

## UNITED STATES PATENT OFFICE

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## METAL PICKLING PROCESS

Albert Klamroth, Cologne-Mulheim, and Hans Ahrens, Leverkusen-Wiesdorf, Germany, assignors to I. G. Farbenindustrie Aktiengesellschaft, Frankfurt-on-the-Main, Germany

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10 Claims. (Cl. 148—8)

The present invention relates to the cleaning and preservation of metallic surfaces wherein the metal is in contact with a liquid of an acid nature. More particularly, the invention relates to the prevention of excessive pitting and embrittlement of a metal when subjected to a pickling process by treatment with a dilute solution of a non-oxidizing acid.

Certain objects of the present invention are to prevent the acid pickle liquor from attacking clean portions of the surface of a metal; to obviate over-pickling, embrittlement and pitting of the articles treated; to minimize the amount of metal lost in pickling; to increase the efficiency of the pickling operation; to prolong the effective life of the pickling bath; and particularly to facilitate the pickling operation. Other and further objects of the invention will be apparent from the following description and accompanying table.

In the art of pickling, the metal is treated with a dilute acid to remove oxides such as 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 free acid. The acid removes the rust and scale, but unfortunately, from the pickling standpoint, unless some agent to prevent such action is present, it attacks the cleaned metal itself thereby causing loss of metal and producing an evolution of hydrogen gas, which escapes into the air, carrying with it a fine spray of the acid liquor from the pickling bath and producing an atmosphere possessing corrosive properties and one which is injurious to health and damaging to equipment.

By the present invention, these objectionable features of the pickling process are substantially overcome or reduced to a minimum. To accomplish to as great an extent as possible the objects set forth in accordance with the present invention, there is added to the pickling bath, a regulating agent or ingredient which acts to restrain the action of the acid from attacking clean metal but assists in removing the rust, scale and other deposits, or in other words the regulator or inhibitor causes the acid selectively to remove such materials without appreciably attacking the clean portions of the metal under treatment.

The pickle regulator or inhibitor, as disclosed in the present application, comprises an organic

sulfoxide. The following sulfoxides have proved to be very effective as solvent inhibitor: benzylsulfoxide, dibenzylsulfoxide, diphenylenesulfoxide, polymerized diethylenesulfoxide, thioanthrenesulfoxide. In general all organic sulfoxides of the aliphatic as well as of the aromatic series yield good results in metal pickling.

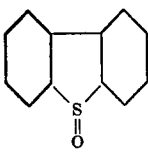
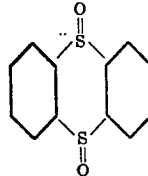
The sulfoxides may be employed as inhibitors with advantage in a number of operations, as for example, in the commercial pickling of iron and steel, in the removal of rust of corrosion products from the interior of piping where it is inconvenient to dismantle the piping, in the preparation of metals 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 sulfoxides to be very efficient inhibitors where employed in the acid treatment of ferrous metals, but also in the treatment of other metals, such as zinc, tin and aluminium.

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.

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 carbohydrates, etc.

The following table shows the results of some tests made with the addition of different sulfoxides to pickling baths at different temperatures.

The tests were performed by using band iron pieces of 8x1.6x0.075 cm. and having a weight of about 5 grams; as acid 100 ccs. of sulfuric acid of 20% concentration were employed, and each test was executed with 0.1% of sulfoxide calculated on the metal.

	Kind of sulfoxide	Reaction time	Temperature	Decrease in weight
		Hours	° C.	Grams
10	Benzylsulfoxide $C_6H_5CH_2-S(=O)-CH_2C_6H_5$	2 2 2	60 80 90	0.02 0.025 0.03
15	Diphenylsulfoxide $C_6H_5-S(=O)-C_6H_5$	2 2	60 90	0.02 0.03
	Diphenylenesulfoxide	2	60	0.02
20				
25	Polymerized diethylenesulfoxide $(C_2H_4-S(=O)-C_2H_4)_x$	2 2	60 90	0.01 0.015
30	Thioanthrenesulfoxide	2	60	0.04
35				
40	No addition	1	80	2.7

A test executed with only 0.01 gram of a sulfoxide gave the following result:

	Hours	° C.	Grams decrease
45 Benzyl sulfoxide	2	70	0.02
Do	2	90	0.03

We do not wish to be limited to the specific sulfoxides 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 a non-oxidizing acid solution containing an organic sulfoxide.

2. The process of treating metals, which comprises subjecting the metal to a non-oxidizing acid solution containing an aromatic sulfoxide.

3. The process of treating metals, which comprises subjecting the metal to a non-oxidizing acid solution containing benzylsulfoxide.

4. The process of treating metals, which comprises subjecting the metal to a non-oxidizing acid solution containing an aliphatic sulfoxide.

5. The process of treating metals, which comprises subjecting the metal to a non-oxidizing acid solution containing polymerized diethylenesulfoxide.

6. A solution of the type adapted for the acid treatment of metals which contains an organic sulfoxide.

7. A solution of the type adapted for the acid treatment of metals which contains an aromatic sulfoxide.

8. A solution of the type adapted for the acid treatment of metals which contains benzylsulfoxide.

9. A solution of the type adapted for the acid treatment of metals which contains an aliphatic sulfoxide.

10. A solution of the type adapted for the acid treatment of metals which contains polymerized diethylenesulfoxide.

ALBERT KLAMROTH.  
HANS AHRENS.