252. COMPOSITIONS,
148

Examine

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CHEMICAL REAGENT

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The invention relates to inhibitors or restrainers useful in chemical and electrochemical processes for preventing or retarding the evolution of hydrogen at the surfaces of metals immersed in the solution or for otherwise preventing or retarding the chemical action of acids on metals. The invention is particularly applicable to chemical processes wherein metals such as iron, steel, nickel, etc., are subjected to the action of acids for removing scale, rust or oxide from the surfaces thereof. Such processes are often referred to as pickling processes and are widely used in manufacturing establishments.

My invention consists in the discovery of a series of chemical compounds which when added to certain chemical reagents act to inhibit the undesired reactions of said reagents without interfering with the desired reactions thereof. For instance when added to a pickling bath of a composition that would ordinarily have a corrosive action upon metals, such compounds serve to retard the corrosive action on the metals and the consequent evolution of hydrogen without interfering materially with the desired function of dissolving the oxide, rust or scale found on the surface of the metal.

There are many advantages in the use of a pickling bath having incorporated therein an inhibiting agent for retarding the chemical action of the acid on the metal. For example, such a composition is useful in removing the layer of iron oxide which is formed on steel or iron during the rolling of sheets, the drawing of wires or rods, the spinning of thin shapes and the annealing of shapes prior to an application of a coating of vitreous enamel, glass, tin, zinc or other metal or paint, varnish enamel, lacquer or other protective or decorative coating. Another use of the process is in the removing of the metallic oxide or carbonate forming on copper or other non-ferrous materials. Another advantageous use is in eliminating the scale forming in pipes and in the tubes of automobile radiators which often seriously interferes with the proper flow and circulation of the fluid through the radiator. My invention is applicable generally to the removal of oxides and scales from metals by a pickling process and the use of the inhibiting agents not only prevents or diminishes the attack of the metals themselves by the acid but also creates more healthful working conditions surrounding the pickling bath. The evolution of hydrogen gas, which is an incident of the attack of the metal by the acid, results in the carrying into the surrounding air of a certain amount of the acid of the bath in the form of a spray which is injurious to the operators and wasteful of the acid material.

In its broader aspects, my invention contemplates the use of the inhibiting agents hereinafter more fully described in connection with any chemical or electrochemical solution or reagent which under normal conditions of operation will evolve hydrogen at the surface of a metal immersed therein. In other words, my invention provides a means for causing desired chemical or electrochemical reactions to take place and without substantially decreasing the rate of said reactions causing an inhibiting action retarding or actually preventing the evolution of hydrogen which would normally take place without the presence of the inhibiting agents.

As a further example of the utility of my invention, it may sometimes be found desirable to use the new inhibiting agents in connection with electroplating processes. It is well known that in the electrodeposition of certain metals hydrogen is liberated at the cathode in addition to the metal which it is desired to plate. By using the inhibiting agents in accordance with my invention the evolution of hydrogen at the cathode may be retarded without correspondingly retarding the deposition of the metal. Thus the efficiency of the plating process is increased and

148

certain undesirable characteristics of the plated metal caused by the evolution of hydrogen may be eliminated.

The new inhibiting agents which I have discovered may be described as cyclic organic compounds of nitrogen. I have found that while in general all of such compounds possess some inhibiting properties, there are certain particular classes of compounds which are much more effective as inhibitors than any compounds heretofore suggested for similar purposes. I have found, for instance, that the derivatives of quinoline in which a substituent is attached to the carbon atom of the quinoline nucleus are more effective inhibitors than pure quinoline itself. I have also found that derivatives of acridine in which a substituent is attached to the carbon atom of the acridine nucleus are more effective inhibitors than pure acridine itself. I have discovered that in general the more complex molecules which may be designated as derivatives of quinoline or acridine exhibit greater inhibiting powers than the less complex molecules. I have further found that certain complex derivatives of the above mentioned cyclic organic compounds of nitrogen will function to almost entirely prevent the evolution of hydrogen when a pure metal is immersed in an acid bath. In other words, I have discovered certain compounds which when used as inhibiting agents will permit acid solutions to dissolve the scale, rust or oxides associated with a metal but will prevent the metal itself being substantially corroded by the action of the acid.

While there are a large number of compounds coming within the purview of this invention, I will refer more specifically to some of the more important compounds with which I have made careful tests to determine the degree of inhibiting power which they possess.

The first group of compounds to which I will refer may be designated as derivatives of quinoline. The following substances have all been found to have markedly superior inhibiting properties to quinoline itself:

Phenylquinoline
2-methylquinoline (quinaldine)
Crude quinaldine
6-methylquinoline
2,4-dimethylquinoline

Another series of compounds useful as inhibiting agents are the derivatives of acridine, of which the following will serve as examples:

Methylacridine
Phenylacridine
3,6-dimethyl-2,7-diethyl diaminoacridine hydrochloride
3,6-diaminoacridine
3,6-dimethyl-2,7-diaminoacridine ethylchloride

Another group of compounds are derivatives of naphthacridine, of which the following are representative:

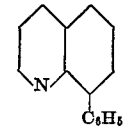
Phenyldinaphthacridine
α-β dinaphthacridine
Fluorenenaphthacridine
β-β dinaphthacridine
α-α dinaphthacridine
Diphenanthracridine

A further group of important inhibiting agents are the following:

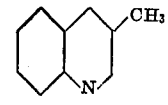
Diquinolyl
Diquinolylmethane
Dimethyldiquinolyl

While in its broader aspects, my invention contemplates the use of any of the substances heretofore enumerated as inhibiting agents, this application also refers more particularly to the class of compounds designated above as the derivatives of quinoline, some of which are listed below together with their probable structural formulas:

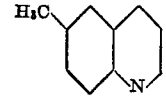
α-phenylquinoline



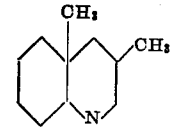
2-methylquinoline



6-methylquinoline



2,4-dimethylquinoline



My invention also contemplates an inhibiting agent formed by substituting one or more chlorine, bromine, amino, hydroxyl or other radicals for one or more of the hydrogen atoms on the quinoline nucleus as, for example, 8-hydroxy quinoline.

The compounds mentioned above may ordinarily be used as inhibiting agents either in the pure state or in the relatively impure form resulting from commercial methods of manufacturing the same. It has been found that in many cases the impure compounds are more efficient inhibitors than the chemically pure substances. For example, crude or impure quinaldine is more effective than pure quinaldine. This may possibly be due to the presence of small amounts of more complex

derivatives in the impure material. The inhibiting compounds may be introduced into the chemical reagent not only in the form of a free base as indicated in some of the formulas given above, but may also be used in the form of a salt as, for example, the hydrochloride of the base.

The amount of the inhibiting agent to be used for any given chemical solution depends not only upon the efficiency of the inhibiting agent but also on operating conditions and the exact results desired in the particular process. In general it may be said that with the compounds mentioned above as the inhibiting agents, 1% or less of the compound added to the solution will be sufficient to obtain the maximum effect although there is apparently no disadvantage other than increased cost in adding larger amounts if so desired. There is, however, a certain relation between the amount of inhibiting agent added and its efficiency.

For example, it has been found that the addition of .15% by weight of 6-methylquinoline to a pickling bath containing 7.5% sulphuric acid inhibits the action of the acid on iron to the extent of 59.7% at 60° C., whereas the addition of 1.5% of the same substance inhibits the action of the acid 93.2% under otherwise similar conditions.

The amount of inhibiting action desired may vary for different manufacturing conditions. For example, in pickling thin sheet steel for light enameled ware it is desirable to use sufficient inhibitor to effect as much as 98% inhibition, whereas in pickling thicker sheets for heavy enamel as little as 80% inhibition might be desired. Thus according to my invention, the inhibiting agent may be added in amounts sufficient only to retard the evolution of hydrogen or on the other hand a suitable inhibiting agent of high efficiency may be added in larger amounts in order to substantially prevent the evolution of hydrogen. By adding 100 millimols per liter of 2-4 dimethylquinoline to a sulphuric acid solution I have obtained 99.0% inhibition to the attack of pure iron. Similarly, the addition of 100 millimols per liter of 8-hydroxy quinoline has obtained 98.4% inhibiting power under substantially the same conditions.

From the above description it will be noted that my invention relates to the discovery of a series of cyclic organic nitrogen compounds having inhibiting characteristics rendering them very valuable in chemical and electrochemical processes with which they have never heretofore been associated. While I have described certain compounds and certain processes with particularity, it is to be understood that the invention is not necessarily limited thereby except in the light of the claims appended hereto.

What I claim as my invention is:

1. A liquid bath for chemical or electro-chemical purposes comprising a solution which under normal conditions of operation evolves hydrogen at the surface of a metal immersed therein and an inhibitor or restrainer in said solution for diminishing the evolution of hydrogen comprising a derivative of quinoline which contains a univalent substituent attached to a carbon atom of the quinoline nucleus, said substituent being attached to only one carbon atom of the nucleus and said quinoline derivative being free from polyatomic inorganic acid radicles attached to the carbon atoms of the nucleus.

2. A liquid bath for chemical or electro-chemical purposes comprising a solution which under normal conditions of operation evolves hydrogen at the surface of a metal immersed therein and an inhibitor or restrainer in said solution for diminishing the evolution of hydrogen comprising a derivative of quinoline which contains a univalent organic radicle attached to a carbon atom of the quinoline nucleus, said substituent being attached to only one carbon atom of the nucleus and said quinoline derivative being free from polyatomic inorganic acid radicles attached to the carbon atoms of the nucleus.

3. A liquid bath for chemical or electro-chemical purposes comprising a solution which under normal conditions of operation evolves hydrogen at the surface of a metal immersed therein and an inhibitor or restrainer in said solution for diminishing the evolution of hydrogen comprising a derivative of quinoline which contains a hydrocarbon radicle attached to a carbon atom of the quinoline nucleus, said substituent being attached to only one carbon atom of the nucleus and said quinoline derivative being free from polyatomic inorganic acid radicles attached to the carbon atoms of the nucleus.

4. A liquid bath for chemical or electro-chemical purposes comprising a solution which under normal conditions of operation evolves hydrogen at the surface of a metal immersed therein and an inhibitor or restrainer in said solution for diminishing the evolution of hydrogen comprising a derivative of quinoline which contains an alkyl radicle attached to a carbon atom of the quinoline nucleus, and free from polyatomic inorganic acid radicles attached to the carbon atoms of the nucleus.

5. A liquid bath for chemical or electro-chemical purposes comprising a solution which under normal conditions of operation evolves hydrogen at the surface of a metal immersed therein and an inhibitor or restrainer in said solution for diminishing the evolution of hydrogen comprising a derivative of quinoline which contains a methyl radicle attached to a carbon atom of the quinoline nucleus, and free from polyatomic inorganic acid radicles

attached to the carbon atoms of the nucleus.

6. A liquid bath for chemical or electrochemical purposes comprising a solution which under normal conditions of operation evolves hydrogen at the surface of a metal immersed therein and an inhibitor or restrainer in said solution for diminishing the evolution of hydrogen comprising a derivative of quinoline which contains a substituted methyl group and free from polyatomic inorganic acid radicles attached to the carbon atoms of the nucleus.

7. A liquid bath for chemical or electrochemical purposes comprising a solution which under normal conditions of operation evolves hydrogen at the surface of a metal immersed therein and an inhibitor or restrainer in said solution for diminishing the evolution of hydrogen comprising quinaldine.

8. The process of inhibiting or restraining the evolution of hydrogen at the surface of a metal immersed in a liquid reagent which consists in introducing into the liquid reagent a derivative of quinoline which contains a univalent substituent attached to a carbon atom of the quinoline nucleus, said substituent being attached to only one carbon atom of the nucleus and said quinoline derivative being free from polyatomic inorganic acid radicals attached to the carbon atoms of the nucleus.

9. The process of inhibiting or restraining the evolution of hydrogen at the surface of a metal immersed in a liquid reagent which consists in introducing into the liquid reagent a derivative of quinoline which contains a univalent organic radical attached to a carbon atom of the quinoline nucleus, said substituent being attached to only one carbon atom of the nucleus and said quinoline derivative being free from polyatomic inorganic acid radicals attached to the carbon atoms of the nucleus.

10. The process of inhibiting or restraining the evolution of hydrogen at the surface of a metal immersed in a liquid reagent which consists in introducing into the liquid reagent a derivative of quinoline which contains a hydrocarbon radical attached to a carbon atom of the quinoline nucleus, said substituent being attached to only one carbon atom of the nucleus and said quinoline derivative being free from polyatomic inorganic acid radicals attached to the carbon atoms of the nucleus.

11. The process of inhibiting or restraining the evolution of hydrogen at the surface of a metal immersed in a liquid reagent which consists in introducing into the liquid reagent a derivative of quinoline which contains an alkyl radical attached to a carbon atom of the quinoline nucleus, and free from polyatomic inorganic acid radicals attached to the carbon atoms of the nucleus.

12. The process of inhibiting or restraining the evolution of hydrogen at the surface of a metal immersed in a liquid reagent which consists in introducing into the liquid reagent a derivative of quinoline which contains a methyl radical attached to a carbon atom of the quinoline nucleus, and free from polyatomic inorganic acid radicals attached to the carbon atoms of the nucleus.

13. The process of inhibiting or restraining the evolution of hydrogen at the surface of a metal immersed in a liquid reagent which consists in introducing into the liquid reagent a derivative of quinoline which contains a substituted methyl group and free from polyatomic inorganic acid radicals attached to the carbon atoms of the nucleus.

14. The process of inhibiting or restraining the evolution of hydrogen at the surface of a metal immersed in a liquid reagent which consists in introducing into the liquid reagent quinaldine.

In testimony whereof I affix my signature.

FRED H. RHODES.