This invention relates to the cleaning and preservation of the surfaces of iron and steel products and more particularly to improvements in the art of pickling iron and steel with dilute solutions of mineral acids.

In the manufacture of iron and steel products such as sheet, rod, wire and other shapes which are subjected to hot rolling, drawing, forging, annealing and other processes, particularly those involving heating of the metal, a scale is formed thereon which it is necessary to remove for reasons well known in the art. Pickling is a process in which the metal is subjected to the action of a dilute mineral acid bath, most commonly of sulfuric acid but sometimes of hydrochloric acid or a mixture of sulfuric and hydrochloric acids, which removes the scale. Unless some material is added to the pickling bath in the nature of an "inhibitor", or selective controlling agent, the acid not only removes the scale but also attacks and consumes the underlying metal. Such attack results in metal loss and pitting of the metal surface. It produces hydrogen gas and acid fumes due to spray caused by bubbles of the gas rising to the surface of the bath. There is an unnecessary consumption of acid with decreased life of the bath. The metal surface is left in a condition liable to rapid corrosion. The hydrogen evolved also causes "acid brittleness" of the steel which is highly undesirable. Moreover, steel contains both iron and carbon and when acid dissolves the iron, the carbon, which is insoluble, remains on the surface of the steel as a black sludge.

A closely related problem is the storage or transportation of dilute sulfuric acid in ferrous metal containers such as tank cars. The use of inhibitors in the acid prevents or reduces the rate of attack of the acid to the point where such metal containers can be used.

The present invention has for its principal object the improvement of inhibitors. More particularly the objects are to provide an inhibitor which reduces attack on the clean metal to a minimum; which reduces the amount of sludge formed in pickling baths; which reduces the consumption of acid and prolongs the life of the bath; which passivates the metal surface rendering it, to a considerable degree, resistant to corrosion; which enables pickling baths to be used at higher temperatures; which leaves the surface of the metal chemically clean and ready for the application of finishing coatings such as plating, painting or lacquering; and which improves the appearance of the pickled metal by leaving a uniformly whiter (i.e., more silvery) surface, thus improving its salability. Other incidental objects and advantages are the elimination of gases and fumes in the pickling process and the prevention of acid brittleness of the steel.

The foregoing objects are attained, in accordance with this invention, by the use in dilute solutions of mineral acids used for pickling of the novel inhibitors hereinafter described. These inhibitors selectively control the action of the acid solution so that it attacks and removes the scale with great efficiency but does not attack the clean metal surface to any appreciable degree. Moreover the surface of the metal is left chemically clean, has a white or silvery lustrous appearance without spots or blemishes, and is highly passive toward oxidation.

The invention resides in the discovery that greatly improved results are obtained, in comparison with known inhibitors, by using as a selective controlling agent a mixture of di ortho xenyl thiourea and an alkali metal sulfate to which there is preferably added a suitable wetting agent; it has also been discovered that the addition to this combination of a small amount of glue still further improves the results.

The wetting agent, which is an ingredient of the inhibitor of the invention, should be one which does not hydrolyze in solution and it is also important that it should not break down or decompose in an acid pickling bath, such as the usual dilute sulfuric acid solution of from 3% to 15%. It is preferred to use a wetting agent of the alkylaryl sulfonate type rather than a sulfated alcohol.

The term "alkali metal sulfate" is used herein and in the claims to denote the sulfates of sodium and potassium. It is preferred to use Glauber's salt (sodium sulfate dehydrate) though anhydrous sodium sulfate, the monohydrate or heptahydrate may be used equally well, if appropriate changes in the proportions of the ingredients of the inhibitor are made to compensate for the varying amounts of water of crystallization in the different salts. Potassium sulfate may also be used in the same manner as sodium sulfate.

The glue used in the inhibitor is preferably animal bone glue. Bone glue commercially known as 60 to 75 gram glue is well suited to this use. Hide glue is not as desirable because of properties attributable to the chemicals used in preparing the hides from which it is derived.

For a better understanding of the invention and to enable those skilled in the art to practice
the same the following specific examples are given by way of illustration.

Example I.—Equal parts by weight of di ortho xenyl thiourea and sodium decyl benzene sulfo-

name "Santonmerse D" (a wetting agent) are ground together in the dry state in a ball mill to a

particular steel to be pickled.

In making up a pickling bath the required amount of water is usually put into the tank first

and the acid then added. Such baths are usually operated at from 140° to 190° F. When the bath

is brought up to the desired temperature the dry inhibitor is added to the path, in which it is

stantly dissolved. Or, if desired, the inhibitor can be preliminarily mixed in a bucket of the

of the metal pickled is not as white and the apparent Selective affinity of the inhibitor is not as

in the following ranges: the di ortho xenyl thiourea 5% to 10%; the wetting agent 1.25% to 10%; the

Glauber's salt 75% to 87%; and the glue 3% to 10%. These ranges, however, are not to be taken

endless. It is to be understood that the invention is not limited to the features herein specifically

described but can be carried out in other ways without departing from its spirit, within the purview of

What is claimed is:

1. An inhibitor for substantially preventing the dissolution of iron or steel in dilute solutions of

2. An inhibitor for substantially preventing the dissolution of iron or steel in dilute solutions of

3. An inhibitor for substantially preventing the dissolution of iron or steel in dilute solutions of

4. An inhibitor for substantially preventing the dissolution of iron or steel in dilute solutions of

5. An inhibitor for substantially preventing the dissolution of iron or steel in dilute solutions of

about 10% sodium decyl benzene sulfonate, from about 75% to about 87% Glauber's salt, and from about 3% to about 10% bone glue.

6. A pickling bath for iron and steel products comprising water, a non-oxidizing mineral acid, and an inhibitor comprising minor proportions by weight of di ortho xylene thiourea, bone glue, and a wetting agent stable in the acid solution, and a major proportion by weight of sodium sulfate.

7. A pickling bath for iron and steel products comprising water, a non-oxidizing mineral acid, and an inhibitor comprising, by weight, from about 5% to about 10% di ortho xylene thiourea, from about 1.25% to about 10% sodium decyl benzene sulfonate, from about 75% to about 87% Glauber's salt, and from about 3% to about 10% bone glue.

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