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PICKLING OF METALS

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20 Claims. (Cl. 252—150)

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This invention relates to the cleaning of metallic surfaces and particularly to processes and compositions which employ steel pickling inhibitors herein described in conjunction with an acid.

Pickling solutions for removing oxides from the surfaces of metals ordinarily consist largely of a dilute solution of an inorganic acid such as sulfuric or hydrochloric acid. The acid although it dissolves the oxides and scale, also attacks the metal to some extent so that the acid is largely consumed and a certain amount of metal is lost. It also appears that the hydrogen liberated by the action of the acid on the metal has a serious embrittling effect upon the metal being treated. The escaping hydrogen also carries with it a fine spray of the acid liquor from the pickling bath which produces an atmosphere possessing corrosive properties and one which is injurious to health and damaging to equipment.

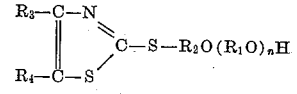
By the present invention, these objectionable features of the pickling process are substantially overcome or reduced to a minimum. More specifically, some of the objects of the present invention are to obviate over-pickling, embrittlement and pitting of the articles treated; to minimize the amount of 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 examples.

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 an inhibitor or regulating agent 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 inhibitor causes the acid selectively to remove such materials without appreciably attacking the clean portions of the metal under treatment.

The new class of pickle regulators may be classed as hydroxy polyether derivatives of mercapto thiazoles. Hydroxy ethyl mercapto thiazoline is known to be a pickling inhibitor but it is not soluble in the pickling baths and special techniques have been attempted in order to disperse the material in the acid cleaning solutions. However, it has now been found in accordance with the present invention that the hydroxy polyether derivatives of mercapto thiazoles are highly effective pickle regulators which are at the same time soluble in the pickling baths. The

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new inhibitors contain at least two ether linkages and one or more hydroxyl groups. Thus, the new class of pickling inhibitors may be represented by the general formula



where R_1 and R_2 are like or unlike alkylene groups, where n is an integer and where R_3 and R_4 are members of the group consisting of hydrogen atoms and hydrocarbon groups but either R_3 or R_4 must be a hydrocarbon group. R_2 may also contain a hydroxyl group.

The new inhibitors may be prepared by condensing a mercapto thiazole with ethylene oxide, propylene oxide, epichlorhydrin, glycerol chlor hydrin, glycide, glycol, glycerol, polyglycerol, and the like. Two or more of these reactive compounds may also be caused to react consecutively. The condensation is advantageously carried out in the presence of alkaline reacting agents or nickel sulfate as catalysts.

Examples of mercapto thiazoles which will condense with the above mentioned reactive compounds to give excellent pickling inhibitors are 2-mercapto thiazoles wherein either or both carbon atoms in the 4 or/and 5 positions of the thiazole nucleus possess an alkyl, cyclo alkyl, aralkyl, or aryl substituent. Among the hydrocarbon groups contemplated are methyl, ethyl, propyl, isopropyl, butyl, amyl, cyclohexyl, benzyl, phenyl, and the like. The preferred substituents are alkyl groups containing less than 6 carbon atoms.

The ready solubility of the new inhibitors in the pickling baths is an important quality. The problem of dispersing insoluble inhibitors is a troublesome one and the presence of undissolved particles in the cleaning bath frequently results in spotting and staining of the metal pieces. Solubility determinations carried out in cold dilute acid with condensation products of a 2-mercapto thiazole and ethylene oxide and of a 2-mercapto thiazole and propylene oxide revealed that the solubility increased with increasing values of n in the foregoing formula. Alkyl substituted 2-mercapto thiazole-ethylene oxide condensation products in which the value of n was greater than 1 were completely soluble in hot pickling baths in the amounts normally used and produced clear haze free pickling baths. In general the preferred value of n is within the range of 2–30.

It is usually preferred to employ between about one hundredth of one percent and three hun-

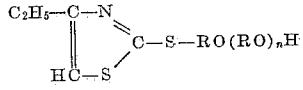
dredths of one percent by weight based on the pickling bath. However, the composition, concentration, temperature of operation, and other factors vary with different baths and similarly the optimum concentration of inhibitor will vary somewhat depending upon the particular conditions employed. The concentration of inhibitor based on the quantity of 100 percent acid contained in the pickling bath is usually between about two tenths of one percent and half of one percent.

The following is to be understood as illustrative of the preparation of the new inhibitors and is not to be construed as limitative thereof.

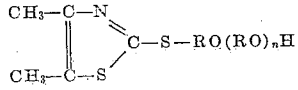
Example

36.3 parts by weight (substantially 0.25 mol) of a 15/85 mixture of 2-mercapto-4-ethyl thiazole and 2-mercapto-4,5-dimethyl thiazole was dissolved in 200 parts by weight of a 5% sodium hydroxide solution. Thereto was added with agitation 20.1 parts by weight (substantially 0.25 mol) of ethylene chlor hydrin and the reaction mix heated for 3 hours at a temperature of 60°–65° C. The resultant condensation product was washed with water and found to be a brown oil only slightly soluble in hydrochloric acid. This brown oil is believed to be the equimolecular condensation product of the mixture of mercapto thiazoles and ethylene chlorohydrin and for this compound in the above described general formula n equals zero.

The brown oily equimolecular condensation product was then placed in a suitable reaction vessel with a small quantity of potassium hydroxide. While agitating, ethylene oxide was admitted through an Alundum thimble at a temperature of 118° C. Samples were taken at intervals and tested for their inhibiting value. In this manner a series of condensation products were prepared possessing 15% by weight



and 85% by weight

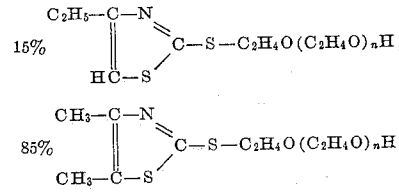


where R is an ethylene group and n is an integer. While n is a whole number in the case of any given molecule, it is convenient to designate n as a function of the average molecular weight and more particularly the total molecular weight equivalents of ethylene oxide actually reacted with each molecular weight of the 15/85 mixture of mercapto thiazoles. Accordingly, the value of n in the table below is the number of mols of ethylene oxide reacted per mol of the 15/85 mixture of mercapto thiazoles and therefore assumes fractional values.

As specific embodiments of the invention which are to be understood as illustrative of the invention and not limitative thereof, typical examples of the preferred class of materials were employed in the metal pickling process under conditions which duplicated, so far as possible those commonly followed in commercial practice. A portion of one of the preferred class of compounds was incorporated in a pickling bath and its value as an inhibitor determined in the following manner: A test piece of 28 gauge hot rolled tin plate steel stock, approximately 4" x 3" in dimension, was immersed in the pickling bath

comprising substantially 750 cc. of a water solution containing approximately 6% by weight of 66° Bé. sulfuric acid and a small amount of one of the inhibitors above described. The temperature of the bath was maintained at substantially 80° C. The steel test piece after thoroughly cleaning and pre-pickling for a few minutes in the absence of inhibitor and drying was weighed before immersion in the bath, and after 40 minutes' pickling the test piece was again weighed, the difference between the two weights representing the metal loss during pickling. The metal loss compared with the metal loss of a similar test piece treated in an analogous manner but without the use of any inhibitor provides a measure of the inhibiting value of the compound employed. The results obtained on testing typical examples of the preferred class of materials are given in the following table. The metal loss is reported as the average of duplicate determinations.

Table



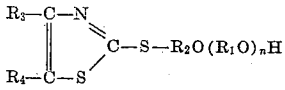
Value of n	Total Amount, Grams	Loss of metal, in Grams	Remarks
Blank—no inhibitor		0.7764	Strips pitted.
0.0	0.0936	0.0405	Inhibitor only slightly soluble. Oily droplets remained in bath.
3.9	0.0936	0.0082	Inhibitor completely soluble. Pickled strips clean and bright.
3.9	0.2340	0.0065	
8.65	0.0936	0.0112	
8.65	0.2340	0.0080	

It is apparent from the data set forth that introducing ether groups into the molecule enhances solubility in the pickling bath and that compounds containing approximately four ether linkages are not only completely soluble but possess excellent inhibiting efficiency. Comparing the loss in weight of the steel test strips to the loss when no inhibitor was employed, it is obvious that a great saving in metal is effected by use of the new inhibitors.

Other methods of employing inhibitors of the class hereinbefore set forth in the acid pickling of metals are apparent to those skilled in the art to which the invention pertains. The products described may be employed in the presence of foaming agents, ionizable substances or other materials ordinarily used. Thus the preferred class of materials may be employed as the sole inhibitor or they may be employed in conjunction with other materials exhibiting an inhibiting action or with inert fillers, dispersing agents, etc. Other non-oxidizing mineral acids than sulfuric acid may be used in the pickling bath in conjunction with the preferred class of inhibitors in the manner hereinbefore set forth. Smaller quantities of the new inhibitors than those indicated may be employed, as for example, 0.01% by weight based upon the weight of one hundred percent acid has been found satisfactory. The new pickling inhibitors in general wherein n is an integer from 4 to 9 have been found economical and efficient.

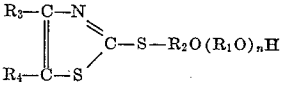
What is claimed is:

1. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a non-oxidizing mineral acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



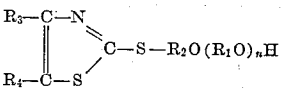
where R_1 and R_2 are alkylene groups, where n is an integer greater than one but not more than thirty, and where R_3 and R_4 are selected from the group consisting of hydrogen atoms and hydrocarbon groups containing not more than seven carbon atoms but where no more than one of the group consisting of R_3 and R_4 can be hydrogen.

2. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a non-oxidizing mineral acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



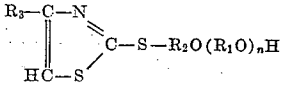
where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer greater than one but not more than thirty, and where R_3 and R_4 are aliphatic groups containing less than six carbon atoms.

3. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a non-oxidizing mineral acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



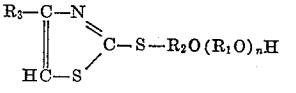
where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer greater than one but not more than thirty, and where R_3 and R_4 are methyl groups.

4. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a non-oxidizing mineral acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer greater than one but not more than thirty, and where R_3 is an aliphatic group containing less than six carbon atoms.

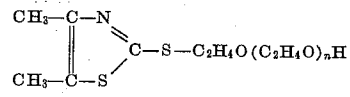
5. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a non-oxidizing mineral acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer

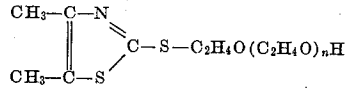
greater than one but not more than thirty, and where R_3 is an ethyl group.

6. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals, of a compound of the structure



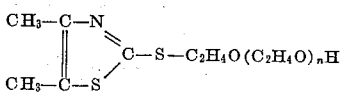
where n is greater than one but not more than thirty.

7. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a hydrochloric acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



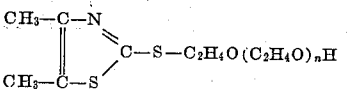
where n is greater than one but not more than thirty.

8. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



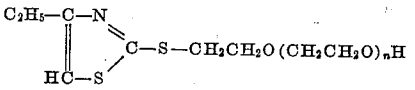
where n is approximately four.

9. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



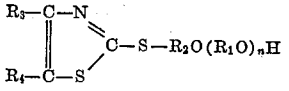
where n is approximately nine.

10. A process of pickling a ferrous metal which comprises subjecting the metal to be pickled to the action of a sulfuric acid solution containing a small proportion sufficient to inhibit the action of the acid on ferrous metals of a compound of the structure



where n is approximately four.

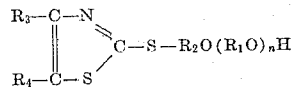
11. A mineral acid pickling bath for metal products which comprises a non-oxidizing mineral acid solution containing 0.01% to 0.03% by weight of a compound of the structure



where R_1 and R_2 are alkylene groups, where n is an integer greater than one and not more than thirty, and where R_3 and R_4 are selected from

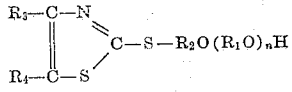
the group consisting of hydrogen atoms and hydrocarbon groups containing not more than seven carbon atoms, but where no more than one of the group consisting of R_3 and R_4 can be hydrogen.

12. A mineral acid pickling bath for metal products which comprises a non-oxidizing mineral acid solution containing 0.01% to 0.03% by weight of a compound of the structure



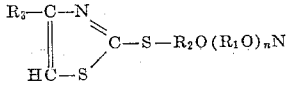
where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer greater than one but not more than thirty, and where R_3 and R_4 are aliphatic groups containing less than six carbon atoms.

13. A mineral acid pickling bath for metal products which comprises a non-oxidizing mineral acid solution containing 0.01% to 0.03% by weight of a compound of the structure



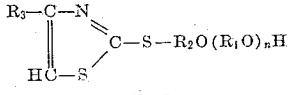
where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer greater than one but not more than thirty, and where R_3 and R_4 are methyl groups.

14. A mineral acid pickling bath for metal products which comprises a non-oxidizing mineral acid solution containing 0.01% to 0.03% by weight of a compound of the structure



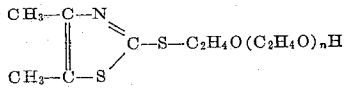
where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer greater than one but not more than thirty, and where R_3 is an aliphatic group containing less than six carbon atoms.

15. A mineral acid pickling bath for metal products which comprises a non-oxidizing mineral acid solution containing 0.01% to 0.03% by weight of a compound of the structure



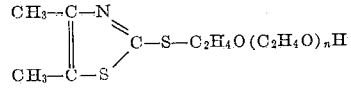
where R_1 and R_2 are alkylene groups containing less than four carbon atoms, where n is an integer greater than one but not more than thirty, and where R_3 is an ethyl group.

16. A mineral acid pickling bath for metal products which comprises a sulfuric acid solution containing 0.01% to 0.03% by weight of a compound of the structure



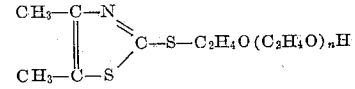
where n is greater than one but not more than thirty.

17. A mineral acid pickling bath for metal products which comprises a hydrochloric acid solution containing 0.01% to 0.03% by weight of a compound of the structure



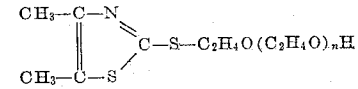
where n is greater than one but not more than thirty.

18. A mineral acid pickling bath for metal products which comprises a sulfuric acid solution containing 0.01% to 0.03% by weight of a compound of the structure



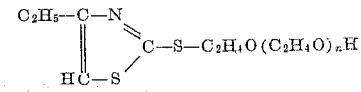
where n is approximately four.

19. A mineral acid pickling bath for metal products which comprises a sulfuric acid solution containing 0.01% to 0.03% by weight of a compound of the structure



where n is approximately nine.

20. A mineral acid pickling bath for metal products which comprises a sulfuric acid solution containing 0.01% to 0.03% by weight of a compound of the structure



where n is approximately four.

RICHARD O. ZERBE.

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