

Patented May 29, 1934

1,961,096

UNITED STATES PATENT OFFICE

1,961,096

INHIBITING PROCESS AND PRODUCT

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No Drawing. Application March 31, 1932,
Serial No. 602,388

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 reaction 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 interfering 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 the reaction products of sulfocyanic acid with coal-tar pyridine bases possess a marked inhibiting action on the evolution of hydrogen.

By "coal-tar pyridine bases", I include both the

coal-tar bases normally found in coal-tar, such for example as pyridine, quinolin, acridine, etc., or methyl-substituted compounds thereof, such as the picolines, the lutidenes, etc., and the mixed coal-tar bases obtained by the usual acid extraction of coal-tar oils; and I prefer the latter. Any desired mixtures of these coal-tar pyridine bases may also be used; and they may be pure, partially refined, or crude materials.

Without in any way limiting my invention to any theory, the reaction of sulfocyanic acid with the coal-tar pyridine bases may be in the nature either of an addition or a substitution reaction, or both reactions may be present; or the reaction may also involve the polymerization of the sulfocyanic acid or the formation of condensation products which either remain dissolved in the reaction mixture or react with the coal-tar pyridine bases to form addition or substitution products.

In carrying out the reaction of sulfocyanic acid with a coal-tar pyridine base, the sulfocyanic acid is preferably formed in the presence of said base by the metathetical reaction of a sulfocyanide with a mineral acid. The sulfocyanide is desirably an alkali-metal sulfocyanide, sodium for example, or an alkaline-earth sulfocyanide, or ammonium sulfocyanide, and effective examples of the mineral acid are hydrochloric acid and sulfuric acid; as will be illustrated in examples given below, which describe the production of the inhibitor reagent according to the present invention.

While the reaction of the coal-tar pyridine bases with the sulfocyanic acid may be carried out at ordinary room temperature, it is preferable to carry it out at a somewhat higher temperature, desirably at approximately 100° C. The reaction may be carried out either at normal atmospheric pressure or at higher pressure. A higher pressure is often desirable when a high reaction temperature is maintained, particularly in case such reaction temperature is above the normal boiling point of the reaction mixture.

It is recognized that some of the coal-tar pyridine bases have been employed as inhibiting reagents in and of themselves; and also that sulfocyanic acid may of itself have some inhibiting action. However, I have discovered that the herein disclosed reaction products of sulfocyanic acid with said coal-tar pyridine bases possess an unexpected and powerful inhibiting activity far superior to anything obtainable with the bases alone, the sulfocyanic acid alone, or the additive value of the activities of these two materials.

The following examples illustrate the produc-

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tion of the inhibitor reagent of the present invention.

Example I

To 100 cc. of a 50—50 mixture by volume of coal-tar pyridine bases and 18° Bé. hydrochloric acid is added 10–15 gms. of ammonium sulfocyanide. The reaction of the ammonium sulfocyanide with the hydrochloric acid forms the sulfocyanic acid required for this reaction. This reaction mixture is then agitated and heated until a homogeneous solution is obtained.

The reaction is then continued at a temperature of 100° C. for about ten hours.

The reaction product is a dark red liquid containing a small amount of crystalline material (ammonium chloride) which may be filtered off or separated by sedimentation.

As another method of obtaining the products of the above example, I may extract coal tar oils with hydrochloric acid in the usual manner of extracting pyridine bases, and then react this product with ammonium sulfocyanide as above described.

Example II

This example is the same as Example I, save that the reaction temperature is raised to about 115° to 120° C., and that the reaction need be continued for only about five hours. This reaction is desirably carried out under an elevated pressure, of about 2 atmospheres.

Example III

This example is the same as either Example I or Example II, save that instead of using ammonium sulfocyanide I use about 15 grams of sodium sulfocyanide.

Example IV

This example may be the same as any of Examples I, II, and III, save that I use about 40% sulphuric acid instead of 18° Bé. hydrochloric acid.

In all these examples, the coal-tar pyridine bases may be any of those indicated, used singly, or any mixture of them.

Instead of ammonium or sodium sulfocyanide, any metal salt of sulfocyanic acid may be employed with equally good results, but I prefer the ammonium, alkali-metal, or alkaline-earth salts mainly because of the greater economy in cost of reagent. If desired, sulfocyanic acid itself may be employed.

Hydrochloric acid or sulfuric acid of any desired concentration may be employed; or, instead of these acids, other mineral acids may be used such for example as phosphoric acid.

I do not limit myself to any specific concentration of coal-tar pyridine bases; nor is there any limitation on the concentration of sulfocyanic acid or its inorganic salts in making up the inhibitor reagent herein disclosed.

Furthermore, it is possible in some cases to use concentrations of reacting materials to obtain either liquid or solid (or semisolid) reaction products, 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, 1% or less added to the acid or salt solution will be sufficient to obtain the maximum effect, although larger amounts may be used if so desired.

As a specific example of the inhibiting action of the inhibitor reagents coming within the scope of this invention, when applied to the "pickling

process", 0.008 of 1% by weight of the reaction product of sulfocyanic acid with coal-tar pyridine bases, as in the examples given, when added to a pickling solution at 82° C., containing 6% sulfuric acid, inhibited the action of the acid on a piece of sheet iron to the extent of about 99% for a forty-minute pickling period.

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.

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 product of the reaction of sulfocyanic acid with a coal-tar pyridine base.

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 a product of the reaction of a coal-tar pyridine base with a mineral acid and an inorganic sulfocyanide.

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 a coal-tar pyridine base with a mineral acid and ammonium sulfocyanide.

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 a coal-tar pyridine base with a mineral acid and sodium sulfocyanide.

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 at a temperature above 25° C. of sulfocyanic acid with a coal-tar pyridine base.

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 at approximately 100° C. of sulfocyanic acid with a coal-tar pyridine base.

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<p>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 at a temperature above 25° C. of a coal-tar pyridine base with a mineral acid and an inorganic sulfocyanide.</p>	<p>of the reaction of a coal-tar pyridine base with a mineral acid and an inorganic sulfocyanide.</p>	80
<p>8. 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 at approximately 100° C. of a coal-tar pyridine base with a mineral acid and an inorganic sulfocyanide.</p>	<p>11. A pickling bath, comprising sulfuric acid containing a product of the reaction of a coal-tar pyridine base with hydrochloric acid and ammonium sulfocyanide.</p>	85
<p>9. 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 sulfocyanic acid with a coal-tar pyridine base.</p>	<p>12. A pickling bath, comprising sulfuric acid containing a product of the reaction of a coal-tar pyridine base with hydrochloric acid and sodium sulfocyanide.</p>	90
<p>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 sulfocyanic acid with a coal-tar pyridine base at approximately 100° C.</p>	<p>13. 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 sulfocyanic acid with a coal-tar pyridine base at a temperature above 25° C.</p>	95
<p>25 solution containing a small amount of a product</p>	<p>14. 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 sulfocyanic acid with a coal-tar pyridine base at approximately 100° C.</p>	100
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