among the numerous substances which have a high inhibiting power, the alkylated and arylated derivatives of thiourea, such as di-n-butyl-thiourea, diethyl-thiourea and di-o-tolyl-thiourea, are particularly well known. Mention may also be made of o-, m- and p-tolyl-thiourea, ethyl-thiourea and phenyl-thiourea.

In general, these substances are slowly soluble in water. Therefore, it is necessary to add emulsifiers to these inhibiting substances in order to distribute them uniformly in the pickling medium. Thus, for example, if a condensation product of nonyl phenol with ethylene oxide is added to dibutyl-thiourea, the inhibiting power of dibutyl-thiourea reaches 99%.

During pickling, the concentration of the salts of the metals treated increases gradually in the acid solutions. The non-ionic emulsifiers are generally found to be sensitive to the action of the metal salts. Consequently, the inhibitor is no longer properly emulsified in the pickling medium. Furthermore, a part of the inhibitor is removed either by the pickled articles in the form of a cream or by settling to the bottom of the pickling bath.

In order to overcome these drawbacks, it has been proposed to add cationic detergents, such as quaternary ammonium compounds.

According to the present invention, there are provided new pickling inhibiting compositions comprising:

(a) From about 2 to 25 parts by weight of an alkyl- or aryl-substituted thiourea.

(b) From about 5 to 75 parts by weight of a non-ionic agent consisting essentially of a condensation product of at least 5 moles of ethylene oxide for each mole of a compound selected from the group consisting of a naphthal, a xylene and a mixture of xylens.

(c) From about 0 to 60 parts by weight of an organic solvent.

The inhibiting power of these compositions is maintained even in baths having a high concentration of salts of the metals treated. Therefore, the present invention also improves the advantages generally attributed to pickling inhibitors such as a saving of metal and of the acid used; the pickling is more uniform and more hygienic.

As indicated above, component (a) of the inhibiting compositions according to the present invention is an alkyl- or aryl-substituted thiourea. Among these substances, there is preferably used an alkyalted derivative of thiourea, with alkyl groups containing from 1 to 5 carbon atoms and more, particularly dibutyl-thiourea.

Component (b) is a non-ionic agent consisting essentially of a condensation product of from 5 to 30 moles of ethylene oxide for each mole of a compound selected from the group consisting of a naphthal, a xylene and a mixture of xylens. The non-ionic agents preferably used are condensation products of from 8 to 25 moles of ethylene oxide for each mole of a naphthal and condensation product from 5 to 15 moles of ethylene oxide for each mole of a mixture of xylens. These non-ionic agents are not emulsifiers or possess only a very low emulsifying power.

In order to make handling and storage easier, the inhibiting compositions may in addition, contain a suitable organic solvent, which has been indicated above as component (c). Examples of such solvents are halogenated hydrocarbons, alcohols, ketones and phenols and especially, aliphatic or alicyclic amines. An amount of an organic solvent sufficient to maintain the homogeneity of the mixture under normal storage conditions is used.

The inhibiting compositions of the invention can be prepared by mixing the constituents, in suitable proportions, in any order; for 1 part of alkyl- or aryl-substituted thiourea are used from 0.25 to 10 parts, preferably from 1 to 5 parts of the non-ionic agent.

These compositions can, if desired, also contain surface active agents such as usually added to commercial pickling inhibitors.

The present invention also includes the acid solutions prepared from these inhibiting compositions. The choice of the acid solution obviously depends on the nature of the metal to be cleaned. Use is generally made of an aqueous solution of sulfuric, hydrochloric, phosphoric or sulfuric acid, or potassium hydrogen sulfate.

The mixture of the substituted thiourea and of the non-ionic agent is added to the acid solution in concentrations of about 0.01 to 1%, preferably 0.025 to 0.25% by weight, referred to the concentration of the acid.

These inhibited acid solutions may be used directly or after suitable dilution for metal pickling or cleaning.

The use of the inhibiting compositions of the invention is however not limited to pickling processes, but they may also be used to protect metals against corrosion and, in general, to inhibit any corrosive effect of an acid upon a metal surface.

The following examples illustrate the improved inhibiting power produced by the compositions of this invention. Examples 1 and 2 are given for the purpose of comparison. In order to obtain comparable results in the tests, it is obvious that it is not possible to carry out actual pickling with metals coated with an oxide scale.

The method used in the test described in the examples is closely related to industrial practice.

A number of metal sheets coated with oxides are pickled for a definite period of time. A tared metal sheet with ground surfaces is introduced at regular intervals. These operations are continued until the bath is exhausted.

The inhibiting power is determined from the weight loss of the metal sheet with ground surfaces. This is done for different states of exhaustion of the bath and consequently for an increase in concentration of dissolved metal salts.

The comparison is always made with an uninhibited bath at the same state of exhaustion.
Example 1

Use is made of an acid pickling bath which contains sulfuric acid (200 g. of H₂SO₄ per liter) at a temperature of 95° C. Dibutyl-thiourea in a concentration of 0.2 g. per 1000 g. of 100% sulfuric acid is used as inhibitor. The inhibiting power is determined in a fresh bath (start of pickling). The average inhibiting power is 68.2%.

This example shows that dibutyl-thiourea added to the pickling bath without an emulsifier dissolves poorly and, consequently, has only a low efficiency.

Example 2

An acid pickling bath containing sulfuric acid (200 g. of H₂SO₄ per liter) is used at a temperature of 85° C. A mixture of 20 parts of dibutyl-thiourea, 20 parts of monoy phenol condensed with 30 moles of ethylene oxide and 60 parts of trichlorehylenes is used as inhibiting composition. This mixture is added to the acid bath in a concentration of 1 g. per 1000 g. of 100% sulfuric acid. The inhibiting power is determined and the following values are found:

(a) In a fresh bath, I=99.4%.
(b) In a bath containing 34 g. iron per liter, I=98.3%.
(c) In a bath containing 80 g. iron per liter, I=89%.
(d) In a bath containing 120 g. iron per liter, I=78%.

(The bath replenished with sulfuric acid after exhaustion.)

This example shows the inhibiting action of dibutyl-thiourea in the presence of a non-ionic emulsifier. The inhibition is almost perfect at the start of pickling but a decrease of the action during pickling is observed.

Example 3

An acid pickling bath containing sulfuric acid (200 g. of H₂SO₄ per liter) is used at a temperature of 85° C. A mixture of 15 parts of dibutyl-thiourea, 70 parts of beta-naphthol condensed with 11 moles of ethylene oxide and 15 parts of cyclohexylamine is used as inhibiting composition. 1.33 g. of this mixture is added per 1000 g. of 100% sulfuric acid. The inhibiting power is determined and the following values are found:

(a) In a fresh bath, I=99.5%.
(b) In a bath containing 80 g. iron per liter, I=98.9%.
(c) In a bath containing 120 g. iron per liter, I=97.9%.

(The bath replenished with sulfuric acid after exhaustion.)

This example shows the inhibiting action of dibutyl-thiourea in the presence of a non-ionic agent according to the invention. The perfect inhibition at the start of pickling is almost fully maintained during pickling.

Example 4

An acid pickling bath is used which contains sulfuric acid (200 g. of H₂SO₄ per liter) at a temperature of 85° C. A mixture of 15 parts of dibutyl-thiourea, 70 parts of a mixture of xylenols condensed with 10 moles of ethylene oxide and 15 parts of cyclohexylamine is used as inhibiting composition. 1.33 g. of this mixture is added per 1000 g. of 100% sulfuric acid. The inhibiting power is determined and the following values are found:

(a) In a fresh bath, I=99.6%.
(b) In a bath containing 80 g. iron per liter, I=98.6%.

Example 5

An acid pickling bath which contains hydrochloric acid (70 g. of HCl per liter) is used at a temperature of 25° C. 0.5 g. of the mixture used in Example 3 is added per liter of acid solution. The inhibiting power is determined and the following values are found:

(a) In a fresh bath, I=98.4%.
(b) In a bath containing 31 g. iron per liter, I=98.3%.

Example 6

An acid pickling bath containing phosphoric acid (150 g. of phosphoric acid per liter) is used at a temperature of 80° C. A mixture of 15 parts of dibutyl-thiourea, 70 parts of beta-naphthol condensed with 11 moles of ethylene oxide and 15 parts of cyclohexylamine is used as inhibiting composition. This mixture is added to the acid bath in a concentration of 1.8 g. per 1000 g. of 85% phosphoric acid. The inhibiting power is determined and the following values are found:

(a) In a fresh bath, I=99.1%.
(b) In a bath containing 34 g. iron per liter, I=99.1%.
(c) In a bath containing 80 g. iron per liter, I=98%.

Example 7

A pickling bath containing potassium hydrogen sulfate (200 g. of KHSO₄ per liter) is used at a temperature of 85° C. A mixture of 15 parts of dibutyl-thiourea, 70 parts of beta-naphthol condensed with 11 moles of ethylene oxide and 15 parts of cyclohexylamine is used as inhibiting composition. 2 g. of this mixture is added per 1000 g. of 99% solid potassium hydrogen sulfate. The inhibiting power is determined and the following values are found:

(a) In a fresh bath, I=99%.
(b) In a bath containing 34 g. iron per liter, I=99.1%.
(c) In a bath containing 80 g. iron per liter, I=98.9%.

Example 8

A descaling bath containing sulfamic acid (100 g. of NH₄HSO₃ per liter) is used at a temperature of 65° C. A mixture of 15 parts of dibutyl-thiourea, 70 parts of beta-naphthol condensed with 11 moles of ethylene oxide and 15 parts of cyclohexylamine is used as inhibiting composition. 10 g. of this mixture is added per 1000 g. of 99% solid sulfamic acid.

In order to reproduce pickling of metal plates coated not only with oxides, but also with calcareous inclusions, there is proceeded as follows. A quantity of calcium carbonate nearly equal to half the quantity of acid is introduced gradually in the pickling bath. A corresponding quantity is added in the same way to an uninhibited bath.

This method makes it possible to reproduce the effect of carbon dioxide and soluble calcium salts, observed in industrial practice.

After four hours' pickling, the inhibiting power determined according to the usual method is 99.6%.

I claim:

1. An inhibiting composition for metal pickling consisting essentially of (a) a member selected from the group consisting of alkyl-thiourea, the alkyl-thiourea, the alkyl-thiourea and (b) a substantially non-emulsifying non-ionic surface active agent consisting of a condensation product of from 5 to 30 moles of ethylene oxide per mole of a compound selected from the group consisting of beta-naphthol and xylene, the proportion of (a) to (b) being about 2 to 25 parts by weight of (a) per about 5 to 75 parts by weight of (b).

2. An inhibiting composition for metal pickling consisting essentially of (a) dibutyl-thiourea and (b) a substantially non-emulsifying non-ionic surface active agent consisting of a condensation product of from 5 to 30 moles of ethylene oxide per mole of beta-naphthol, the proportion of (a) to (b) being about 2 to 25 parts by weight of (a) per about 5 to 75 parts by weight of (b).

3. An aqueous acid pickling solution, normally corrosive towards metal surfaces, containing dispersed therein about 0.01 to 1% by weight, based on the weight of the acid of an inhibiting composition according to claim 1.

4. An aqueous acid pickling solution, normally corrosive towards metal surfaces, containing dispersed therein about 0.01 to 1% by weight, based on the weight of the acid of an inhibiting composition according to claim 1.
sive towards metal surfaces, containing dispersed therein about 0.01 to 1% by weight, based on the weight of the acid of an inhibiting composition according to claim 2.

6. An aqueous acid pickling solution, normally corrosive towards metal surfaces, containing dispersed therein about 0.01 to 1% by weight, based on the weight of the acid of an inhibiting composition according to claim 3.

7. A process for pickling a metal selected from the group consisting of iron and steel, which comprises immersing the metal in an acid bath containing dispersed therein about 0.01 to 1% by weight, based on the weight of the acid of an inhibiting composition as defined in claim 1.

8. A process for pickling a metal selected from the group consisting of iron and steel, which comprises immersing the metal in an acid bath containing dispersed therein about 0.01 to 1% by weight, based on the weight of the acid of an inhibiting composition as defined in claim 2.

9. A process for pickling a metal selected from the group consisting of iron and steel, which comprises immersing the metal in an acid bath containing dispersed therein about 0.01 to 1% by weight, based on the weight of the acid of an inhibiting composition as defined in claim 3.

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