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PICKLING INHIBITOR COMPOSITION

Filed July 6, 1965

Fig. 1.

MILD STEEL IN SULFURIC ACID WITH INHIBITOR

6 HOURS AT 165°F

Fig. 2.

MILD STEEL IN SULFURIC ACID WITH INHIBITOR

6 HOURS AT 200°F

Fig. 3.

MILD STEEL IN PHOSPHORIC ACID WITH INHIBITOR

6 HOURS AT 165°F

Fig. 4.

MILD STEEL IN PHOSPHORIC ACID WITH INHIBITOR

6 HOURS AT 200°F

INVENTOR

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Fig. 5.
**PICKLING INHIBITOR COMPOSITION**

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3 Claims. (Cl. 252—149)

This application is a continuation-in-part of my copending application Ser. No. 285,060, filed June 3, 1963, now abandoned.

This invention relates to inhibitor composition for acid solutions employed in the surface treatment of metals, and more particularly to special formulations for these inhibitor compositions.

The treatment of metal surfaces with strong acids for the purpose of removing metal oxides and scale, is generally referred to as "pickling." Many methods of preparing a metal surface for processes such as electrodeposition, chemical coating and machining. In a pickling process, a metal object containing, for example, a high percentage of iron, is immersed in an aqueous acid bath, commonly called "pickling liquor." On immersion, the metal oxide, iron oxide in this instance, and scale are removed by direct attack of the acid on points on the metal surface at which the iron oxide or scale attaches.

Deposits of oxide and scale are usually quite pessimal to the constituents of the pickling liquor, and slough off rapidly because of the action of the acid. Of course, at the same time that the pickling liquor is attacking the metal surface directly beneath the unwanted coating, it is also attacking the already clear metal surfaces and dissolving off appreciable quantities of metal. Furthermore, acids are often used needlessly in this type of chemical process.

In order to prevent such attack on clean metal, pickling inhibitors are generally added to the pickling liquor. Each type of pickling inhibitors slows down acid attack on clean surfaces only more than acid attack on scaled surfaces. Thus, the rate of scale removal by pickling is substantially the same as without the inhibitor, while the loss of metal by solution in acid is decreased. Many of the more successful pickling inhibitors are organic sulfon compounds, particularly mercaptans.

There are, however, other problems which occur in a pickling operation besides dissolution of metal from clean surfaces. For example, the attack of acid on metal to produce a metal salt plus hydrogen naturally results in a loss of acid by entrapment with the escaping hydrogen. Acid can also be lost by fuming, particularly nitric acid. Thus, it is apparent that, even with an excellent pickling inhibitor, there are many practical considerations which must be taken care of before the entire pickling process can be operated in an economical fashion.

It is an object of this invention to provide a pickling inhibitor formulation which reduces acid consumption either by metal attack fuming or entrapment, which decreases heat loss from the bath, which effectively prevents acid attack on bright metal, which is effective in low concentration and which is economical to use. Other objects of this invention will become apparent from the following description:

FIGS. 1 to 5 inclusive represent corrosion charts which will be referred to hereinafter.

In fulfillment of the above and other objects, this invention provides a pickling inhibitor formulation comprising a dialkyl thiourea, a polyoxyethylene glycol ester of a resin acid mixture derived from tall oil, an alkoxylated quaternary ammonium compound, propylene glycol, a nonylphenol polyoxyethylene ether, and water.

The polyoxyethylene glycol ester of the resin acid mixture, one of the constituents of my novel pickling inhibitor formulation, is represented by the following formula: 

\[ H-(O-C\_\_H\_\_2H\_\_2)-O-RE \]

wherein \( n \) is a number from 6-20, preferably 15, and \( RE \) is the residue of a resin acid of the group consisting of dextrotripinamic, levopimaric, abietic, isodexotripinamic, dihydroabietic, tetrahydroabietic, dehydroabietic, and neoabietic acids. The structures of these acids are fully disclosed in Vol. III of "The Terpenes" by Sammon and Barton, Cambridge, 1952. Typical polyoxyethylene esters of resin acids include compounds with the following formulas:

\[ H(O-C\_\_H\_\_2H\_\_2-O)_{10}-O \]; abietate

\[ H(O-C\_\_H\_\_2H\_\_2-O)_{15}-O \]; levopimarate

\[ H(O-C\_\_H\_\_2H\_\_2-O)_{20}-O \]; neoabietate

I prefer to use a commercially available mixture of resin acids derived from hydrolysis of tall oil rather than a pure resin acid to esterify the polyoxyethylene glycol, which part of the molecule is also derived from a commercial mixture in which one given molecular species predominates, \( HO(CH_2\_CH_2-O)_n-H \) or

\[ HO(CH_2\_CH_2-O)_n-H \]

Another of the ingredients of the novel pickling inhibitor formulation provided by this invention is an alkoxylated quaternary ammonium derivative which can be represented as follows:

\[ \begin{align*}
R \quad (R'O)_nH \\
R \quad (R'O)_nH
\end{align*} \]

wherein \( R \) is an aliphatic hydrocarbon radical containing from 6 to 22 carbon atoms, \( R' \) is a lower alkyl radical, \( X \) is ethylene, 1,2-propylene or trimethylene, \( X' \) is an anion and \( x \) is a positive integer having a sum total in the range 2-50. In the above formula, the term "lower alkyl" means alkyl radicals having less than four carbon atoms such as methyl, ethyl and propyl. Likewise, the term "alkyllic" includes alkyl, cycloalkyl, alkylene, cycloalkylene and alkynyl radicals such as, for example, cyclohexyl, cyclocnenyl, hexyl, dectyl, undecenyl, bicyclooctenyl, tetradecynyl, octadecynyl and the like. The anion represented by \( X \) can be any anion including inorganic ions such as chloride, bromide, fluoride, phosphate, sulfate and the like as well as organic anions such as p-toluenesulfonate, trichloroacetate and the like. However, anions of strong acids having a \( pK_a=2 \) or less are preferred. In general, the precise nature of the anion is not critical inasmuch as the quaternary ammonium compounds are strong electrolytes and ionizes substantially completely in solution. A typical alkoxylated quaternary ammonium derivative has the following formula:

\[ \begin{align*}
Cu_2H_2 \\
O\_\_H\_\_2 \\
Cu_{10}H_2
\end{align*} \]

The dialkyl thioureas which are useful in preparing my novel formulation can be represented by the following formula:

\[ \begin{align*}
8 \quad Alk-NH-O-NH-alk' \\
8 \quad Alk-NH-O-NH-alk'
\end{align*} \]

wherein alk and alk' are alkyl groups of from 1-5 carbon atoms including such groups as methyl, ethyl, n-propyl, n-buty1, sec-buty1, isobuty1, isopropanyl, n-amyl, etc. The above thioureas may be either symmetrically or unsymmetrically substituted with alkyl groups. The preferred group of thioureas are those in which the sum of the carbon atoms in alk and alk' is from 2-8.

The non-ionic surfactant constituent of the novel formulations of this invention can be any of the commercially used surfactants readily available from commercial sup-
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I prefer to use, however, a nonylphenol polyethylene glycol ether in which the polyethylene glycol chain contains from 6 to 15 (preferably 13) moles of ethyleneoxy residues per nonyl phenol residue.

Typical nonylphenol polyethylene glycol ethers include compounds of the following structures:

\[ \text{C}_9\text{H}_{17}\text{O}(-\text{CH}_2-\text{CH}_2-O)_n\text{H} \]

My preferred formulations contain the above constituents in percentages by volume, each of the ingredients being present in an amount equal to or at least 0.75% by volume of the whole composition.

Dialkylthiourea \( \quad 3.5 \) to \( 5.0 \)
Polyoxyethylene glycolester of resin acid \( \quad 10.5 \) to \( 14.0 \)
Nonylphenol polyethylene glycol ether \( \quad 7.5 \) to \( 1.0 \)
Propylene glycol \( \quad 5.0 \) to \( 6.0 \)
Water \( \quad 10 \) to \( 15 \)

Formulations coming within the above range include the following:

(I) 5% dibutyl thiourea

\[ \text{CaH}_2\text{H}_2\text{H}_2\text{H}_2\text{O}(-\text{CH}_2-\text{CH}_2-\text{O})_n\text{H} \]

10% \( \text{H}(\text{O}-\text{CH}_2-\text{CH}_2)_n\text{OH} \)
10% propylene glycol
50% water

(II) 3.5% di-isobutyl urea

\[ \text{CaH}_2\text{H}_2\text{H}_2\text{H}_2\text{O}(-\text{CH}_2-\text{CH}_2-\text{O})_n\text{H} \]

60% propylene glycol
10% water

Although the above formulas are preferred ones, the actual operative ratios of dialkyl thiourea to alkylated quaternary ammonium halide can vary from 1 to 9 to 1 to 1.

In actual use, a pickling inhibitor formulation falling within the ranges listed above is added to a pickling bath so as to provide from about 0.1% to about 0.3% of the dialkyl thiourea in the bath. Thus from about 0.2 to about 9 volumes of pickling formulation are added per 100 volumes of acid bath. Our novel inhibitor formulation can be used with various acids including sulfuric acid, hydrochloric acid, acetic acid, perchloric acid, phosphoric acid, sulfamic acid and the like. My novel inhibitor formulations are also effective with mixtures of the above acids. Concentrations of acid in the acid bath can vary from about 1% to about 15% by weight and bath temperatures can vary from about 50° to about 210° F. Among the metals whose corrosion rate in an acid pickling bath can be decreased by the addition to the bath of a pickling inhibitor formulation provided by this invention are included: mild steel, stainless steel, aluminum, copper, cast iron, zinc, high carbon, phosphorized steel and the like.

This invention is further illustrated by the following specific examples:

**EXAMPLE 1**

Corrosion test on low carbon wire

One hundred and two cubic centimeters of aqueous 12% 66° B. sulfuric acid was poured into each of two beakers. 0.03 gram of the following pickling inhibitor compositions was added to beaker #1; 50 parts propylene glycol, 10 parts water, 20 parts of

\[ \text{CaH}_2\text{H}_2\text{H}_2\text{O}(-\text{CH}_2-\text{CH}_2-\text{O})_n\text{H} \]

5 parts di-n-butyl thiourea, 1 part of

\[ \text{H}(\text{O}-\text{CH}_2-\text{CH}_2)_n\text{OH} \]

wherein RE is a resin acid derived from tall oil by hydrolysis and 14 parts of a polyoxyethylene quaternary ammonium halide corresponding to the formula

\[ \text{CaH}_2\text{H}_2\text{H}_2\text{O}(-\text{CH}_2-\text{CH}_2-\text{O})_n\text{H} \]

Beaker #2 was kept as a control beaker. The two beakers were heated to 200° F. Three pieces of six inch long low carbon steel wire were added to each beaker and the wire pieces were picked for 30 minutes. At the end of this time, the acid was poured off and diluted to its original volume of 102 cc. The diluted solutions were then titrated for acid and iron content. Table 1 gives the results of this experiment.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beaker 1</td>
</tr>
<tr>
<td>Amount of inhibitor added (g.)</td>
</tr>
<tr>
<td>Original vol. (cc.)</td>
</tr>
<tr>
<td>Vol. after picking (cc.)</td>
</tr>
<tr>
<td>Evaporation loss (g.)</td>
</tr>
<tr>
<td>Evaporation loss (percent)</td>
</tr>
<tr>
<td>Amount of iron in final solution (percent)</td>
</tr>
<tr>
<td>Amount of acid in original solution (percent)</td>
</tr>
<tr>
<td>Amount of acid in final solution (percent)</td>
</tr>
<tr>
<td>Percent acid used</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

Corrosion test on low carbon wire

An experiment similar to Example 1 was carried out using 100 cc. of aqueous 10% 66° B. sulfuric acid. 0.05 gram of the pickling inhibitor from Example 1 was added to beaker #1. Both beakers were heated to 180° F. Three six-inch pieces of low carbon steel wire were added to each beaker and the wire was picked for thirty minutes. After the end of the pickling period, the acid was poured off and diluted to its original volume. Table 2 gives the results of this experiment.

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beaker 1</td>
</tr>
<tr>
<td>Amount of inhibitor added (g.)</td>
</tr>
<tr>
<td>Original vol. (cc.)</td>
</tr>
<tr>
<td>Vol. after picking (cc.)</td>
</tr>
<tr>
<td>Evaporation loss (g.)</td>
</tr>
<tr>
<td>Evaporation loss (percent)</td>
</tr>
<tr>
<td>Amount of iron in final solution (percent)</td>
</tr>
<tr>
<td>Amount of acid in original solution (percent)</td>
</tr>
<tr>
<td>Amount of acid in final solution (percent)</td>
</tr>
<tr>
<td>Amount of acid used (percent)</td>
</tr>
</tbody>
</table>

**FIGURES 1-5** Graph the corrosion rate of mild steel or stainless steel in sulfuric or phosphoric acid versus the percent inhibitor concentration. The inhibitor employed was the same as that used in Example 1.

The invention claimed is:

1. A pickling inhibitor formulation consisting of the following ingredients:
   (a) a dialkyl thiourea wherein the alkyl groups have from 1-5 carbon atoms,
(b) an alkoxylation quaternary ammonium salt of the formula
\[
\begin{array}{c}
\text{R} \quad \text{(O'R)} \quad \text{H} \\
\text{R'} \quad \text{(O'R)} \quad \text{H}
\end{array}
\]
wherein \( R \) is an aliphatic hydrocarbon radical having from 6–22 carbon atoms; \( R' \) is a lower alkyl radical having from one to four carbon atoms; \( R'' \) is a member of the group consisting of ethylene, 1,2-propylene and trimethylene; \( X^- \) is chloride, bromide, fluoride, phosphate, sulfate, p-toluene, or trichloroacetate; and \( y \) and \( z \) are positive integers whose sum lies in the range 28–32.

(c) a polyoxyethylene glycol esterified with isodextrapimmaric, dihydroabietic, tetrahydroabietic, dehydroabietic, abietic, neoabietic, dextropimaric or levopimaric acids having from 6–20 oxyethylene residues in the ester portion of said molecule.

(d) a nonyl phenol polyoxyethylene ether having from 6–15 ethylenoxy residues in the polyoxyethylene glycol chain, and

(e) propylene glycol, each of the above ingredients being present in an amount equal to at least 0.75% by volume of the whole composition.

2. A pickling inhibitor formulation consisting of:
(a) from 3.5–5.0% by volume of a dialkyl thiourea wherein the alkyl groups have from 1–5 carbon atoms,
(b) from 10.5–14.0% by volume of an alkoxylation quaternary ammonium salt of the formula:
\[
\begin{array}{c}
\text{R} \quad \text{(O'R)} \quad \text{H} \\
\text{R'} \quad \text{(O'R)} \quad \text{H}
\end{array}
\]
wherein \( R \) is an aliphatic hydrocarbon radical having from 6–22 carbon atoms; \( R' \) is a lower alkyl radical having from one to four carbon atoms; \( R'' \) is a member of the group consisting of ethylene, 1,2-propylene, and trimethylene; \( X^- \) is chloride, bromide, fluoride, phosphate, sulfate, p-toluene sulfonate, or trichloroacetate; and \( y \) and \( z \) are positive integers whose sum lies in the range 28–32,

(c) from 0.75–1.0% by volume of a polyoxyethylene glycol ester of a resin acid of the group consisting of abietic, neoabietic, dextropimaric, isodextrapimmaric, dehydroabietic, dehydroabietic, and levopimaric acids,

(d) from 15–20% by volume of a nonyl phenol polyethylene glycol ether having 6–15 ethylenoxy residues per nonyl phenol residue,

(e) from 50–60% by volume of propylene glycol, and

(f) from 10–15% by volume of water.

3. A pickling inhibitor formulation consisting of:
(a) 5% by volume of dibutyl thiourea,
(b) 14% by volume of an ethoxylated quaternary ammonium halide of the formula:
\[
\begin{array}{c}
\text{C}_n\text{H}_{2n} \quad \text{(CH}_2\text{-CH(OH)O)}_n\text{H} \\
\end{array}
\]
(c) 1% by volume of a compound of the formula \( \text{H(O-CH}_2\text{-CH}_2\text{)}_{15} \text{-O-RE} \) wherein RE is a member of the group consisting of abietic, neoabietic, dextropimaric, isodextrapimaric, dihydroabietic, tetrahydroabietic, dehydroabietic and levopimaric acids,

(d) 20% by volume of a compound represented by the formula:
\[
\begin{array}{c}
\text{C}_n\text{H}_{2n+2} \quad \text{(CH}_2\text{-CH(OH)}_2\text{H} \\
\end{array}
\]
(e) 50% by volume of propylene glycol, and

(f) 10% by volume of water.

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