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PRESERVATION OF METALLIC SURFACES

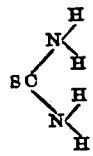
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The present invention relates to the cleaning and preservation of a metallic surface wherein the surface is in contact with liquids of an acid nature. More particularly, the invention relates to the prevention of excessive pitting and embrittlement of metals when subjected to a pickling process. The invention includes the provision of a regulator or inhibitor for causing the acid solution selectively to attack unclean portions of metallic surfaces immersed therein to the substantial exclusion of corrosive action upon the clean portions of the metal surface.

In the pickling process, the metal is treated with a dilute acid to remove rust, scale or other deposits. The acid solution in removing such deposits in the absence of any material preventing such action, also attacks clean portions of the metal thereby causing pitting or over-pickling of portions of the metallic surface. Such pitting is particularly detrimental and undesirable when the metal is to be plated, painted or galvanized and cold worked.

By means of the present invention the objectionable features of the pickling process are substantially overcome and eliminated. To accomplish this in accordance with the present invention, there is added to the pickling bath or other acid solution employed, a regulating agent or ingredient which acts to restrain the action of the acid in removing the scale or deposits, or in other words, the ingredients causes the acid selective to remove oxides and the like without materially attacking the clean portions of the metal surface.

The regulators or inhibitors which are disclosed in the present application comprise the unsymmetrically substituted thioureas, wherein one or more of the hydrogen atoms attached to separate nitrogen atoms in the formula



are unsymmetrically substituted, that is, are replaced by different alkyl or aryl groups.

The invention will be readily understood from the following description and examples. In the examples set forth for carrying out the metal pickling process, conditions were imposed 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 picking liquor in the manner as hereinafter set forth was, however, from three to four times that ordinarily followed in practice for the acid concentrations employed.

The test pieces of steel were approximately three inches square, cut from a sheet after the annealing process and having a carbon content of 0.04%. These pieces of steel were immersed in about 500 cc. of a sulphuric acid solution containing approximately 8% of 66° Baumé acid and a small quantity of one of the preferred type of inhibitors. Although the quantity of inhibitor used may vary between relatively wide limits, it has been found that particularly favorable results are realized when the proportion of inhibitor is from 0.01 to 0.1 of 1% of the weight of the acid solution employed. However, the amount of inhibitor used may if necessary or desirable be increased to that quantity which forms a saturated solution of the acid solution employed.

The test pieces were subjected to the action of the pickle liquor for approximately one hour at a temperature of from 176 to 185° F. (80 to 85° C.). For this acid concentration, it is commercial practice to pickle at approximately between 150–190° F., for from fifteen to twenty minutes. In all cases the results were compared with similar tests wherein the steel pieces were subjected under the conditions set forth to the action of an acid solution of the strength specified above but containing no inhibitor. Comparisons of the loss in weight suffered by the various test pieces give at once a measure of the inhibiting action exerted by the compunds tested. The unsymmetrically substituted thioureas hereinbefore stated as effective for preventing excessive deterioration of metals immersed in or subjected to the action of an acid solution

have been employed in the following manner.

A solution was prepared for use in pickling metals comprising about 500 cc. of sulphuric acid containing approximately 8% of 66° Baumé acid and about 0.10 grams of phenyl-p-tolyl-thiourea added. The resulting solution contained approximately 0.02% by weight of the substituted thiourea. Iron test strips were then immersed in the solution for about sixty minutes while maintaining the solution at a temperature of from 80 to 85° C. The loss in weight of the test strips resulting from the pickling treatment was found to be only about 11.6% of the loss that resulted when a similar test strip was pickled under the same conditions in an acid solution containing no inhibitor. In other words, the inhibitor decreased by about 8/9 the metal loss due to solvent action of the acid on the metal. When this loss was calculated on the surface exposed to the solution, it amounted to .00090 grams per square inch of surface exposed as compared with a loss of .00777 grams per square inch where no inhibitor was employed.

Identical tests made in which, however, symmetrically substituted thioureas, for example di-p-tolyl-thiourea and di-alpha-naphthyl-thiourea were used as inhibitors showed a much greater loss per square inch of surface exposed. The losses amounted to 0.0017 and .0036 grams respectively per square inch of surface exposed.

A similar test carried out in the manner as described, except that o-tolyl-m-xylyl-thiourea was employed as an inhibitor, yielded a result showing that the solvent action of the acid on the metal was decreased about 7/8. The loss of metal per square inch of surface exposed was 0.00094 grams as compared with a loss of 0.00777 grams per square inch of surface exposed where no inhibitor was employed.

A further test was made in which phenyl-o-tolyl-thiourea was used as an inhibitor. An acid solution of the strength mentioned and containing only 0.01% by weight of the inhibitor was found to be effective for obtaining the object desired. Such a solution was found to pickle test pieces of iron and steel in such a manner that the loss in weight due to the solvent action of acid was .00133 grams per square inch as compared to the loss of .00777 grams per square inch of surface exposed where no inhibitor is used.

As another example of the preferred type of inhibitor, a test was made in which an acid solution of the strength mentioned contained 0.02% by weight of o-tolyl-p-tolyl-thiourea. Such a solution was found to pickle iron and steel strips in such a manner that the loss was found to be .00127 grams per square inch as compared to the loss of .00777 grams per square inch of exposed surface where no inhibitor was used.

Other unsymmetrical substituted thioureas have also been found to possess a desirable inhibiting effect when employed in quantities comprising less than 1% of the pickle solution. Thus, for example, tests similar to those hereinbefore stated have been made in which o-tolyl-p-dimethyl-amino-phenyl-thiourea, phenyl-p-amido-phenyl-thiourea, p-dimethyl-amino-phenyl-thiourea have been found to exhibit desirable inhibiting qualities.

It is evident from the various examples hereinbefore set forth, that the unsymmetrical substituted thioureas 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 desirable, however, to use a greater quantity of inhibitor than will completely dissolve in the solution employed.

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 of the process described are apparent to those skilled in the art to which the invention pertains, wherein metals other than the one particularly described may be similarly treated or wherein different acids or different acid concentrations may be employed, or the times of treatment may be varied or different temperatures employed. The invention is to be considered as limited solely by the following claims wherein the invention is claimed as broadly as possible in view of the prior art.

What is claimed is:

1. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulphuric acid solution containing a small proportion of an unsymmetrically substituted thiourea.

2. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulphuric acid solution containing a small proportion of an unsymmetrically di-substituted thiourea.

3. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulphuric acid solution containing a small proportion of phenyl-p-tolyl-thiourea.

4. A pickling bath for iron and steel products comprising sulphuric acid containing a dissolved unsymmetrically substituted thiourea.

5. A pickling bath for iron and steel products comprising sulphuric acid containing a dissolved unsymmetrically di-substituted thiourea.

6. A pickling bath for iron and steel products comprising sulphuric acid containing not more than 1% of dissolved phenyl-p-tolyl-thiourea.

7. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulphuric acid solution containing a small proportion of an unsymmetrically di-aryl-substituted-thiourea.

8. A pickling bath for iron and steel products comprising sulphuric acid containing a dissolved unsymmetrically di-aryl-substituted-thiourea.

In testimony whereof I hereunto affix my signature.

JAMES C. VIGNOS.