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SOLVENT INHIBITOR FOR THE ACID TREATMENT OF METALS

No Drawing.

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This invention relates to the acid treatment of metals. It has been known for some time that oxides, salts, rust and other corrosion products may be removed from the surfaces of metals by suitable treatment in an acid bath. One of the disadvantages connected with such a treatment of a metal has been the degree to which the acid bath attacked the free metal in addition to the undesirable corrosion products. For the purposes of inhibiting this solvent action on the free metal certain types of substances have been heretofore added to the acid bath. Examples of such inhibitors are mouldy flour, size or glue, the sulfonation product of slaughter house waste, the acid extract of coal sludges from the sulfuric acid treatment of coal tar or petroleum, carbazole, pyridine, aniline, quinoline, etc. None of these substances, however, afford all that could be wanted with respect to desirable qualities as inhibitors.

We have found that certain mercaptans possess to a very marked degree the desirable properties of inhibiting the action of acids upon metals, while permitting the acids to attack undesirable corrosion products. The inhibiting quality is possessed to a very marked degree by mercaptans of the class R-SH in which R is either an alkyl or aryl nucleus. The effectiveness as inhibitors varies somewhat with the particular mercaptan, the concentration of acid, the kind of acid, the kind of metal, and the temperature at which the acid solution is maintained. The inhibiting action, however, is not restricted to any particular mercaptan or to any particular condition of concentration temperature or kind of acid. Under all conditions the rate of solution of the free metal is materially reduced.

As an example of the effectiveness of mercaptans, mild steel was treated with an aqueous solution containing 5% sulphuric acid; the acid bath was maintained at a temperature of 60° C. Two samples of equal weight from the same batch of steel were treated in two separate acid solutions under the above conditions, and to one of the solutions was added 0.03% of thio phenol. The untreated,

or blank sulphuric acid solution, dissolved 100 parts of free metal during the same time in which the sulphuric acid solution containing thio phenol dissolved 3.9 parts of free metal. Translated to terms of percentage, the thio phenol inhibited the solution of the metal to the extent of 96.1%.

Under the same conditions employing the same amounts of differing mercaptans, the following results were obtained:

Mercaptan	Per cent inhibition
Thio phenol	96.1
Thio beta naphthol	93.1
Benzyl mercaptan	99.93
Iso amyl mercaptan	99.93
Iso propyl mercaptan	99.84

Amino substituted mercaptans, such as 2-amino-5-ethoxy-thiophenol and 1-mercapto-2-amino-anthraquinone show satisfactory inhibiting properties.

The mercaptans may be employed as inhibitors with advantage in a number of operations, as for example, in the commercial pickling of iron and steel, in the removal of rust of corrosion products from the interior of piping where it is inconvenient to dismantle the piping, in the preparation of metals for electroplating where it is desirable to remove oxides and other corrosion products without removing the free metal and particularly without injuring the surface of the metal. We have found the mercaptans to be very efficient inhibitors where employed in the acid treatment of ferrous metals.

The amount of inhibitor employed will, of course, vary in accordance with the requirements of the operator. For example, in the pickling of heavy, cheap materials, such as, for instance, iron castings, an inhibition of 75 to 90% might be quite satisfactory to the pickler, while in the case of relatively valuable material, such as the finer grades of iron or seamless tubing, the pickler might be dissatisfied with less than 99% or even better inhibition. The amount of inhibition varies somewhat with the kind and amounts of inhibitor employed, although any measurable quantity of inhibitor will produce some retardation of solution.

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adding
agent

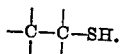
It is sometimes advantageous to mix with the inhibitor a substance which will cause the former to readily become wet with acid, or which will tend to disperse it quickly and thoroughly throughout the acid. Any of the substances ordinarily used for dispersing materials in an acid medium may be applied, such for example as cellulose sulfite pitch, Turkey red oil, Twitchell's reagent, aldehyde condensation products of naphthol sulfonic acids, petroleum sludge acids, some of the higher aldehydes, water soluble carbohyrates, etc. We may also accomplish the dispersion of the inhibitor by first dissolving it in strong acid, such for example as 96° sulfuric acid or strong hydrochloric acid. We may, in fact, in some cases where the inhibitor is not affected adversely by strong acid, market it in solution in strong sulfuric acid, such as 60° or 66° acid.

In the pickling of metal products, such as plates and tubes, in dilute sulfuric acid, it has been found that the use of an inhibitor may slow up the pickling action materially; it may even double the time required for pickling. Since this is a disadvantage in the use of pickling agents, we have been interested in finding a method to accomplish the pickling operation more quickly in the presence of inhibitors. We may accomplish this by using with the inhibitor, and preferably mixing with it before addition to the acid, a metallic chloride such for example as sodium chloride, in such quantity that hydrochloric acid will be formed in amounts sufficient to substantially reduce the time required for pickling.

We do not wish to be limited to the specific mercaptans listed above, which it should be understood are given only as examples; nor do we wish to be limited to the amounts of inhibitor or conditions under which the inhibitor is used. Nor do we wish to be limited to any particular acid since any acid normally useful in pickling operations may be employed. On the contrary, we desire our invention to be limited only as defined in the appended claims.

We claim:

1. The process of treating metals which comprises subjecting the metal to an acid solution containing a mercaptan of the type:



2. The process of treating metals which comprises subjecting the metal to an acid solution containing a compound of the type R-SH in which R is a hydrocarbon group directly attached to the S atom.

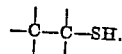
3. The process of treating ferrous metals which comprises subjecting the metal to an acid solution containing a mercaptan compound of the type R-SH in which R is a

hydrocarbon group directly attached to the S atom.

4. The process of treating ferrous metals which comprises subjecting the metal to a sulphuric acid solution containing a mercaptan compound of the type R-SH in which R is a hydrocarbon group directly attached to the S atom.

5. In the pickling of metals the step which comprises subjecting the metal to an acid bath containing a mercaptan compound of the type R-SH in which R is a hydrocarbon group directly attached to the S atom.

6. A solution of the type adapted for the acid treatment of metals which contains a mercaptan of the type:



7. A solution of the type adapted for the acid treatment of metals which contains a mercaptan of the type R-SH in which R is a hydrocarbon group directly attached to the S atom.

8. A solution of the type adapted for the acid treatment of ferrous metals which contains a mercaptan of the type R-SH in which R is a hydrocarbon group directly attached to the S atom.

9. The process of treating ferrous metals which comprises subjecting the metal to a sulphuric acid solution containing thiophenol.

10. The process of treating ferrous metals which comprises subjecting the metal to a sulphuric acid solution containing benzyl mercaptan.

11. The process of treating ferrous metals which comprises subjecting the metal to a sulphuric acid solution containing iso-propyl mercaptan.

12. A solution of the type adapted for the acid treatment of metals which contains thiophenol.

13. A solution of the type adapted for the acid treatment of metals which contains benzyl mercaptan.

14. A solution of the type adapted for the acid treatment of metals which contains iso-propyl mercaptan.

In testimony whereof we affix our signatures.

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