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INHIBITED ACID BATH AND USE

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This invention relates to inhibitors for metal-pickling baths, and more particularly to inhibitors comprising organic sulfonic acid compounds.

As a preliminary treatment prior to electroplating or other surface treatments of metals, it is common practice to subject the metal surface to a treatment with acid agents, particularly with solutions of mineral acids, in order to remove layers of metal oxides, grease, and other substances which might interfere with the surface treatment. Such pretreatments are commonly referred to as pickling processes. However, in order to prevent the acid agent employed from directly attacking the virgin metal, the acid agent or pickling solution is modified with substances which are usually referred to as inhibitors. For example, for the purpose of pickling or removing rust from the surface of iron objects, inhibitors are added to the acid bath which serve to prevent, to a large extent, the non-corroded metal surface from being attacked by the acid pickling bath after the overlying layer of rust or foreign matter has been removed by the pickling bath. The same principle can be applied to the pre-treatment of objects made from other types of metals, such as, for example, from zinc or aluminum.

Since the time when inhibitors were first introduced they have been improved, and new and better inhibitors have been found which combine many desirable physical qualities with improved inhibiting action. Today a satisfactory and desirable inhibitor must fulfill many requirements to meet the demands of industry. For example, a high-grade inhibitor must give a maximum degree of protection within relatively low ranges of concentration; it must also impart a lasting inhibiting effect to acid pickling baths, so that these baths can remain in operation for long periods of time without constant surveillance; furthermore, it is expected of such inhibitors that they be effective over wide ranges of temperature and concentration; moreover, a good inhibitor must be effective when used in conjunction with a variety of pickling acids and metals; finally, a modern inhibitor is expected to be practically non-volatile, even when used in the presence of ordinary or acid-containing steam, non-poisonous, not prone to generating interfering gases, and practically odorless, a property which many of the old sulfur-containing inhibitors generally lacked.

It is therefore an object of the present invention to provide inhibitors for acid pickling baths which will improve the inhibiting action of such baths without interfering with the pickling action.

Another object of this invention is to provide inhibitors for acid pickling baths which will give a maximum degree of inhibiting protection within relatively low ranges of concentration.

Another object of this invention is to provide inhibitors for acid pickling baths which will impart a lasting inhibiting effect to such baths.

Still another object of this invention is to provide inhibitors for acid pickling baths which will give effective inhibiting protection over wide ranges of concentration and temperature.

A further object of this invention is to provide inhibitors for acid pickling baths which can be used in conjunction with a large variety of pickling acids and metals.

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Finally, it is an object of the present invention to provide inhibitors which are practically non-volatile, non-poisonous, odorless, and will not generate interfering gases.

Other objects and advantages will become apparent as the description of our invention proceeds.

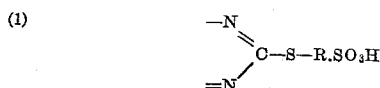
We have found that certain organic sulfonic acids or their salts have excellent corrosion-preventing properties and are excellent inhibitors which meet all of the requirements of modern inhibitors as set forth above.

More particularly, we have found that organic sulfonic acids having the general structural formula

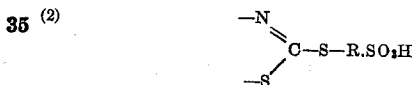


or their salts are valuable inhibitors for acid pickling baths. In the above formula, G represents an organic radical which contains a carbon atom linked, on one hand, exclusively to heteroatoms and, on the other hand, to the $-RSO_3H$ radical through a sulfur atom and R is a bivalent aliphatic radical containing from 1 to 6 carbon atoms which may carry one or more substituents.

Compounds of the following classes are examples of the types of sulfonic acids or their salts which may be used as corrosion-preventing agents in accordance with our invention:



This class of sulfonic acids is derived from thiourea, for example, as well as from 2-thioimidazoles or 2-benzimidazoles if the carbon atom and the nitrogen atoms form a part of a heterocyclic ring system.



This structure occurs in sulfonic acids which are derived, for example, from 2-mercaptothiazoles or 2-mercaptobenzothiazoles, or from thiocyanides.



Sulfonic acids having this structure are derived, for example, from 2-thiobenzoxazoles and 2-thiocumazoles (2-thiobenzometoxazines).



Sulfonic acids having this structure are derived, for example, from dithiocarbamic acids.



Sulfonic acid compounds having this type of structure are derived from thioxanthic acids or trithiocarbonic acids.



Sulfonic acid compounds having this type of structure are derived from xanthic acids.



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Sulfonic acids having this type of structure are derivatives of carbaminothiol acids.

In the above examples, R represents an aliphatic radical having from 1 to 6 carbon atoms, as defined above, and the open bonds may be linked to hydrogen atoms or to aliphatic, cycloaliphatic or aromatic hydrocarbon radicals. The hydrocarbon radicals attached to the open bonds may also be interconnected by linkage bonds and may, in addition, carry substituents or contain further heteroatoms or heteroatom groups.

Sulfonic acid compounds of the type herein referred to can be obtained by very simple methods and with excellent yields; for example, by reacting the corresponding sulfhydryl compounds or enolizable thiocarbonyl compounds with cyclic anhydrides of oxyalkanesulfonic acids (sulftones).

The following sulfonic acid compounds are examples of compounds having the above general structural formula which can be used as corrosion-preventing additives or inhibitors for acid pickling baths in accordance with our invention:

Betaine salts of isothiurea-S-butane- ω -sulfonic acid
 Betaine salts of N-phenyl-isothiurea-S-propane- ω -sulfonic acid
 2-mercaptobenzothiazole-S-propane- ω -potassium sulfonate
 Rhodanic acid-S-n-propylester- ω -sodium sulfonate
 2-thiobenzoxazole-S-propane- ω -sodium sulfonate
 2-thiometoxazine-S-butane- ω -potassium sulfonate
 N,N-dimethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
 N,N-diethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
 N,N-pentamethylene-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
 N-butyl-dithiocarbamic acid-n-butylester- ω -sodium sulfonate
 N-p-tolyl-dithiocarbamic acid-n-propylester- ω -potassium sulfonate
 Dithiocarbamic acid-n-propylester-potassium sulfonate
 S-phenyl-trithiocarbonic acid-n-propylester- ω -sodium sulfonate
 Isopropyl-xanthogenic acid-n-butylester- ω -sodium sulfonate
 n-Butyl-xanthogenic acid-n-propylester- ω -sodium sulfonate
 Carbaminothiolic acid-n-propylester-potassium sulfonate

and the like.

Instead of the sodium and potassium salts, other salts of inorganic or organic alkaline compounds can be used equally effectively.

In order to prove the high degree of effectiveness of the sulfonic acid compounds as inhibitors for pickling baths in accordance with our invention, a series of tests were performed the results of which are tabulated in the table below.

In these tests, a piece of sheet iron having a surface area of about 18 cm.² was submerged in a 2 N solution of hydrochloric or sulfuric acid. The degree of corrosive attack of the acid on the metal surface was continuously determined by measuring the amount of hydrogen given off. From the rate of corrosion of the system iron-2 N hydrochloric acid and iron-2 N sulfuric acid at 23° C., a series of comparative control values were determined; thereafter the rates of corrosion of the systems iron-2 N hydrochloric acid-inhibitor and iron-2 N sulfuric acid-inhibitor were similarly determined and recorded in terms of percentage fraction of corrosion-preventing power of the systems. In all cases the amount of inhibitor added was 1 gm. per liter of 2 N acid.

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The individual inhibitors investigated in compiling the values of the table below were the following:

- I. Dithiocarbamic acid-n-propylester- ω -sodium sulfonate.
- II. N,N-dimethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
- III. N,N-diethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
- IV. N,N-diethyl-dithiocarbamic acid-n-butylester- ω -sodium sulfonate
- V. N,N-diisopropyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
- VI. N,N-dibutyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
- VII. N,N-pentamethylene-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
- VIII. N-butyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate
- IX. Isopropyl-xanthogenic acid-n-propylester- ω -sodium sulfonate
- X. Butyl-xanthogenic acid-n-propylester- ω -sodium sulfonate
- XI. Trithiocarbonic acid-bis-n-propylester- ω -sodium sulfonate
- XII. 2-mercaptobenzothiazole-S-propane- ω -sodium sulfonate
- XIII. 2-mercaptobenzothiazole-S-butane- ω -sodium sulfonate
- XIV. Rhodanic acid-S-propane- ω -sodium sulfonate
- XV. The betaine salt of isothiurea-S-propane- ω -sulfonic acid

Product	Corrosion-Preventing effect, Percent	
	2 N HCl	2 N H ₂ SO ₄
I.	88.6	97.5
II.	97.9	99.1
III.	99.2	99.8
IV.	99.6	100.0
V.	96.1	98.5
VI.	100.0	100.0
VII.	99.4	99.7
VIII.	100.0	100.0
IX.	97.7	97.0
X.	98.6	100.0
XI.	98.5	not observed
XII.	99.6	99.8
XIII.	100.0	100.0
XIV.	not observed	87.0
XV.	not observed	85.9

The addition of the sulfonic acid inhibitors to acid pickling baths in accordance with our invention does not require any change in the practices usually followed in treating the surfaces of metal objects with acid solutions.

The amounts of sulfonic acid inhibitors required to give the desired inhibiting effects in accordance with our invention vary within rather wide limits and depend largely upon the type of acid agent employed to make up the pickling solution, upon the metal treated, and under certain circumstances also upon the temperature at which the acid treatment takes place. However, as a rule it is sufficient to add from 0.01 to 0.5% of inhibitor based upon the weight of acid present.

The sulfonic acid inhibitors can be used in accordance with our invention in conjunction with other known corrosion-preventing agents without any danger of incompatibility.

The inhibitors of our invention are effective in pickling baths made from mineral acids as well as from inorganic or organic acid salts of such mineral acids.

Finally, pickling baths modified with the sulfonic acid inhibitors in accordance with our invention can be used upon any type of metal capable of being subjected to an acid surface treatment for the purpose of cleaning, etching, removal of rust and dirt, and the like.

While we have disclosed specific embodiments of our

invention, we wish it to be understood that the invention is not limited to such embodiments, and that various changes and modifications can be made without departing from the spirit of our invention or the scope of the appended claims.

We claim:

1. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight, based upon the weight of acid, of N,N-diethyl-dithiocarbamic acid-n-butylester- ω -sodium sulfonate.

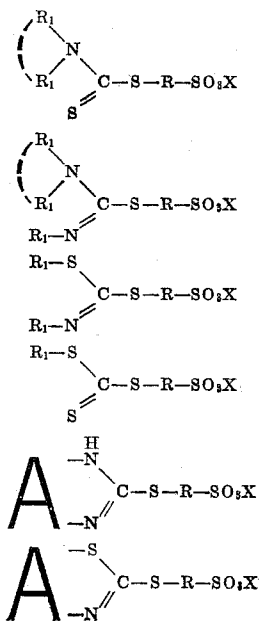
2. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight, based upon the weight of acid, of N,N-dibutyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate.

3. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight, based upon the weight of acid, of N-butyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate.

4. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight, based upon the weight of acid, of 2-mercaptobenzothiazole-S-propane- ω -sodium sulfonate.

5. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight, based upon the weight of acid, of 2-mercaptobenzothiazole-S-butane- ω -sodium sulfonate.

6. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of an acid selected from the group consisting of sulfuric and hydrochloric acid which contains from about 0.01 to about 0.5% by weight based upon the weight of the acid, of at least one organic sulfonic acid component having a structural formula selected from the group consisting of:

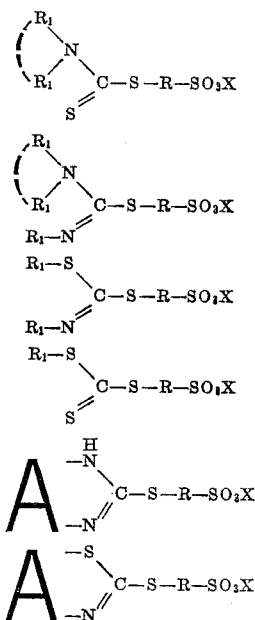


wherein R is a bivalent alkyl radical having from 1 to 6 carbon atoms; R₁ is a radical selected from the group consisting of hydrogen, lower alkyl radicals having from 1 to 4 carbon atoms, and phenyl radicals and R₁—R₁ represents two R₁ groups joined to form a pentamethylene radical which together with the nitrogen atom form a piperidine radical; A is a radical having a structure selected from the group consisting of —CH=CH— and



and X is selected from the group consisting of hydrogen, potassium and sodium atoms.

7. As a composition for cleansing the surfaces of metal objects, an aqueous solution of an acid selected from the group consisting of hydrochloric acid and sulfuric acid and from about 0.01 to about 0.5% by weight, of acid, of at least one inhibitor selected from the group consisting of organic sulfonic acids having a structural formula selected from the group consisting of:



wherein R is a bivalent alkyl radical having from 1 to 6 carbon atoms; R₁ is a radical selected from the group consisting of hydrogen, lower alkyl radicals having from 1 to 4 carbon atoms, and phenyl radicals and R₁—R₁ represents two R₁ groups joined to form a pentamethylene radical which together with the nitrogen atom form a piperidine radical; A is a radical having a structure selected from the group consisting of —CH=CH— and



and X is selected from the group consisting of hydrogen, potassium and sodium atoms.

8. The method of cleansing the surfaces of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon the weight of acid, of dithiocarbamic acid-n-propylester- ω -sodium sulfonate.

9. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon the weight of acid, of N,N-dimethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate.

10. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon the weight of acid, of N,N-diethyl-dithiocarbamic acid-n-propylester- ω -sodium sulfonate.

11. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon the weight of acid, of N,N-diisopropyl-dithiocarbamic acid-n-propyl- ω -sodium sulfonate.

12. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon the weight of acid, of N,N-pentamethylene-dithiocarbamic acid-n-propylester- ω -sodium sulfonate.

13. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon the weight of acid, of trithiocarbonic acid-bis-n-propylester- ω -sodium sulfonate.

14. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon

the weight of acid, of rhodanic acid-S-propane- ω -sodium sulfonate.

15. The method of cleansing the surface of metal objects which comprises contacting said objects with an aqueous solution of a mineral acid selected from the group consisting of hydrochloric acid and sulfuric acid, and from about 0.01 to about 0.5% by weight based upon the weight of acid, of the betaine salt of isothioureia-S-propane- ω -sulfonic acid.

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