

UNITED STATES PATENT OFFICE

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MEANS OF CLEANING AND PROTECTING METAL SURFACES

No Drawing.

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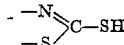
The present invention relates to a process of cleaning and preserving metal surfaces and to a process of removing scale and rust therefrom. The invention relates particularly to any and all processes wherein a metal surface is subjected to the action of an acid and comprises adding to the acid solution employed, a relatively small proportion of a suitable compound or mixture of compounds of the type hereinafter set forth, in order to diminish and substantially inhibit the pitting and roughening of the clean metal surface by the action of the acid thereon.

The invention is particularly applicable for use in the pickling of iron or steel wire, sheets or other like metallic objects, but is useful and readily adaptable in many other processes, such as for cleaning or freeing iron or steel in any form from rust, oxide or other deposits by means of dilute acids. Thus, the process hereinafter set forth is adaptable to the removal of deposits collecting within a water or steam circulating or distributing system and also for removing scale, such as boiler scale or the like from sheets and tubes. The preferred type of acid inhibitors may likewise be added to the acid transported in an acid tank car to prevent corrosion of the car by the acid and can likewise be used to diminish excessive corrosion by water in systems employing mine waters. The inhibitors disclosed are also adapted for use in the acid solution employed in treating mineral oil fractions in petroleum refineries as well as in other industrial applications wherein an acid other than highly concentrated acid is in contact with a metal surface.

Certain objects of the invention are, then, to prevent the pickle liquor from attacking clean portions of the surface of a metal; to obviate overpickling embrittlement and pitting of the articles treated; to prevent the escape of gases, vapors and acid spray from the pickle vat; to minimize the amount of metal lost in pickling; to increase the efficiency of the pickling operation and to prolong the effective life of the pickling bath and particularly to speed the pickling operation. Other and further objects of the invention will be apparent from the follow-

ing description and accompanying examples.

In addition to the sulfuric acid liquor ordinarily employed in the pickling step, the preferred composition for use therewith necessary to accomplish the various objects set forth, includes a compound or mixture of compounds having the property of lessening or inhibiting the solvent action of the acid employed upon the metal treated. As such inhibitors, the present invention discloses the use of mercaptans, that is compounds containing the C—SH grouping, and preferably those mercaptans wherein the sulph-hydrate group is attached to a carbon atom of a thiazole group, that is, the



group. Derivatives of mercaptans, such as the sulfids, disulfids, thiocyanates, sulfonates and the like as well as reaction products thereof, have also been found effective when employed as inhibitors. Although the preferred class of inhibitors have been used successfully, if desired they may be employed in conjunction with a foaming agent and/or with an organic solvent for the inhibitor.

In the examples hereinafter set forth of the preferred and improved means of carrying out the pickling process, conditions were employed which duplicated, so far as possible, those commonly followed in commercial practice, so far as concerned acid concentrations and temperatures employed. The heating of the metallic test strips in the pickling liquor was, however, from three to four times that ordinarily followed in practice for the acid concentrations employed.

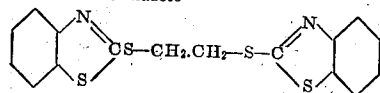
Test pieces of steel approximately three inches square were cut from a sheet after the annealing process had been carried out. The steel employed had a carbon content of approximately 0.04%. These pieces were then immersed in approximately 500 cc. sulfuric acid containing 8% by weight of 66° Baumé acid together with the quantity of inhibitor indicated in the table following. The test pieces were then subjected to the action of the pickle liquor for substantially an hour while being maintained at a tem-

perature of from 176 to 185° F. (80 to 85° C.). For this acid concentration, commercial practice is to pickle at approximately 165° F. (73.8° C.) for from fifteen to twenty minutes. In all cases, the results were compared with similar tests wherein no inhibitor was employed. The results obtained from one series of tests wherein a number of different mercaptans were tested as inhibitors are as follows:

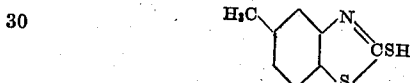
Inhibiting compound employed	Amount in gms.	Average iron loss in gms.
No inhibitor	0.00	0.357
Ethylene dithio-dibenzo thiazole	0.10	0.055
Ethylene dithio-dibenzo thiazole	0.05	0.064
Mercapto tolyl thiazole	0.10	0.019
Mercapto tolyl thiazole	0.05	0.014
Ethylene dithio-dimercapto tolyl thiazole	0.010	0.033
Ethylene dithio-dimercapto tolyl thiazole	0.05	0.040
Mercapto-benzo-thiazole thiocyanate	0.01	0.110
Mercapto-benzo-thiazole thiocyanate	0.05	0.090
Thio phenol	0.1	0.051

The inhibiting compounds set forth in the table possess the following chemical structures:

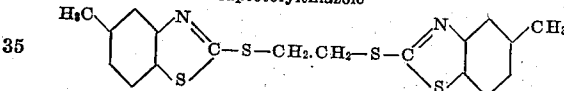
Ethylene dithiodibenzothiazole



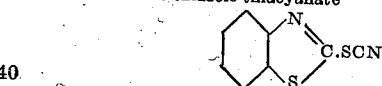
Mercapto-tolyl-thiazole



Ethylene dithiodimercaptotolylthiazole



Mercapto-benzo-thiazole-thiocyanate



and thiophenol C_6H_5SH .

The results given show that the loss in weight suffered by the iron test pieces when subjected to the pickle liquor containing an inhibitor is very much less than that resulting under similar conditions when no inhibitor is present in the acid bath.

Another series of tests were carried out under the conditions previously described but employing different inhibitors. The results so obtained were as follows:

Inhibiting compound employed	Amount in gms.	Average iron loss in gms.
None		0.315
Mercapto-benzo-thiazole	0.01	0.056
Mercapto-benzo-thiazole	0.05	0.036
Potassium mercapto-benzo-thiazole	0.01	0.020
Potassium mercapto-benzo-thiazole	0.05	0.016

The results of the foregoing tests corre-

spond in general to the first group of results set forth and show that mercaptan compounds, and particularly mercapto-thiazole compounds, when used in extremely small quantities in the pickle liquor, greatly decrease the solvent action of the acid upon the articles pickled. Even greater savings could, of course, be realized by the use of greater quantities of the inhibitor. In every case, the test pieces when taken from the pickle solution were clean and bright and particularly free from surface roughness or pitting.

The compounds of the type disclosed herein have also been found to be effective as inhibitors when used in the form of a sulfonated compound. Such compounds were prepared by treating the mercaptan with a suitable proportion of concentrated sulfuric acid and then heating the mixture at from 100 to 150° C. until fumes of sulfur dioxide were no longer evolved. Solvents of the inhibitors may also be employed in the pickle bath if desired. Thus, glycerine C_3H_5OH , ethylene-glycol C_2H_4OH , and other materials have been used as solvents in the process set forth. The following tests were carried out in accordance with the procedure hereinbefore described and the results set forth were obtained:

Compound	Amount used	Amount of iron loss
Ethylene dibenzo-thiazole sulfonated	0.01 gms.	0.047 gms.
Ethylene dibenzo-thiazole sulfonated	0.05 gms.	0.05 gms.
Ethylene glycol saturated with mercapto-benzo-thiazole	0.85 cc.	0.029 gms.
1 part mercapto-benzo-thiazole sulfonated with 25 parts 66° Bé. sulfuric acid	0.5 gms.	0.007 gms.
None	0.00	0.210 gms.

In the pickling process as carried out, it is customary to agitate the pickle liquor. Inasmuch as hydrogen or other gases are at times evolved in quite appreciable volumes during the process, the effect of agitation and gas evolution frequently results in the spattering of droplets of the acid solution. The loss of such acid is avoided and a consequent improvement of conditions in the vicinity of pickling baths results when a material is added to the acid liquor which forms a persistent foam blanket over the surface thereof. Such blanket not only serves substantially to prevent the spattering of the acid solution but also materially decreases the loss of gases when hydrochloric acid and the like are employed.

It has been found that when the salt of an aromatic primary amine, such as aniline sulfate, acetate and hydrochloride is treated with an aliphatic aldehyde, for example with aldol, the resulting product possesses an appreciable action as a pickle inhibitor but is particularly effective when employed in conjunction with other inhibitors because of its foam producing qualities. Thus, a series of

tests were carried out in the manner hereinbefore described in detail and the following results were thereby obtained:

5	Composition of inhibitor used	Amount used	Amount of iron loss
	None.....	None.....	0.213 gms.
	Potassium mercapto-benzo-thiazole plus aniline sulphate treated with aldol.....	0.05 gms..	0.020 gms.
10	Mercapto tolyl thiazole plus aniline sulphate treated with aldol.....	0.05 gms..	0.018 gms.
	10 cc. foamer, 20 cc. 66° Bé. sulphuric acid, 20 cc. glycerine, 1 gram mercapto-benzo-thiazole.....	0.85 cc....	0.022 gms.
	10 cc. foamer, 20 cc. 66° Bé. sulphuric acid, 20 cc. ethylene glycol, 1 gram mercapto-benzo-thiazole.....	0.85 cc....	0.021 gms.
15	20 cc. foamer, 20 cc. 66° Bé. sulphuric acid, 1 gram mercapto-benzo-thiazole.....	0.85 cc....	0.011 gms.
	20 cc. foamer, 20 cc. 66° Bé. sulphuric acid, 20 cc. ethylene glycol, 1 gram mercapto-benzo-thiazole.....	0.85 cc....	0.007 gms.

From the results set forth, it is evident that mercaptan compounds and derivatives thereof comprise a class of effective inhibitors in processes wherein metals are subjected to the action of an acid. Greater inhibiting action has been found to be produced by the use of a larger quantity of the various compounds than that set forth in the examples. It is not, however, necessary to employ an acid solution containing more than 1% by weight of the inhibiting compound. Equally characteristic results were also realized by the use of acids other than sulfuric, such as hydrochloric and nitric acids in the pickling bath and also in the treatment of other metals. Thus, copper, bronzes, and other alloys of various metals have been subjected to treatment by a pickle liquor in the presence of one of the preferred type of inhibitors set forth with the result that the loss of metal due to solvent action of the acid thereon was very materially decreased.

The examples hereinbefore set forth are to be understood as illustrative only and not at all limitative of the scope of the invention. Other examples are apparent to those skilled in the art to which the invention pertains wherein different acid concentrations, times of treatment and temperatures may be employed. The invention is to be considered as limited solely by the following claims wherein the invention is claimed as broadly as is possible in view of the prior art.

What is claimed is:

1. A metal treating compound comprising a highly ionized mineral pickle acid solution containing less than 1% by weight of a sulfonated mercaptan.

2. A metal treating compound comprising a highly ionized mineral pickle acid solution containing less than 1% by weight of a sulfonated mercapto aryl thiazole compound.

3. A pickling bath for iron and steel products comprising a highly ionized mineral pickle acid, a foaming agent, and a sulfonated mercaptan compound.

4. A pickling bath for iron and steel products comprising a highly ionized mineral pickle acid, a foaming agent, a sulfonated mercaptan compound and a solvent for said mercaptan.

5. A pickling bath for iron and steel products comprising sulfuric acid, a foaming agent, a sulfonated mercapto aryl thiazole compound, and an organic hydroxy compound as a solvent for said thiazole compound.

6. A pickling bath for iron and steel products comprising sulfuric acid, an aldehyde reaction product of the salt of an amine, a sulfonated mercapto-benzo-thiazole compound, and a polyhydroxy alcohol.

7. A pickling bath for iron and steel products comprising sulfuric acid, the aldol reaction product of aniline hydrochloride, a sulfonated mercapto-benzo-thiazole and ethylene glycol.

8. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion of a sulfonated mercaptan.

9. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion of a sulfonated mercapto-aryl-thiazole compound.

10. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion of a foaming agent and a sulfonated mercaptan compound.

11. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion of a foaming agent, a sulfonated mercaptan compound and a solvent for said mercaptan.

12. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion of a foaming agent, a sulfonated mercapto-aryl-thiazole compound and an organic hydroxy compound as a solvent for said thiazole compound.

13. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion of an aldehyde reaction product of a salt of an amine, a sulfonated mercapto-benzo-thiazole compound and a polyhydroxy alcohol.

14. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sul-

furic acid solution containing a small proportion of the aldol reaction product of aniline hydrochloride, a sulfonated mercaptobenzo-thiazole and ethylene glycol.

5 In testimony whereof I hereunto affix my signature.

JAMES C. VIGNOS.

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