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MEANS OF PRESERVING METALLIC SURFACES

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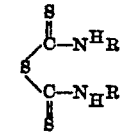
The present invention relates to the cleaning and preservation of a metallic surface wherein the surface is in contact with liquids of an acid nature. More particularly, the invention relates to the prevention of excessive pitting and embrittlement of metals when subjected to a pickling process. The 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 any corrosive action upon the clean portions of the metal surface.

In the art of pickling, the metal is treated with a dilute acid to remove rust, scale or other deposits. The acid solution removes the rust and scale, but in the absence of any material preventing such action, also attacks clean portions of the metal thereby causing pitting or over-pickling of the 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 ingredient causes the acid selectively 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 organic sulfur-containing compounds of a type wherein two sulfur atoms are joined to a single carbon atom, such carbon being also linked to a nitrogen atom. Such compounds are designated as thiuram sulfids and include mono and disulfid compounds represented as follows:



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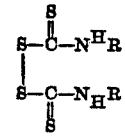


wherein R represents alkyl groups which may be the same or unlike groups.

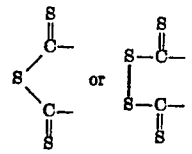
The invention will be readily understood from the following description and examples. In the examples set forth for carrying out the metal pickling process, conditions were imposed which duplicated, so far as possible, those commonly followed in commercial practice, so far as concerned acid concentrations and temperatures employed. The heating of the metallic test strips in the pickling 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.

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. of sulfuric acid solution containing approximately 8% by weight of 66° Baumé acid together with a small quantity of one of the preferred type of inhibitor. Although the quantity of inhibitor taken 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.

The test pieces were subjected to the action of the pickle liquor for approximately an

hour while being maintained at a temperature 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 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 compounds tested.

Thiuram mono and disulfids, which as hereinbefore indicated contain the grouping



respectively, have been found to be effective for preventing excessive deterioration of metals immersed in or subjected to the action of an acid solution. Thus a solution was prepared for use in pickling metals comprising 500 cc. of sulfuric acid containing approximately 8% by weight of 66° Baumé. To this acid solution there was added about 0.01 grams of di-allyl-thiuram disulfid. The resulting solution contained approximately 0.002% of the disulfid. 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 exposure to the pickling solution was observed to be only about 7.5% of the loss that resulted when a similar test strip was pickled under the same conditions in an acid solution containing no inhibitor. That is, the inhibitor decreased by about 13/14 the metal loss due to solvent action of the acid on the metal. This loss when calculated on the surface exposed to the solution amounted to but 0.00155 grams per square inch of surface exposed as compared with a loss of 0.0172 grams per square inch where no inhibitor was employed.

A similar test carried out in the manner as described, except that dimethyl-alpha-naphthyl-thiuram disulfid was employed in place of the inhibitor specified in the example, yielded a result showing that the solvent action of the acid on the metal was decreased by approximately 12/13. In other words, the loss in metal per square inch of surface exposed to the acid solution was but 0.0013 grams as compared with a loss of 0.0172 grams per square inch where no inhibitor was employed.

A further test was completed wherein di-ethyl-di-o-tolyl-thiuram disulfid was employed as an inhibitor in the manner as described. An acid solution of the strength mentioned and containing only 0.002% by weight of the inhibitor was found to be particularly effective for the object desired. Such a solution was found to pickle iron and steel strips in such a manner that the acid loss due to solvent action of the acid was only 3.8% as great as that taking place when no inhibitor was employed. This loss distributed over the area of surface exposed to the pickle solution amounted to only 0.00066 grams per square inch as compared with a loss of 0.01722 grams per square inch when no inhibitor was employed.

Other thiuram sulfids have also been found to possess a desirable inhibiting effect when employed in quantities comprising less than 1% of the pickle solution. Thus, tests similar to those hereinbefore set forth have been carried out wherein diethyl-diphenyl-thiuram disulfid, ethyl-thiuram disulfid, di-piperidyl thiuram disulfid and the like were employed as inhibitors and found to retard the action of acid upon a metal. By proceeding in a like manner, similar beneficial effects were ascertained to be exercised when thiuram disulfids were employed in a pickle liquor comprising hydrochloric acid. Other metals such as copper and the like were also protected from undue corrosion by acids when the preferred type of inhibitors were employed in the pickling liquor. It is evident from the various examples hereinbefore set forth, that thiuram mono and disulfids 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 nor is it desirable to use a greater quantity 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 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 possible in view of the prior art.

This application is a division of application Serial No. 246,917 filed on even date.

What is claimed is:

1. The process of cleaning a metal surface which comprises treating such metal with a sulfuric acid solution containing a small proportion of a thiuram disulfid.

2. The process of cleaning a metal surface

which comprises treating such metal with a sulfuric acid solution containing a small proportion of a dialkyl-diaryl-thiuram-disulfid.

3. The process of cleaning a metal surface which comprises treating such metal with a sulfuric acid solution containing a small proportion of a diethyl-di-o-tolyl-thiuram-disulfid.

4. A pickling bath for iron and steel products comprising a pickle acid containing a dissolved dialkyl-diaryl thiuram compound.

5. A pickling bath for iron and steel products comprising sulfuric acid containing a dissolved diethyl-di-o-tolyl thiuram compound.

6. A pickling bath for iron and steel products comprising sulfuric acid containing from 0.01% to not more than 1% of dissolved diethyl di-o-tolyl thiuram disulfid.

7. A pickling bath for iron and steel products comprising a pickle acid containing an aryl substituted thiuram disulfid.

In testimony whereof I hereunto affix my signature.

JAMES C. VIGNOS.