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CLEANING OF METALLIC SURFACES

Richard O. Zerbe, Nitro, W. Va., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

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18 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 atomsphere 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 mercaptothiazolines. Hydroxy ethyl mercaptothiazoline is known to be a pickling inhibitor but it is not soluble in the pickling baths and special

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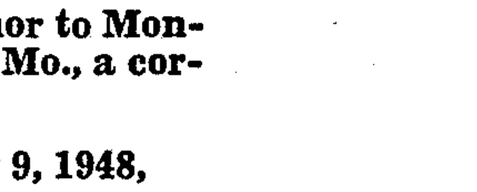
techniques have been attempted in order to disperse the material in the acid cleaning solutions. However, it has now been found in accordance with the present invention that the hydroxy polyether derivatives of mercaptothiazolines are highly effective pickle regulators which are at the same time soluble in the pickling baths. The 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 alkylene groups and n is an integer.

The new inhibitors may be prepared by condensing a mercaptothiazoline with ethylene oxide, propylene oxide, epichlorhydrin, glycerol α 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 advantangeously carried out in the presence of alkaline reacting agents or nickel sulfate as catalysts.

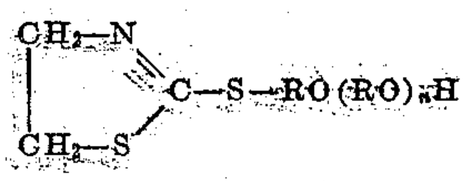
Examples of mercaptothiazolines which will condense with the above mentioned reactive compounds to give excellent pickling inhibitors are 2-mercaptothiazoline and substituted 2-mercaptothiazolines wherein one or more of the hydrogen atoms attached to the carbon atoms in the 4 and 5 positions of the thiazoline nucleus are replaced by saturated and unsaturated hydrocarbon groups such as alkyl, alkylene, aryl, aralykyl, or cycloaliphatic groups.

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 2-mercaptothiazoline and ethylene oxide and of 2-mercaptothiazoline and propylene oxide revealed that the solubility increased with increasing values of n in the foregoing formula. Mercaptothiazoline-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 hundredths 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.

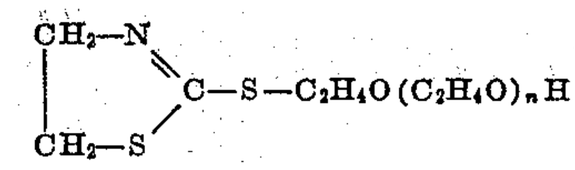
As exemplary of the preparation of the new inhibitors 2-mercaptothiazoline was condensed with ethylene oxide in varying ratios. 23.8 parts by weight (substantially 0.2 mol) of 2-mercaptothiazoline and 0.25 parts by weight of powdered potassium hydroxide were charged into a suitable reaction vessel. The mixture was melted by immersing in an oil bath and the ethylene oxide was admitted to the melt through an Alundum thimble at 118° C. Samples were taken at intervals and tested for their inhibiting value. In this manner a series of compounds were prepared possessing the structural formula



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 mercaptothiazoline. Accordingly, the value of n in the table below is the number of mols of ethylene oxide reacted per mol of mercaptothiazoline 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 place 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 determination.

Table



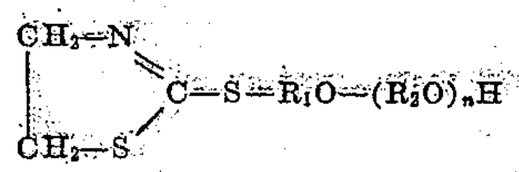
Value of n	Total Amount, Grams	Loss of metal, in Grams	Remarks
Blank—no inhibitor		0.7764	strips pitted.
0.2	0.0936		Inhibitor not soluble. White wax remained in bath.
0.95	0.0936	0.0145	Inhibitor not completely soluble. Oily droplets remained in bath.
2.8	0.0936	0.0098	Inhibitor completely soluble. Pickled strips clean and bright.
2.8	0.2340	0.0088	Do.
7.5	0.0936	0.0093	Do.
7.5	0.2340	0.0075	Do.

It is apparent from the data set forth that introducing more than one ether group into the molecule enhanced solubility in the pickling bath and that compounds containing approximately three ether linkages are not only completely soluble but possess higher 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.

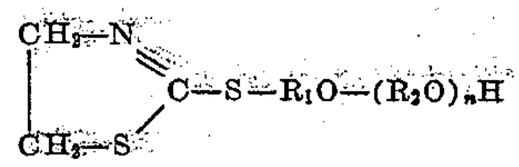
What is claimed is:

1. A process of pickling a metal consisting essentially of subjecting the metal to be pickled to the action of a heated non-oxidizing mineral acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



where R_1 and R_2 are alkylene groups and n is an integer greater than one.

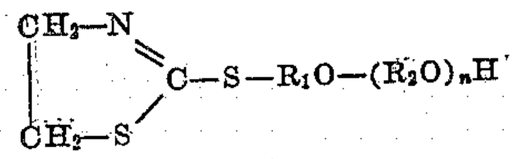
2. A process of pickling a metal consisting essentially of subjecting the metal to be pickled to the action of a heated non oxidizing mineral acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



where R_1 and R_2 are alkylene groups of less than 4 carbon atoms and n is an integer greater than one but not more than 30.

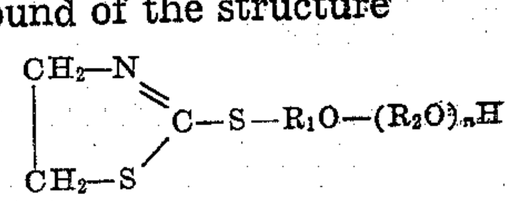
3. A process of pickling a metal consisting

ssentially of subjecting the metal to be pickled o the action of a heated non oxidizing mineral cid solution containing a small amount sufficient to inhibit the action of the acid on the metal f a compound of the structure



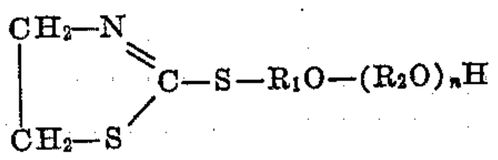
where R_1 and R_2 are alkylene groups of less than carbon atoms and n is approximately three.

4. A process of pickling a metal consisting ssentially of subjecting the metal to be pickled o the action of a heated non oxidizing mineral acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



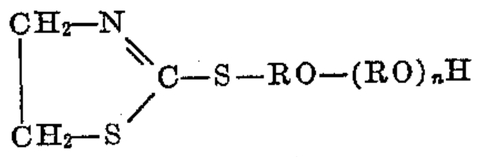
where R_1 and R_2 are ethylene groups and n is an integer greater than one but not more than 30.

5. A process of pickling a metal consisting essentially of subjecting the metal to be pickled to the action of a heated non oxidizing mineral acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



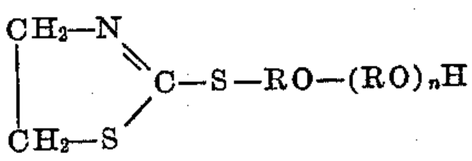
where R_1 and R_2 are propylene groups and n is an integer greater than one but not more than 30.

6. A process of pickling a metal consisting essentially of subjecting the metal to be pickled to the action of a heated sulfuric acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



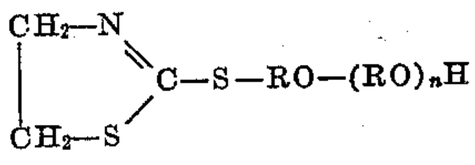
where R is an ethylene group and n is an integer greater than one but not more than 30.

7. A process of pickling a metal consisting essentially of subjecting the metal to be pickled to the action of a heated sulfuric acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



where R is an ethylene group and n is approximately three.

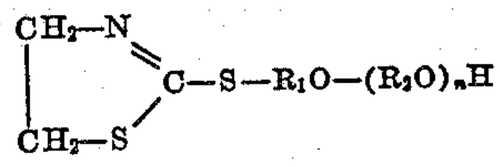
8. A process of pickling a metal consisting essentially of subjecting the metal to be pickled to the action of a heated sulfuric acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



where R is an ethylene group and n is approximately eight.

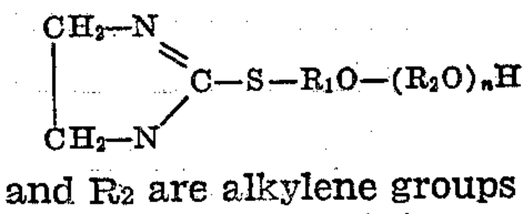
9. A pickling bath for metal products consisting essentially of a non oxidizing mineral acid

solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



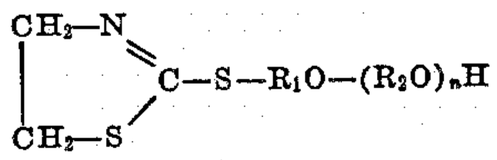
where R_1 and R_2 are alkylene groups and n is an integer greater than one.

10. A pickling bath for metal products consisting essentially of a non oxidizing mineral acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



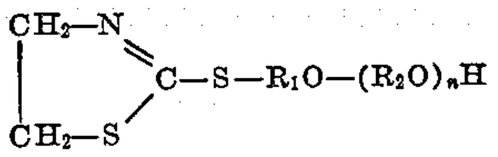
where R_1 and R_2 are alkylene groups of less than 4 carbon atoms and n is an integer greater than one but not more than 30.

11. A pickling bath for metal products consisting essentially of a non oxidizing mineral acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



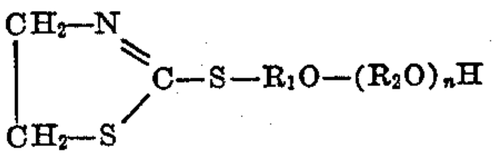
where R_1 and R_2 are alkylene groups of less than 4 carbon atoms and n is approximately three.

12. A pickling bath for metal products consisting essentially of a non oxidizing mineral acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



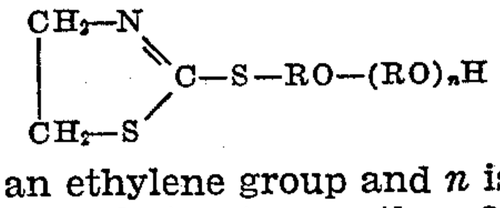
where R_1 and R_2 are ethylene groups and n is an integer greater than one but not more than 30.

13. A pickling bath for metal products consisting essentially of a non oxidizing mineral acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



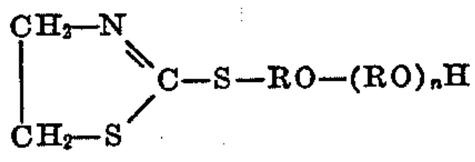
where R_1 and R_2 are propylene groups and n is an integer greater than one but not more than 30.

14. A pickling bath for metal products consisting essentially of a sulfuric acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



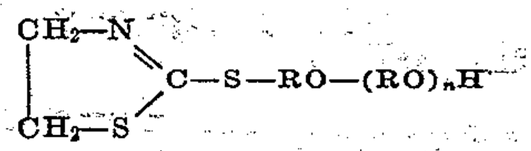
where R is an ethylene group and n is an integer greater than one but not more than 30.

15. A pickling bath for metal products consisting essentially of a sulfuric acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



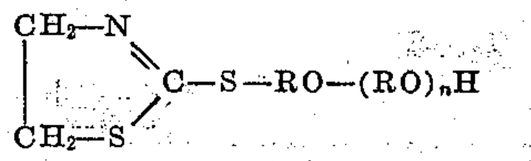
where R is an ethylene group and n is approximately three.

16. A pickling bath for metal products consisting essentially of a sulfuric acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



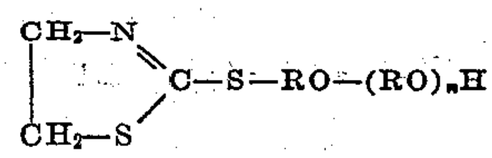
where R is an ethylene group and n is approximately eight.

17. A process of pickling a metal consisting essentially of subjecting the metal to be pickled to the action of a heated hydrochloric acid solution containing a small amount sufficient to inhibit the action of the acid on the metal of a compound of the structure



where R is an ethylene group and n is an integer greater than one but not more than 30.

18. A pickling bath for metal products consisting essentially of a hydrochloric acid solution containing 0.01 to 0.03 percent by weight based on the pickling bath of a compound of the structure



where R is an ethylene group and n is an integer greater than one but not more than 30.

RICHARD O. ZERBE.

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