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PICKLING INHIBITOR AND PROCESS

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This invention relates to inhibitors for acids, and to processes employing the same, and is particularly directed to processes and compositions which employ, in conjunction with an acid, an inhibitor comprising a substituted thiourea containing a hydrogenated aryl group.

Pickling and metal cleaning operations frequently involve the use of a bath of dilute, non-oxidizing acids such as sulfuric, hydrochloric, acetic, formic, aqueous solutions of acid sulfates, and the like. Such baths are used for numerous purposes, a typical example of which is the pickling of iron or steel articles such as wire, sheet, and other manufactures. The composition, concentration, temperature of operation, and other factors vary with different baths, but in every instance the primary function of a bath is the removal of undesirable incrustations. As soon as the base metal becomes exposed, it is, in the absence of an inhibitor, attacked by the bath with subsequent damage to the article and with an unnecessary consumption of acid.

It has already been proposed to add organic inhibitors to metal cleaning and pickling baths to diminish the attack of the clean base metal by the acids. Among the inhibitors heretofore employed are the thioureas, and by the use of aryl substituted thioureas a considerable diminution of undesirable acid attack is accomplished.

I have found that substituted thioureas which contain a hydrogenated aryl group are of exceptionally high efficiency as inhibitors and are possessed of numerous desirable qualities. Such substituted thioureas are prepared, generally, by the reaction of a hydrogenated aromatic amine with carbon disulphide.

The following example illustrates the production and use of a novel compound of this invention.

Example:

The product of this example, symmetrical di-1-methylcyclohexyl thiourea, was prepared as follows: 87.5 g. of 1-methylcyclohexylamine, 55 g. of carbon disulfide, 0.8 g. of sulfur, and 200 g. of water were placed in a one liter round bottom flask and heated under reflux. An oil first separated from the reaction mixture which was converted into a solid after about 14 hours refluxing. The reaction mixture was cooled, giving 150 g. of crude crystalline product which was recrystallized from 150 g. of alcohol. The final product was a white powder which melted at 202–203° C. and was found to have a nitrogen content of 10.37% as compared with 10.44% as the calculated value for the thiourea. It has a slight aro-

matic odor which is not objectionable. The product is not completely soluble in five per cent sulfuric acid, but is substantially so.

The product of this example, dimethylcyclohexyl thiourea, displays a very high efficiency as an inhibitor. When 0.001% of dimethylcyclohexyl thiourea was employed with a five per cent sulfuric acid pickling solution, the corrosion of steel was reduced almost ninety-nine percent. Under the same conditions, the same amount of diorthotolyl thiourea reduced the corrosion only about sixty per cent.

The inhibitor of this example, dimethylcyclohexyl thiourea, displayed very high efficiency, as seen above, when only a small amount was present. It is noted that when only 0.0006% was used, the corrosion was reduced sixty per cent. It is believed that it is the presence of the reduced aryl substituent which results in the marked increase in efficiency noted with the compounds of this invention.

Numerous other cyclohexyl thioureas may be used according to this invention. I may, for instance, use symmetrical di-cyclohexyl thiourea, symmetrical di-3-methylcyclohexyl thiourea, symmetrical di-1-hydroxycyclohexyl thiourea, alpha-cyclohexyl beta-ethyl thiourea, tetracyclohexyl thiourea, alpha-alpha-dicyclohexyl thiourea, alpha-cyclohexyl-beta-methylcyclohexyl thiourea or monocyclohexyl thiourea. Such substituted thioureas containing at least one cyclohexyl group constitute the preferred inhibitors of this application.

The best results have been obtained using thioureas substituted with a cyclohexyl group, but thioureas with other hydrogenated aromatic groups may advantageously be employed. I may, for instance, use symmetrical di-decahydro-alpha-naphthyl thiourea.

While the inhibitors of this invention may be employed in widely varying amounts, it is usually desired to use between about one one-thousandth and one per cent by weight.

The inhibitors of my invention are compatible with conventional dispersing and foaming agents, such as sulfite cellulose waste, saponin, soap bark, and gum arabic, and may advantageously be employed in conjunction therewith. The inhibitors of my invention may, of course, be used in conjunction with acids for purposes other than metal cleaning as are inhibitors known to the art.

While I have shown certain specific compounds above, it will be understood that I do not intend to be limited thereto as numerous substi-

tuted thioureas containing a hydrogenated aryl group may readily be prepared by those skilled in the art.

I claim:

- 5 1. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of an acid cleaning solution in the presence of a small amount of a substituted thiourea containing a hydrogenated aryl group.
- 10 2. In a process of cleaning and pickling metals, the step comprising subjecting the metal to the action of an acid cleaning solution in the presence of a small amount of a substituted thiourea containing a cyclohexyl group.
- 15 3. In a process of cleaning and pickling met-

als, the step comprising subjecting the metal to the action of an acid cleaning solution in the presence of a small amount of dimethylcyclohexyl thiourea.

4. A pickling and cleaning composition comprising a non-oxidizing acid and a substituted thiourea containing a hydrogenated aryl group.

5. A pickling and cleaning composition comprising a non-oxidizing acid and a substituted thiourea containing a cyclohexyl group.

6. A pickling and cleaning composition comprising a non-oxidizing acid and dimethylcyclohexyl thiourea.

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