

UNITED STATES PATENT OFFICE

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CLEANING AND PRESERVATION OF METALLIC SURFACES

No Drawing.

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The present invention relates to the cleaning and preservation of metallic surfaces wherein the surface is in contact with liquid 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 clean portions of the metal surface.

Certain objects of the invention are to prevent the pickle liquor from attacking clean portions of the surface of a metal; to obviate over pickling, 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 following description and accompanying examples.

In the art of pickling, the metal is treated with a dilute acid to remove rust, scale and other deposits, after which the metal is preferably washed with water and dipped into an alkaline bath to remove the last traces of the free acid. The acid removes the rust and scale but unfortunately, from the pickling standpoint, it attacks the cleaned metal itself, producing an evolution of hydrogen gas, which escapes into the air carrying with it a fine spray of the pickling bath producing an atmosphere possessing corrosive properties and one which is highly injurious to health.

By the present invention these objectionable features of the pickling process are substantially overcome. To accomplish this in accordance with my invention there is added to the pickling bath a regulating agent or ingredient which acts to restrain the action of the acid in removing the rust, scale and other deposits, or in other words it selectively removes said materials without materially attacking the free metal. At the same time the

said regulating agent or ingredient produces a foam, which acts as a blanket over the surface of the pickle liquor, thereby substantially preventing the escape of appreciable quantities of particles of pickle liquor into the atmosphere.

The regulator or inhibitor and foam-producing agent, as disclosed in the present application, comprise sulfonated organic compounds and preferably sulfonated creosote oils; that is, the creosote oil of commerce which has been treated with sulfuric acid. Creosote oil is generally regarded as the fraction obtained during the distillation of coal tar, which is collected between the light oil fraction and the anthracene fraction. It may or may not include the middle oils or those portions of them remaining after partial or complete removal of tar acids or naphthalene.

One method by means of which the preferred material may be prepared follows: Substantially one part by weight of creosote oil and substantially two parts by weight of approximately 66° Bé. commercial sulfuric acid were mixed in a suitable container equipped with a means of agitation. After the materials were thoroughly mixed, heating with agitation was continued until substantial sulfonation of the oil had taken place, for example, for about 1.5 hours at approximately 120 to 125° C. The resulting product was then passed into a storage tank where it was allowed to stand for a sufficient period of time to permit a complete separation of the unsulfonated oil from the product. The unreacted oil thus separated was added to a succeeding batch of creosote oil to be sulfonated.

Other methods for the preparation of the preferred materials have been employed wherein different ratios and concentrations of acid and different periods of heating and temperatures were used. Thus, in the use of fuming sulfuric acid a shorter heating period or a lower temperature may be employed.

In the example 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 longer than that ordinarily followed in commercial 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 containing approximately 8% by weight of 66° Bé. acid together with a small quantity of the preferred type of inhibitor.

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 150 to 190° F. (66 to 88° C.) for from 5 to 10 minutes. In all cases, the results were compared with similar tests wherein the steel pieces were subjected, under the condition set forth, to the action of an acid solution of the strength specified above but containing no inhibitor. Comparison of the loss in weight suffered by the various test pieces gives at once a measure of the inhibiting action of the compound tested.

The following table shows a comparison between the loss in weight in the steel test pieces when the preferred inhibitor was used and when no inhibitor was used.

Inhibiting compound employed	Amount of inhibitor employed	Average iron loss in grams	Loss of weight in grams per sq. inch of surface exposed
Sulfonated creosote oil.....	1 cc.	0.0172	.00095
Sulfonated creosote oil.....	0.5 cc.	0.0467	.00260
Sulfonated creosote oil.....	.02 g.	0.185	.0103
Sulfonated creosote oil.....	.05 g.	0.174	.0097
Sulfonated creosote oil.....	.10 g.	0.170	.0094
None.....		0.396	.0220

The results given show in all cases that the loss in weight suffered by the test pieces when subjected to the pickle liquor containing the preferred inhibitor is very much less than that resulting under similar conditions when no inhibitor is present in the acid. In all tests as carried out in the above indicated manner sulfonated creosote oil not only inhibited the action of the acid on the cleaned metal, but also produced a very satisfactory foam, thus substantially prohibiting the carrying of small particles of the acid liquor into the surrounding atmosphere.

A sample of commercial creosote oil from which the tar acids and bases were removed was fractionated and cuts made every 5° C. rise in temperature. These fractions were sulfonated and on testing in the manner hereinbefore described, all inhibited the action of the pickle liquor on the steel test pieces. The

tar acids and the sulfonated distillation residue likewise functioned as inhibitors.

Tests were also made in the manner described on the inhibiting action of the following sulfonated aromatic compounds: sodium benzene sulfonate, sulfonated guaiacol, sulfonated benzyl disulfid, sulfonated cresylic acid, naphthalene disulfonic acid, sulfonated di-p-tolyl-ethane, sulfonated di-xylyl ethane, sulfonated diphenyl-urea, phenol sulfonic acid, sulfonated alpha-naphthylamine, sulfonated diphenyl-guanidine. All of these materials showed favorable results as inhibitors.

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 sulfuric acid solution containing a small proportion of sulfonated creosote oil.
2. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution to which is added a small proportion of creosote oil treated with sulfuric acid.
3. A process of pickling iron and steel products which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution to which is added a small proportion of creosote oil heated with sulfuric acid at approximately 120 to 125° C.
4. A pickling bath for iron and steel products comprising sulfuric acid containing a small proportion of sulfonated creosote oil.
5. A pickling bath for iron and steel products comprising sulfuric acid to which is added a small proportion of creosote oil treated with sulfuric acid.
6. A pickling bath for iron and steel products comprising sulfuric acid to which is added a small proportion of creosote oil heated with sulfuric acid at approximately 120 to 125° C.

In testimony whereof I hereunto affix my signature.

JAMES C. VIGNOS.