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PICKLING INHIBITOR

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This invention relates to improvements in pickling and cleaning of metals and in inhibiting or retarding the action of acids on metals. More particularly the invention relates to improvements in inhibitors for acids, solutions containing these inhibitors for cleaning or pickling metals, and methods of cleaning or pickling metals and removing oxides or scale therefrom.

Such metallic substances as ferruginous metals, aluminum, zinc, nickel and others are, as is well known, subject to surface corrosion when exposed to the atmosphere and certain chemicals. Metal surfaces that are thus affected and that have become coated with scale, particularly mill scale formed in sheet rolling or other operations, rust and the like are generally treated with a pickling solution to remove the objectionable material. The pickling solution generally contains an acid, and a so-called inhibitor that is added for the purpose of preventing dissolution of the metal without interfering with the dissolution action of the acid on the objectionable material.

It is of considerable advantage to employ as inhibitors, substances that have a high solubility in pickling acid solutions, that are readily wetted by acids, and that, by rinsing with water, are easily and completely washable from metal along with carbon smut and other debris. It is also an advantage to employ compounds that do not have a disagreeable odor and that are not irritating to the skin and mucous membranes of workmen.

The above and other advantages are gained by the following invention in which a pickling solution is provided by adding to an acid solution a product obtained by chemical reaction between an aldehyde, certain nitrogen compounds and a thiocyanic acid compound. The condensation products formed include in their molecular structure both sulfur and nitrogen thereby rendering them particularly effective as inhibitors.

The nitrogen compounds from which the thiocyanates are prepared are basic amino compounds of either the aliphatic or straight chain, carbocyclic, or heterocyclic types. They contain one or more amine or imine groups, or tertiary nitrogen atoms, or combinations thereof. It is to be understood in the present instance that the term "amino compound" as herein employed, applies to compounds containing primary, secondary and tertiary amine structures in their configuration and wherein one, two or three atoms of ammoniacal hydrogen have been replaced by other linkages.

Under steel plant working conditions it is de-

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sirable to use compounds that are thermostable. It is noted that in general the presence of alkyl, alkoxy, aralkyl, and especially aryl groups in the amino starting compounds provides increased stability in the inhibitor. For instance, the diphenyl guanidine thiocyanate aldehyde condensation product is more thermostable than the corresponding condensation product made from guanidine thiocyanate.

The stronger the basic characteristics of the amino compound used as a starting material the better the compound is for purposes of the present invention. It is preferred that the amino compound be basic enough to form with thiocyanic acid true thiocyanates of sufficient stability to avoid continuous splitting off of free thiocyanic acid in too great proportions during condensation. The bases employed should preferably have a basicity greater than that expressed by the dissociation constant 10^{-14} .

The presence of water solubilizing groups, such as NH_2 , NH , OH and others, in the amino compound or in the inhibitor product confers upon the inhibitor increased solubility in the acid baths in which it is used.

The following are some of the amino compounds which have been found to be useful in providing the acid inhibitors of the present invention:

Mono- and poly-amines such as dimethylamine, monoethylamine, mono-n-propylamine, di-isopropylamine, tri-n-butylamine, mono-n-butyl diamylamine, dioctylamine, mono-n-dodecylamine, mono-n-octadecylamine, benzyl diethylamine, aniline, p-tertiary-amylianiiline, di-tertiary amylianiiline, N-monoamylaniiline, N,N-diamyl aniline, N-mono-n-butyl aniline, N,N-di-n-butylaniiline, a-naphthylamine, B-naphthylamine, N-n-butyl-a-naphthylamine, o-amino diphenyl, diphenylamine, piperidine, morpholine, phenylmorpholine, phenylmethyl pyrazolone, monoethanolamine, diethanolamine, ethyldiethanolamine, n-butyl mono-ethanolamine, 2-amino-1-butanol, 2-amino-2-ethyl-1,3-propanediol, tris (hydroxymethyl) aminomethane, phenylethanolamine, p-tertiaryamyl phenyl diethanolamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 2,3-diamino-2,3-dimethylbutane, pentamethylene diamine, hexamethylene tetramine, p-phenylene diamine, benzidine.

The above amino compounds, either singly or mixtures of two or more thereof, are readily converted to thiocyanates or perthiocyanates by reaction with thiocyanic acid or a perthiocyanic

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acid, or by the double decomposition of an amine salt and a metal or ammonium thiocyanate.

For the aldehyde component of the new compounds there may be used for example formaldehyde, acetaldehyde, butyraldehyde, crotonaldehyde, acrolein, benzaldehyde, salicylaldehyde, cinnamic aldehyde, furfural, glyoxal, and others and mixtures thereof. Formaldehyde is in general to be preferred on account of its availability, cheapness, and effectiveness.

As to the relative proportion of amino compound and aldehyde to be used, no general rule can be laid down. The ratio depends on the number of active groups in the amino compound molecule, such as NH_2 and thiocyanate groups. One mol of aldehyde is usually employed for each reactive group, and therefore in most cases two mols of aldehyde are sufficient for a particular thiocyanate. However, an excess of for example formaldehyde does no harm, since it is in itself a pickling inhibitor of some limited value and may therefore be left with the reaction product in many cases. A deficiency of aldehyde also is of no grave consequence since practically all amines and all thiocyanates in a sense have some inhibiting value of their own. Where desired, an excess of aldehyde may be removed by means known to the art, such as evaporation in vacuo or otherwise.

When using the pickling inhibitors of the present invention, it is often advantageous to add wetting agents to the pickling baths or to incorporate such agents with the inhibitors themselves. Such commercial wetting agents as a naphthalene sulphonic acid type of wetting agent, known as Aerosol OS, render good service. They should be employed in quantities of about $\frac{1}{2}\%$ of the acid weight of the bath. The addition of wetting agents facilitate the removal of carbon smut from the pickled steel or other metal goods. At the same time, though only very small amounts of the inhibitors are needed in a pickling bath in order to inhibit effectively the solvent action of the acid in the bath on the metal as seen in the following examples, the addition of the wetting agent increases the effectiveness of the inhibitors to such an extent that substantially smaller percentages of the inhibitors give satisfactory results.

Examples

1. 1940 c. c. of an aqueous solution of aniline thiocyanate containing 3.3 mols of the compound, are slowly added to 495 grams (6.6 mols) of a 40% aqueous formaldehyde solution. The mixture is constantly stirred and kept at about 12°C . Slowly a milkiness begins to appear and the color gradually changes to a light yellow due to finely dispersed solid. The color of the solid deepens while the amount increases, until a large quantity of a scarlet colored, finely divided product is produced at the end of the addition of the aniline thiocyanate solution. Filtration and washing with water yields an almost theoretical quantity of the desired aniline thiocyanate formaldehyde condensation product. The new material is a thermosetting resin which does not melt at temperatures up to 300°C . and on heating gradually turns brown and then black. It was found to be a good pickling inhibitor.

2. 230 parts of 2-amino-2-methyl-1-propanol thiocyanate are refluxed with 380 parts of 40% aqueous formaldehyde for six hours. The resultant product is an amber, clear liquid, a little hydrophobic but substantially water soluble. It

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is entirely soluble in a mixture of one part concentrated hydrochloric acid and two parts water. Tests prove it to be an excellent pickling inhibitor.

3. 300 parts of 2-amino-2-ethyl-1,3-propanediol thiocyanate are refluxed with 380 parts of 40% aqueous formaldehyde for six hours. The resultant product is a dark, red-brown, clear liquid rather hydrophobic. Tests prove it to be entirely soluble in a mixture of one part concentrated hydrophobic acid and two parts water. It is a most excellent inhibitor.

4. 230 parts of 2-amino-1-butanol thiocyanate are refluxed with 380 parts of 40% aqueous formaldehyde for six hours. The resultant product is a very deep red-brown, thick-liquid, quite hydrophobic but completely soluble in a mixture of 1 part concentrated hydrochloric acid and 2 parts water. Tests prove it to be a most excellent pickling inhibitor.

This application is a continuation in part of my copending application, Serial Number 463,133, filed October 23, 1942, now U. S. Patent No. 2,425,320.

The term amine is used herein to refer to the nitrogen analogues of alcohols, phenols and ethers in contradistinction to amidines as claimed in the parent application which are nitrogen analogues of acids.

The compounds of the invention as obtained from basic amines and hydroxylated basic amino compounds are useful as rubber accelerators and promoters, as pickling inhibitors, as pest control agents and as synthetic resins and plastics.

I claim:

1. A condensation product of an aldehyde and a preformed thiocyanate salt of a tert-alkylol amine.

2. A condensation product according to claim 1 in which the aldehyde is formaldehyde.

3. A thiocyanate salt of a tert-alkylol amine.

4. A cleaning and pickling composition for metal subject to atmospheric corrosion and for removing oxides and other corrosion products from surfaces of said metal, said composition comprising a pickling acid solution having dissolved therein a relatively small proportion of a reaction product of an aldehyde and a preformed thiocyanate of a basic amino compound selected from the class consisting of basic mono amines, said reaction product being soluble in said pickling acid solution in a proportion which inhibits dissolution of said metal by said acid.

5. The composition of claim 4 in which the aldehyde is formaldehyde.

6. A cleaning and pickling composition for metal subject to atmospheric corrosion and for removing oxides and other corrosion products from surfaces of said metal, said composition comprising a pickling acid solution having dissolved therein a relatively small proportion of a reaction product of an aldehyde and a preformed thiocyanate of a basic amino compound selected from the class consisting of aliphatic mono amines, said reaction product being soluble in said pickling acid solution in a proportion which inhibits dissolution of said metal by said acid.

7. The composition of claim 6 in which the aldehyde is formaldehyde.

8. A cleaning and pickling composition for metal subject to atmospheric corrosion and for removing oxides and other corrosion products from surfaces of said metal, said composition comprising a pickling acid solution having dissolved therein a relatively small proportion of a

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reaction product of an aldehyde and a preformed thiocyanate of a basic amino compound selected from the class consisting of tert-alkylol amines, said reaction product being soluble in said pickling acid solution in a proportion which inhibits dissolution of said metal by said acid.

9. The composition of claim 8 in which the aldehyde is formaldehyde.

10. In a method of cleaning and pickling a metal, the step comprising treating the metal with an aqueous pickling acid solution in which is dissolved in acid-inhibiting proportions a product of reaction between an aldehyde and a preformed thiocyanate of a basic amino compound selected from the class consisting of basic monoamines, said reaction product being soluble in said pickling acid solution in a proportion which inhibits dissolution of said metal by said acid.

11. The process of claim 10 in which the aldehyde is formaldehyde.

12. In a method of cleaning and pickling a metal, the step comprising treating the metal with an aqueous pickling acid solution, in which is dissolved in acid inhibiting proportions, a product of reaction between an aldehyde and a preformed thiocyanate of a basic amino compound selected from the class consisting of tert-alkylol amines, said reaction product being soluble in said pickling acid solution in a proportion which inhibits dissolution of said metal by said acid.

13. The process of claim 12 in which the aldehyde is formaldehyde.

14. A product of the condensation of one mol of a preformed thiocyanate salt of a tert-alkylol primary monoamine and two mols of an aldehyde, said product being characterized as a hydrophobic liquid soluble in a mixture of one part of concentrated hydrochloric acid and two parts of water.

15. The product of claim 14 in which the aldehyde is formaldehyde.

16. A cleaning and pickling composition for metal subject to atmospheric corrosion and for

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removing oxides and other corrosion products from surfaces of said metal, said composition comprising a pickling acid solution having dissolved therein a relatively small proportion of a reaction product of an aldehyde and a preformed thiocyanate of a basic amino compound, selected from the class consisting of the products as set forth in claim 14.

17. The composition of claim 16 in which the aldehyde is formaldehyde

18. In a method of cleaning and pickling a metal, the step comprising treating the metal with an aqueous pickling acid solution in which is dissolved in acid-inhibiting proportions a product of reaction between an aldehyde and a preformed thiocyanate of a basic amino compound selected from the class consisting of the products set forth in claim 14

19. The process of claim 18 in which the aldehyde is formaldehyde.

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