3,535,240
SULFOXIMINE CORROSION INHIBITOR FOR ACID SOLUTIONS
Warren L. Lyness, Mount Healthy, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio
No Drawing. Filed Aug. 24, 1967, Ser. No. 662,901
Int. Cl. E21b
U.S. Cl. 252—8.55

6 Claims

ABSTRACT OF THE DISCLOSURE
The attack of clean ferrous metal surfaces in contact with acid solutions such as pickling baths is inhibited by the use in such baths of unsymmetrical sulfoximines containing at least one long alkyl chain.

FIELD AND BACKGROUND OF THE INVENTION
This invention relates to inhibitors for acid solutions employed with ferrous metals such as in pickling or cleaning baths or oil well acid fracturing.

The treatment of metal surfaces with strong acids for the purpose of removing metal oxides and scale, is generally referred to as "pickling"; "pickling" is one method of preparing a metal surface for processes such as electro-deposition, 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 such as iron oxide 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 pervious to the constituents of the pickling liquor, and slough off rapidly because of the action of the acid. At the same time that the pickling liquor is attacking the metal surface directly beneath the unwanted coating, it is also attacking the already clean metal surfaces and dissolving off quantities of metal, often causing pitting or roughening, i.e., corrosion. Acid is used up needlessly in this type of chemical process. In order to prevent such corrosive attack on clean metal, inhibitors are generally added to the pickling liquor. These inhibitors slow down acid attack on clean surfaces. Thus, the rate of scale removal by pickling is substantially the same as without the inhibitor, while the loss of metal by acid corrosion is decreased.

Similar corrosion problems are encountered when acid solutions are employed in the cleaning of ferrous metal boiler tubes, condensers, heat exchangers and the like. Moreover, the ferrous metal piping, drills and casing involved in oil well acid fracturing also requires similar protective inhibition. Oil well acid fracturing involves the injection of strong acids down the ferrous metal casing of the well to fracture limestone and other minerals at the bottom of the well (by acid reaction). This fracturing increases yields of petroleum from oil-bearing strata.

OBJECTS
It is an object of this invention to provide an acid solution, such as a pickling bath, containing an inhibitor which effectively prevents corrosive acid attack on ferrous 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:

SUMMARY OF INVENTION
The acid compositions of this invention comprise a strong acid in aqueous solution and a corrosion-inhibiting amount of a sulfoximine having the formula:

\[
\text{O} \quad \text{R-S-R'}
\]

wherein R is an alkyl containing 6 to 22 carbon atoms and R' is methyl or ethyl.

DETAILED DESCRIPTION
The sulfoximine corrosion inhibitor compounds employed in the baths of this invention are known and described as detergent compounds in U.S. Pat. 3,255,116 of Jim S. Berry issued June 7, 1966.

The above sulfoximine formula describes the sulfur-oxygen bond and the sulfur-nitrogen bond as being of a semipolar nature, and is thus depicted as a convenient way of representation. R can be straight chain or branched chain alkyl having from 6 to 22 carbon atoms. Examples are listed below. The long chain alkyl can suitably be obtained from synthetic or natural sources.

Examples of sulfoximine inhibitor compounds include the following: hexyl methyl sulfoximine; octyl methyl sulfoximine; decyl methyl sulfoximine, dodecyl methyl sulfoximine, tetradecyl methyl sulfoximine, octadecyl methyl sulfoximine, decyl ethyl sulfoximine, dodecyl ethyl sulfoximine, tetradecyl ethyl sulfoximine, docosyl methyl sulfoximine, hexadecyl ethyl sulfoximine, octadecyl ethyl sulfoximine, eicosyl methyl sulfoximine, tetrapropylene methyl sulfoximine, 2-dodecyl methyl sulfoximine and docosyl methyl sulfoximine.

These sulfoximine inhibitors are employed in the acid solutions such as pickling baths in an effective inhibiting amount, generally about 0.01% to about 0.5% by weight of the solution, e.g., pickling bath. The sulfoximine inhibitors, being surface active agents and detergents, also aid in cleaning the ferrous metal as well as protecting it against corrosion.

The acid solutions, e.g., pickling baths, of this invention contain an effective pickling, cleaning or fracturing amount, generally from about 0.5% to 30% of a strong acid in aqueous solution. These strong acids can be any of the usual pickling, cleaning or oil well fracturing acids such as sulfuric acid, hydrochloric acid, acetic acid, perchloric acid, phosphoric acid, nitric acid and sulfamic acid. Best results of this invention are seen in HCl or H2SO4 solution baths. Ferrous salts such as FeCl3 can also be employed with the acid. Pickling and cleaning bath temperatures preferably range from about 100° F. to about 210° F. Oil well acid fracturing is also generally done with hot acid solutions at a temperature in this range or, in deep wells, the temperature at the bottom may be even higher, e.g., up to 250° F. or more.

The metals whose corrosion rate in an acid solution such as a pickling bath can be decreased by addition to the solution of the corrosion inhibitor of this invention include: mild steel, stainless steel, cast iron, high carbon steel, rephosphorized steel and the like.

The inhibiting action of the sulfoximines can be im-
proved by using along with the sulfoximine, a nonionic ethoxylated surface active agent. Preferably, such mixtures of these materials have a weight ratio in the range of about 5:1 to about 1:5 of sulfoximine to nonionic ethoxylated surfactant.

Nonionic ethoxylated surfactants can be broadly defined as compounds produced by the condensation of alkyne oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which can be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxykylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

(1) One class of nonionic surfactants is marketed under the tradename "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility, has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product.

(2) A alkynaphenolpolyethylene oxide condensates are condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, or none, for example.

(3) Nonionic surfactants can be derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine and include compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 10,000. Such compounds result from the reaction of ethylene oxide with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000.

(4) Other nonionic surfactants include condensation products of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol.

TEST PROCEDURE

In testing the corrosion inhibition capabilities of the baths of this invention, the following technique was followed, employing cold-rolled steel coupons, each weighing about 18 to 18.5 gms. and measuring 2" x 2" x 1 mm. These coupons were:

1. washed with Lava soap;
2. rinsed and dried thoroughly;
3. soaked for 1 minute in uninhibited aqueous 15% HCl solution at room temperature, 70° F.;
4. rinsed and dried thoroughly;
5. weighed;
6. soaked in 200 gms. of the pickling bath being tested for one hour at 180° F. (2 coupons for each test solution);
7. rinsed in water and dried;
8. weighed.

After final weighing the percent protection was calculated from the weight loss and the original coupon weight.

Inhibitor Percent Acid Percent Wt. loss Percent protection
Sulfoximine 0.1 HCl 15 0.009 90.1
Do. 0.2 HCl 15 0.014 90.5
Non. HCl 15 0.050 85.9
Sulfoximine 0.1 5 H3PO4 25 0.045 85.3
Non. 5 H3PO4 25 0.049 80.5
Sulfoximine 0.1 1 H2SO4 20 0.042 85.7
Non. 1 H2SO4 20 0.033 83.3
Sulfoximine 0.1 HCl 15 0.053 82.5
Non. HCl 15 0.022 83.2
Sulfoximine 0.1 5 H3PO4 20 0.015 94.6
Non. 5 H3PO4 20 0.012 93.5
Sulfoximine 0.1 HCl 15 0.021 83.5
Non. HCl 15 0.039 85.4
Sulfoximine 0.1 1 H2SO4 20 0.050 85.6
Non. 1 H2SO4 20 0.083 86.6

EXAMPLE 1

The following table shows the improved results of the inhibited, aqueous acid pickling baths of this invention, as compared to uninhibited baths; the sulfoximine inhibitor was decyl methyl sulfoximine in each case and the above-described test procedure was employed.

Inhibitor Percent Acid Percent Wt. loss Percent protection
Sulfoximine 0.1 HCl 15 0.009 90.1
Do. 0.2 HCl 15 0.014 90.5
Non. HCl 15 0.050 85.9
Sulfoximine 0.1 5 H3PO4 25 0.045 85.3
Non. 5 H3PO4 25 0.049 80.5
Sulfoximine 0.1 1 H2SO4 20 0.042 85.7
Non. 1 H2SO4 20 0.033 83.3
Sulfoximine 0.1 HCl 15 0.053 82.5
Non. HCl 15 0.022 83.2
Sulfoximine 0.1 5 H3PO4 20 0.015 94.6
Non. 5 H3PO4 20 0.012 93.5
Sulfoximine 0.1 HCl 15 0.021 83.5
Non. HCl 15 0.039 85.4
Sulfoximine 0.1 1 H2SO4 20 0.050 85.6
Non. 1 H2SO4 20 0.083 86.6

1 Nonionic is the condensation product of nine moles of ethylene oxide and 3 moles of a mixture of C4 to C8 secondary alcohol (Kyro EO).

The coupons pickled in the sulfoximine-inhibited baths were clean and free from iron oxide and scale. They were quite suitable for zinc coating, copper electropolishing or vitreous enameling.

EXAMPLE 2

Preparatory to zinc galvanizing, a 20-gallon mild steel trash can with a coating of rust and scale is pickled in a 50-gallon aqueous bath comprising 15% HCl and 0.1% decyl methyl sulfoximine inhibitor for 2 hours at 180° F. After pickling the can is bright and clean, but not pitted, and ready for dipping into molten zinc. Octylmethyl sulfoximine or dodecylmethyl sulfoximine at 0.1% levels can also be employed in this example.

EXAMPLE 3

Calcium bicarbonate scale is effectively removed from the tubes of a steel, horizontal-tube evaporator by boiling them for one hour with 1% solution of HCl containing 0.2% dodecylmethyl sulfoximine as an inhibitor. After rinsing with clear water, no pitting or corrosion is seen. 1% sulfamic acid can also be employed in such a scale removal process.

EXAMPLE 4

A hot (200° F.) 15% HCl solution containing 0.2% dodecylmethyl sulfoximine inhibitor is injected into the steel casing of an oil well, 7500 feet deep, for the purpose of fracturing limestone at the bottom of the well. Corrosion of the casing, steel piping and other drilling implements is markedly inhibited, while still achieving effective fracturing.

The foregoing description and examples of this invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variation and modifications therein will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

What is claimed is:
1. An inhibited composition for pickling or cleaning ferrous metal surfaces, or for use in oil well acid fracturing, consisting essentially of an aqueous solution of an acid selected from sulfuric acid, hydrochloric acid, acetic acid, perchloric acid, phosphoric acid, nitric acid, and
sulfamic acid and an effective amount of a sulfoximine corrosion inhibitor therefor having the formula:

\[
\text{O} \\
\text{R} - \text{S} - \text{R}^1 \\
\text{NH}
\]

wherein R is an alkyl containing 6 to 22 carbon atoms and R¹ is methyl or ethyl.

2. The composition of claim 1 wherein the solution is a pickling bath, the inhibitor is dodecyl methyl sulfoximine and the acid is hydrochloric acid or sulfuric acid.

3. The composition of claim 1 wherein the solution is an oil well acid fracturing solution, the inhibitor is dodecyl methyl sulfoximine and the acid is hydrochloric acid or sulfuric acid.

4. The composition of claim 2 wherein the sulfoximine concentration is from about 0.1% to 0.5% by weight.

5. The composition of claim 2 which contains a non-ionic ethoxylate surface active agent at a weight ratio in the range of about 5:1 to about 1:5 of the sulfoximine to the nonionic ethoxylated surfactant.

6. The composition of claim 3 wherein the sulfoximine concentration is from about 0.1% to 0.5% by weight and the acid is hydrochloric acid.

References Cited
UNITED STATES PATENTS
2,801,979 8/1957 Hager et al. ------------ 252—148
3,252,904 5/1966 Carpenter ------------ 252—8.55
3,255,116 6/1966 Berry --------------- 252—95

MAYER WEINBLATT, Primary Examiner
A. RADY, Assistant Examiner

U.S. Cl. X.R.
134—3, 41; 252—146, 148, 151, 391