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INHIBITING PROCESS AND PRODUCT

Orin D. Cunningham, Indianapolis, Ind., assignor to Peter C. Reilly, Indianapolis, Ind.

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15 Claims. (Cl. 148—8)

This invention relates to the prevention or retardation of chemical action of acid or salt solutions on metals in certain chemical and electrochemical processes, and the consequent prevention or retardation of the evolution of hydrogen at the surface of metals immersed in such acid or salt solutions; by certain products herein described as "inhibitors".

The object of the present invention is to produce a highly efficient inhibitor.

My invention is especially useful in what is commonly referred to as the "pickling process", wherein metals, such for example as iron or steel, are subjected to the action of acid solutions for removing the oxide scale from the surface thereof; in which process the presence of very small quantities of the inhibitor reagents of the present invention dissolved in the acid pickling solution results in a very marked retardation of the corrosive action on the metal and the consequent evolution of hydrogen gas, without materially interferring with the action of the acid in removing the scale, rust, or oxide film from the surface thereof. Thereby not only is a material saving in acid and metal effected, but certain objectionable features incident to the pickling operation without an inhibiting reagent are overcome. For example, the evils known as "acid brittleness", "blisters", "black deposits", and "overpickling" are greatly mitigated; and the highly objectionable spray of acid (acid fumes) carried into the atmosphere by the excessive hydrogen gas evolution formed in the absence of inhibiting agent is substantially eliminated.

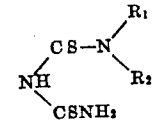
In its broader aspects, however, my invention contemplates the use of the inhibitor reagents of the present invention in acid or salt solutions of any chemical or electrochemical process which under normal conditions will evolve hydrogen at the surface of the metal in contact therewith; and also in the storage of certain corrosive acid or salt solutions. In the electrodepositions of metals, for example, it may find application in retarding the sometimes troublesome evolution of hydrogen at the cathode without in any way interfering with normal operation of the process. It may further be applied in acid cleaning solutions, to retard corrosive action of the acid on the metal, such as, for example, automobile radiator cleaning solutions.

I have discovered that certain of the substituted dithiobiuret compounds posses excellent inhibiting action on the evolution of hydrogen, especially those dithiobiuret compounds which are obtained by the reaction of perisosulfocyanic acid with a substance in the class comprising aniline and its homologs.

By "aniline and its homologs" I include the aromatic primary bases aniline, the toluidines, and the xylidines; and their aliphatic-alkyl-substituted secondary bases methylaniline, ethylaniline, etc., methyltoluidine, ethyltoluidine, etc., methyl xylidine, ethyl xylidine, etc.; as well as the mono-substituted halides of these amino compounds, such as, for example, the chloroanilines, the bromoanilines, the iodoanilines, etc. Any desired mixture of these compounds may also be used; and they may be pure, partially refined, or crude materials.

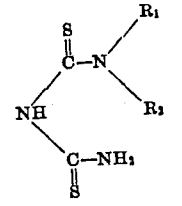
The monosubstituted dithiobiuret compounds herein disclosed may be represented by the following formula:

(1)



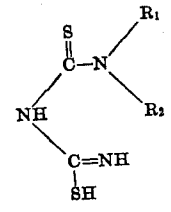
This formula includes two variants:

(2)



or

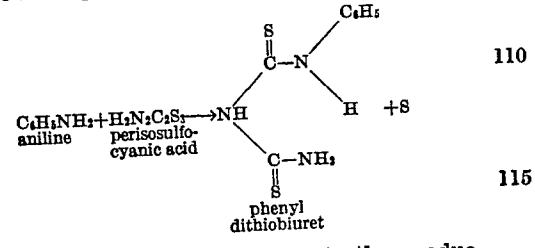
(3)



In these formulas, R_1 represents a hydrocarbon radical or a hydrocarbon radical containing a halogen, and R_2 represents a hydrocarbon radical or hydrogen.

The reaction according to the preferred method of obtaining this type of compound is illustrated by the following equation, which depicts the reaction of aniline with perisosulfocyanic acid to form phenyl dithiobiuret.

(4)



The following examples illustrate the production of the inhibitor reagents of the present invention.

Example 1

To 100 parts by weight of aniline (or of toluidine or xylidine, or of aliphatic-ethyl-substituted aniline, toluidine, or xylidine) are added 100 parts of perisosulfocyanic acid and the reaction mixture heated to 120° C., or thereabout, for 5–10 hours with agitation. These proportions provide an excess of aniline, which I deem it desirable to have as a reaction medium although it is not necessary. The reaction product is a solid material.

Example 2

This example is the same as Example 1, save that the reaction is carried out at 100° C. for about ten hours in the presence of 100 parts by volume of 22° Bé. hydrochloric acid as a reaction medium. The reaction product is a semi-solid material.

Instead of hydrochloric acid as a reaction medium other mineral acids may be used, such as, for example, sulfuric acid. The reaction medium may be employed in any desired proportion or concentration. The reaction may also be carried out in organic reaction mediums, such as benzene or toluene, as well as the excess of aniline provided in Example 1, and any reaction medium may be used which permits the reaction to proceed.

In a similar manner any of the above-mentioned homolog compounds of aniline may be reacted with perisosulfocyanic acid to produce the substituted dithiobiuret type of inhibitor reagent herein disclosed, or a mixture of aniline and its homolog compounds may be employed.

My invention is not limited to any specific proportion of aniline and its homolog compounds, nor is there any limitation on the proportion of perisosulfocyanic acid in the reaction. I prefer to have an excess of the aniline or its homolog compounds, as already stated, but that is not essential.

Furthermore it is possible in some cases to vary the concentrations of the reacting materials, and of the reaction medium, to obtain either liquid or solid (or semi-solid) reaction products as desired, any one of which is effective as an inhibiting reagent.

In general it may be said that in the use of the inhibitor reagents of the present invention one percent or less added to the acid or salt solution is sufficient to obtain optimum effect, although larger amounts may be used if desired.

As a specific example of the inhibiting action of the inhibitor reagents coming within the scope of this invention, when applied to pickling of steel, 0.004 of 1% by weight of the solid reaction product of perisosulfocyanic acid with aniline, produced according to Example 1, when added to a pickling solution of 82° C., containing 6% by weight of sulfuric acid, there was obtained a metal-loss of 2.7 milligrams per square inch for a forty-minute pickling period after de-scaling was complete, as compared to 122.0 milligrams per square inch for the same test without any inhibitor present; and a proportionately reduced evolution of hydrogen.

Under the above pickling conditions the corrosive action on the iron and consequent evolution of hydrogen was substantially prevented without any material interference with the desired function of the pickling operation—namely, the removal of the scale or oxide film from the metal surface.

By regulating the concentration of the inhibitor it is possible to obtain practically any desired degree of inhibiting action.

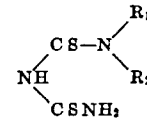
The above example of the use of my inhibitors is illustrative only, and not at all to limit the scope of the invention. For instance, other metals and alloys may be similarly treated, such as copper, nickel, brass, stainless steel, etc. Different pickling acids, or acid concentrations, may be employed, or the period of treatment and the temperature employed may be varied to suit the manufacturing needs.

Mixtures of my various inhibitor reagents with other known inhibitors can be used to advantage to obtain improved results.

These inhibitors can be used in the presence of the foam-producing agents commonly employed in the pickling operation, without detriment to the effect of either.

I claim as my invention:

1. The process of inhibiting the solution of a metal the surface of which is in contact with or immersed in an acid or salt solution, and so inhibiting the consequent evolution of hydrogen, consisting in dissolving in said acid or salt solution a small amount of a substituted dithiobiuret compound having the following formula:



in which R_1 represents a hydrocarbon radical or a hydrocarbon radical containing a halogen, and R_2 represents hydrogen or a hydrocarbon radical.

2. The process of inhibiting the solution of a metal the surface of which is in contact with or immersed in an acid or salt solution, and so inhibiting the consequent evolution of hydrogen, consisting in dissolving in said acid or salt solution a small amount of phenyl dithiobiuret.

3. The process of inhibiting the solution of a metal the surface of which is in contact with or immersed in an acid or salt solution, and so inhibiting the consequent evolution of hydrogen, consisting in dissolving in said acid or salt solution a small amount of a product of the reaction of perisosulfocyanic acid with a substance from the class consisting of aniline and its homologs.

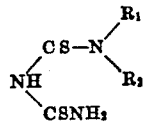
4. The process of inhibiting the solution of a metal the surface of which is in contact with or immersed in an acid or salt solution, and so inhibiting the consequent evolution of hydrogen, consisting in dissolving in said acid or salt solution a small amount of a product of the reaction of perisosulfocyanic acid with aniline.

5. The process of inhibiting the solution of a metal the surface of which is in contact with or immersed in an acid or salt solution, and so inhibiting the consequent evolution of hydrogen, consisting in dissolving in said acid or salt solution a small amount of a product of the reaction of perisosulfocyanic acid with an excess of a substance from the class consisting of aniline and its homologs.

6. The process of inhibiting the solution of a metal the surface of which is in contact with or immersed in an acid or salt solution, and so inhibiting the consequent evolution of hydrogen, consisting in dissolving in said acid or salt solution a small amount of a product of the reaction of perisosulfocyanic acid with an excess of aniline.

7. A liquid bath for chemical and electro-chemical purposes, comprising an acid or salt solution

containing a small amount of a substituted dithiobiuret compound having the following formula:



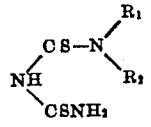
in which R_1 represents a hydrocarbon radical or a hydrocarbon radical containing a halogen, and R_2 represents hydrogen or a hydrocarbon radical.

8. A liquid bath for chemical and electro-chemical purposes, comprising an acid or salt solution containing a small amount of phenyl dithiobiuret.

9. A liquid bath for chemical and electro-chemical purposes, comprising an acid or salt solution containing a small amount of a product of the reaction of perisosulfocyanic acid with a substance from the class consisting of aniline and its homologs.

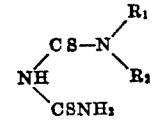
10. A liquid bath for chemical and electrochemical purposes, comprising an acid or salt solution containing a small amount of a product of the reaction of perisosulfocyanic acid with aniline.

11. A pickling bath, comprising sulphuric acid containing a substituted dithiobiuret compound having the following formula:



in which R_1 represents a hydrocarbon radical or a hydrocarbon radical containing a halogen, and R_2 represents hydrogen or a hydrocarbon radical.

12. A new inhibitor for use in the cleaning of metal surfaces with acid or salt solutions, consisting of a substituted dithiobiuret compound having the following formula:



in which R_1 represents a hydrocarbon radical or a hydrocarbon radical containing a halogen, and R_2 represents hydrogen or a hydrocarbon radical.

13. A new inhibitor for use in the cleaning of metal surfaces with acid or salt solutions, consisting of phenyl dithiobiuret.

14. A new inhibitor for use in the cleaning of metal surfaces with acid or salt solutions, consisting of a product of the reaction of perisosulfocyanic acid with a substance from the class consisting of aniline and its homologs.

15. A new inhibitor for use in the cleaning of metal surfaces with acid or salt solutions, consisting of a product of the reaction of perisosulfocyanic acid with aniline.

ORIN D. CUNNINGHAM.