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AMINE INHIBITORS FOR ACIDIC CLEANING SOLUTIONS

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ABSTRACT OF THE DISCLOSURE

Acidic cleaning solutions, which have little or no tendency to corrode metal surfaces, containing amine compounds prepared by reacting a specific amine starting material, formaldehyde and a ketone in the presence of acid, are described. The amine starting material is of the formula

$$CH_3(CH_2)_n-\underset{\underset{HN-Z}{|}}{CH}-R$$

wherein n is an integer ranging from about 2 to about 20, R is selected from the group consisting of hydrogen and $CH_3(CH_2)_{m-1}$, wherein m is an integer ranging from 1 to about 21, and Z is selected from the group consisting of hydrogen and the propylamine radical.

This invention relates to amine compounds. This invention also relates to the use of amine compounds in acidic solutions which are utilized to clean metal surfaces.

It is known to utilize certain amine compounds in acidic solutions which are utilized for cleaning or pickling metal surfaces to remove therefrom unwanted oxide scales and other undesirable corrosion products. The amine compound functions to reduce the tendency of the acidic cleaning solution to corrode the metal surface without interfering wtih the cleaning operation performed by the solution. Materials which so function are generally referred to as "acid inhibitors."

The corrosion of metal surfaces by acidic cleaning solutions is caused by the acids present in the solution. Acids generally used in such metal cleaning or pickling solutions are the so-called "non-oxidizing" acids. Included in this category are inorganic acids, such as hydrochloric acid, phosphoric acid, sulphamic acid, sulphonic acid and sulphuric acid; and organic acids, such as acetic acid, citric acid, formic acid, glycolic acid and oxalic acid.

The acid component of the cleaning solution is effective to rid the metal surface of undesirable deposits thereon, but unfortunately it also tends to attack and corrode the base metal which is desired to be cleansed only. This, of course, is extremely undesirable. To counteract the corrosive effects of the acids, acid inhibitors are added to the cleaning solution.

Amine compounds which function as acid inhibitors in acidic cleaning or pickling solutions are disclosed in U.S. Pat. No. 2,758,970 to Saukaitis and Gardner and assigned to the same assignee as this invention. These amine compounds are the product obtained by the reaction of certain rosin amines with formaldehyde and a ketone. Such reaction is of the type known as a "Mannich reaction." The patent also discloses that the acid salts of the amines described therein are useful as acid inhibitors.

It is also known that rosin amines, which are utilized as the starting material to prepare the amine compounds which are the subject matter of the above mentioned patent, are useful as acid inhibitors. However, the amines of the patent are superior to the rosin amine starting materials because the former exhibit better inhibition properties and because they exhibit a high degree of heat stability. Heat stability is important because the cleaning process is sometimes advantageously carried out at temperatures above ambient.

Although known amine compounds, such as those described above, have been successfully used as acid inhibitors in acidic cleaning and pickling solutions, their use has not always been problem-free. For example, their use leaves something to be desired in pickling applications in which iron tends to build up in the acidic pickling solution.

As an illustration of such an application, it has been observed that in the hydrochloric acid pickling of steel by strip line or batch process, the content of the iron (expressed as Fe^{++}) in a working solution can rise to as high as about 14 to about 17 grams per 100 ml. of solution. The presence of the iron has various undesirable effects on the cleaning process. For example, the iron, which takes the form of the chloride salt in a hydrochloric acid pickling solution, can actually accelerate the corrosion of the steel being treated.

Another undesirable effect produced by the iron is that it causes the acid inhibitor to "oil out" of the pickling solution. This reduces the amount of acid inhibitor which is available to counteract the corrosive effect of the chloride salt and the acid. Moreover, when the acid inhibitor oils out of the cleaning solution, it deposits on the metal surface. Such deposits have a tendency to interfere with subsequent operations to which the steel is subjected, such as for example, cold rolling.

It is therefore an object of this invention to provide new amine compounds which exhibit improved acid inhibition properties and a method for preparing such compounds.

It is another object of this invention to provide acid inhibitors for acidic cleaning or pickling solutions, that is materials which are effective to reduce or prevent the tendency of such solutions to corrode or attack metal surfaces which are subjected to the solutions for cleaning.

It is also an object of this invention to provide improved acidic cleaning or pickling solutions which have little or no tendency to corrode metal surfaces which are subjected to the solutions for the purpose of ridding said surface of undesirable deposits present thereon.

It is a further object of this invention to provide an improved process for cleaning metal surfaces of oxide scales and other undesirable deposits by the use of an acidic cleaning or pickling solution and in a manner such that the metal surface is not attacked and corroded by the solution.

It is still another object of this invention to provide materials for use as acid inhibitors in acidic cleaning or pickling solutions in which iron is present.

In accordance with this invention, it has been found that by selecting certain specific amine starting materials and reacting one or more of them with formaldehyde and a ketone having at least one reactive hydrogen, in the presence of sufficient acid to maintain the pH of the reaction below 7, there is obtained an amine product which exhibits excellent acid inhibition properties in acidic solutions for cleaning metal surfaces. As the reaction is carried out in an acidic medium, the product obtained will contain the acid salt of the amine produced by the reaction. Both the acid salt of the amine and the amine itself exhibit acid inhibition properties, so that either of the products or mixtures thereof can be utilized as the acid inhibitor in acidic cleaning solutions.

The amine starting material utilized in the reaction described above is of the formula

$$CH_3(CH_2)_n-\underset{\underset{HN-Z}{|}}{CH}-R \qquad \text{Formula}$$

wherein n is an integer ranging from about 2 to about 20; R is selected from the group consisting of hydrogen and $CH_3(CH_2)_{m-1}$ wherein m is an integer ranging from 1 to about 21; and Z is selected from the group consisting of hydrogen and the propylamine radical. The above defined amine starting materials, which are precursors for the improved acid inhibitors of this invention, are well-known, as are methods for preparing them. A number of them are commercially available.

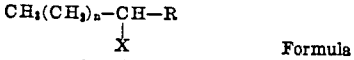
The reaction set forth above to prepare the new and improved acid inhibitors of this invention, that is the reaction of an amine starting material, formaldehyde and ketone, in the presence of an acid, is of the type which can be classified as a Mannich reaction, one well-known in the amine synthesis art. This reaction, which utilizes an amine starting material for synthesizing a different amine compound, consists, in general, of the condensation of an amine with formaldehyde and a ketone having at least one reactive hydrogen atom. Whereas the Mannich reaction is one of general knowledge, it has not heretofore been known to subject the amine starting materials of Formula I above to this reaction to produce the acid inhibitors of this invention.

Although the Mannich reaction has been known and investigated for some time, there exists various uncertainties about the reaction which preclude in many cases a correct prediction of the specific amine compound or mixture of amine compounds that will be produced by the reaction. In this connection, it is noted that the mechanism of the Mannich reaction has not been established. A number of theories on the reaction mechanism have been advanced, but no one theory has been agreed upon as being a correct and full explanation of how the various and many kinds of amines and ketones known to react with formaldehyde do react.

Experience in synthesizing amine compounds by a Mannich reaction has shown that it is not unlikely that the reaction product will comprise in some cases a mixture of amine compounds rather than a specific amine.

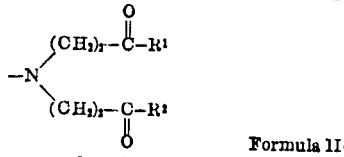
We have found that regardless of the particular amine compound or mixture of amine compounds produced by reacting the amine starting material of Formula I with ketone and formaldehyde as set forth above, the reaction product exhibits excellent acid inhibition properties.

Despite the uncertainties of the specific product that will be produced in a Mannich reaction, it has also been found that by reacting amine starting materials of Formula I above with formaldehyde and a ketone having at least one reactive hydrogen in the presence of sufficient acid to maintain the pH of the reaction below 7, there can be obtained amine compounds of the general formula



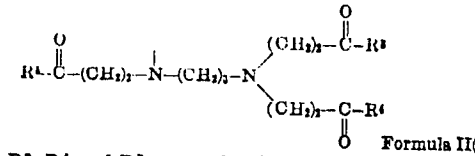
Formula I_I

wherein n is an integer ranging from about 2 to about 20; R is selected from the group consisting of hydrogen and $CH_3(CH_2)_{m-1}$ wherein m is an integer ranging from 1 to about 21; and X is selected from the group consisting of



Formula II(A)

wherein R^1 and R^2 are each a hydrocarbon radical and the group



Formula II(B)

wherein R^3, R^4 and R^5 are each a hydrocarbon radical.

The amines of Formula II above, as well as their acid salts, exhibit excellent acid inhibition properties in acidic cleaning solution. With respect to the acid salts of the amines, it is noted that because the reaction is carried out in an acidic medium and maintained at a pH below 7, the product produced by the reaction will contain the acid salt of the amines represented by Formula II. As the acid salt has acid inhibition properties, it can be used without further treatment as the acid inhibitor in acidic cleaning solutions. On the other hand, if it is desired, the amine itself can be recovered from the acid salt of the amine.

The amines of this invention and their corresponding acid salts have a number of properties which make them particularly suitable and effective as acid inhibitors in acidic cleaning solutions. Such properties include the ability to more effectively prevent or retard the corrosion of the metal being cleaned by the acidic cleaning solution than known acid inhibitors. This is so even when high concentrations of iron are present in the solution. Also, they have the ability to resist "oiling out" of the cleaning or pickling solution, unlike various of the presently available acid inhibitors which tend to oil out due to the presence of iron in the solution. Thus, the use of the compounds of this invention in metal cleaning processes has the advantage that amounts of the compounds are not dissipated due to oiling out and the further advantage that the metal surface is not left with "oiling out" deposits which tend to interfere with operations to which the metal is subsequently subjected.

Another very important property of the compounds of this invention is that they are extremely effective as acid inhibitors even when used in very small amounts. Thus the advantages set forth above can be realized when as little as a few hundredths of a percent, or even less, of the amine compound is present in the acidic cleaning solution.

Any of the available methods may be utilized to prepare the amine compounds of Formula II above. For example, compounds of Formula II above can be prepared by reacting suitable vinyl ketones and amines in the presence of acid or by reacting suitable methylol amines and ketones in the presence of acid. However, it is preferred that they be prepared by a Mannich type reaction.

The formaldehyde component utilized in the reaction to produce the acid inhibitor of this invention is preferably added to the reaction mixture in the form of an aqueous solution, such as for example the conventional 37 weight percent aqueous solution of commerce, or in the form of an organic solution, such as the readily available alcoholic solution known as "Formcel."

According to standard techniques, any material that readily breaks down to yield formaldehyde under the conditions of the Mannich reaction can be utilized instead of the aqueous and alcoholic solutions of formaldehyde referred to above. An example of such material as a source of formaldehyde is paraformaldehyde, a linear polyoxymethylene glycol.

For each mole of amine starting material utilized, there is preferably utilized one mole of formaldehyde for each hydrogen atom attached to a nitrogen atom in the amine starting material, plus about 10 to 20 molar percent excess of formaldehyde.

Any ketone having at least one reactive hydrogen atom can be utilized in the Mannich reaction to prepare the compounds of this invention. Examples of such ketones are the following:

acetone
methylethylketone
isobutylmethyl ketone
diacetone alcohol
2,4-pentanedione
acetonylacetone
phorone
mesityl oxide
cyclopentanone
propiophenone
acetonaphthone
acetophenone
p-methoxyacetophenone
p-chloroacetophenone
2-heptanone
2-undecanone
2-acetylcyclohexanone
butyrophenone
naphthalenone
cyclohexanone
tetrolophenone

With reference to Formulae II(A) and II(B) above, it is noted that the ketone utilized in the reaction is the source of the hydrocarbon radical, that is, R^1 and R^2 of Formula II(A), and R^3, R^4 and R^5 of Formula II(B). From the standpoint of the reaction, it is noted that any ketone having available reactive hydrogen will react according to the Mannich reaction. From the standpoint of acid inhibitor properties of the compounds of this invention, it is noted that the presence of any hydrocarbon radical is effective and, consequently, any ketone capable of reacting as set forth above can be utilized.

Mixtures of ketones may also be utilized to prepare the amines within the scope of this invention. When a mixture of ketones is utilized, there can be obtained compounds wherein R^1 and R^2 of the Formula II(A) above and R^3, R^4 and R^5 of the Formula II(B) above are different hydrocarbon radicals.

When a mixture of ketones is utilized, the less or least reactive ketone or ketones should be added to the reaction mixture and allowed to react to some extent with the amine starting material and formaldehyde components prior to the addition to the reaction medium of the ketone having greatest reactivity. This procedure gives the ketones of lesser activity an opportunity to react with the amine and formaldehyde components.

On the other hand, when a single ketone is utilized, R^1 and R^2 of Formula II(A) above will be the same hydrocarbon radical and similarly R^3, R^4 and R^5 of the Formula II(B) above will be the same hydrocarbon radical.

Preferably, the reaction is carried out using an excess of ketone. On the basis of one mole of amine starting material, there is preferably utilized one mole of ketone for each hydrogen atom attached to a nitrogen atom in the amine starting material, plus an excess of about one to two moles of ketone.

As mentioned, the reaction must be carried out in the presence of sufficient acid to maintain the pH of the reaction medium below 7. An inorganic or organic acid can be utilized.

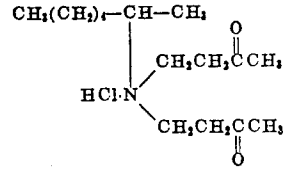
The preferred acid is hydrochloric acid and, when used, the product obtained will be the hydrochloride salt of the amine. Hydrobromic, sulfuric and acetic acids are illustrative of other types of acids that can be utilized.

In a preferred sequence of steps to prepare the compounds of this invention, acid is added to a mixture of the amine starting material and the ketone in amounts sufficient to impart to and maintain the reaction mixture at a pH below 7. Then formaldehyde is added slowly over a period of hours to the reaction mixture as it is continuously stirred. The mixture is then refluxed for a period of hours to maximize yield. The excess ketone may then be distilled off leaving behind amine compounds within the scope of this invention.

Set forth below are illustrative examples of compounds within the scope of this invention and preparation of such compounds.

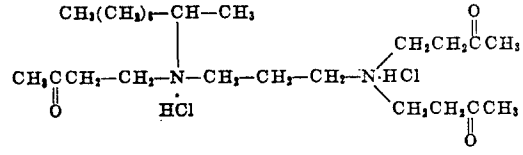
EXAMPLE I

One-half mole of amine starting material of the general Formula I above, wherein *n* is 4, R is methyl and Z is hydrogen, was dissolved in 2 moles of acetone. One-half mole of hydrochloric acid was then added with stirring and cooling. One mole of formaldehyde in the form of a 37 weight percent aqueous solution was then added over a period of 2 hours through a dropping funnel as the mixture was continuously stirred and kept cool. The mixture was then heated to reflux and was so maintained as it was continuously stirred for 24 hours. The pot temperature was 77° C. Thereafter, excess acetone was separated from the reaction mixture by distillation and the distillate obtained amounted to 54 ml. The distillate had a specific gravity of 0.81 (equivalent to 41 g. of acetone). A still residue of 265 g. was left behind and this contained the hydrochloride salt of the amine of the formula



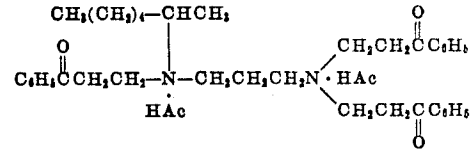
EXAMPLE II

One-half mole of amine starting material of the general Formula I above, wherein *n* is 8, R is methyl and Z is a propylamine radical, was dissolved in 3 moles of acetone. One mole of hydrochloric acid was added slowly with stirring and cooling. Formaldehyde (1.5 moles), as a 37 weight percent aqueous solution, was added slowly, over 2 hours, with stirring and cooling. Then the reaction mixture was heated to reflux, with stirring, for 20 hours. Thereafter, the excess acetone was distilled off, the pot temperature reaching 98° C. There was obtained 89 ml. of distillate having a specific gravity of 0.84. The residue (416 g.) contained the dihydrochloride salt of the amine having the formula



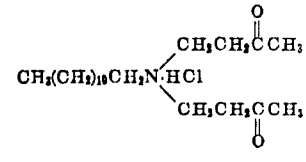
EXAMPLE III

One-half mole of amine starting material of the general Formula I above, wherein *n* is 4, R is methyl and Z is propylamine, was dissolved in 1.5 moles of acetophenone contained in a flask. Acetic acid (1 mole) was added to the flask with stirring and cooling. Formaldehyde (1.5 moles), 40 weight percent in n-butanol, was added slowly, with stirring. Refluxing was carried out for 24 hours, and the mix was distilled up to a pot temperature of 125° C. to provide 58 ml. of mixed distillate. The residue (381 g.) in the flask contained the acetate salt of the amine of the formula



EXAMPLE IV

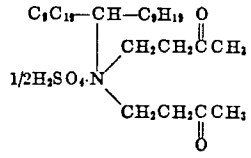
One mole of amine starting material of the general Formula I above, wherein *n* is 10 and R and Z are each a hydrogen atom, was dissolved in 3 moles of acetone. Hydrochloric acid (1 mole) was added slowly, with stirring and cooling. Two moles of formaldehyde as a 37 weight percent aqueous solution was added over a three-hour period with stirring. Refluxing was then carried out for 24 hours at a pot temperature of 85° C. The product was then distilled to a pot temperature of 93° C., when 41 ml. of acetone was distilled off to provide a residue (601.5 g.) containing the hydrochloride salt of the amine of the formula



EXAMPLE V

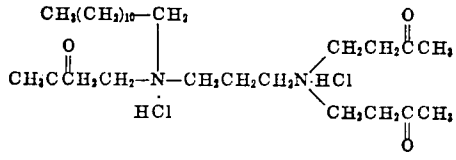
Using the procedure outlined in Examples I–IV above, an amine starting material of the general Formula I above, wherein *n* is 8, R is $CH_3(CH_2)_8$ and Z is hydrogen, was reacted with acetone and formaldehyde in the

presence of sulphuric acid to yield the sulphate salt of the amine of the formula



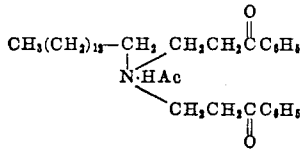
EXAMPLE VI

Using the procedures outlined in foregoing Examples I–IV above, an amine starting material of the general Formula I above, wherein *n* is 10, R is hydrogen and Z is propylamine, was reacted with acetone and formaldehyde in the presence of hydrochloric acid to yield the dihydrochloride salt of the amine of the formula



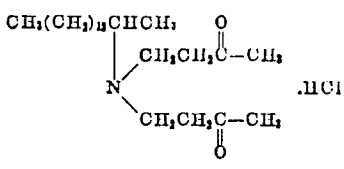
EXAMPLE VII

One-half mole of amine starting material of the general Formula I, wherein *n* is 12, R is hydrogen and Z is hydrogen, was dissolved in 1 mole of acetophenone. One mole of acetic acid was added with cooling and stirring. One mole of formaldehyde as 40 weight percent active in n-butanol solution, was added over a two-hour period with stirring. The solution was then heated and stirred at reflux for 24 hours, the pot temperature reaching 105° C. Water (19 ml.) and butanol (28 ml.) were then distilled off, the pot temperature reaching 124° C. The product (307 g.) contained the acetate salt of the amine of the formula



EXAMPLE VIII

There was added to a flask 1 mole of amine starting material of the general Formula I, wherein *n* is 12, R is methyl, and Z is hydrogen, and 3.5 moles of acetone. To the contents of the flask 116 g. of hydrochloric acid was added drop-wise. The pH of the solution in the flask was approximately 1. Thereupon, 2.1 moles of formaldehyde as a 37 weight percent aqueous solution was added to the contents of the flask. Refluxing was carried out for 24 hours at 76° C. At the end of the 24-hour period, excess acetone and formaldehyde were stripped by distillation to a temperature of 90° C. The reaction product contained the hydrochloride salt of the amine having the formula



As discussed above, the amine compounds of this invention and their acid salts are excellent acid inhibitors in acidic solutions which are utilized to clean metal surfaces. As such they function to remarkably reduce the tendency of the acid in the cleaning solution to corrode and attack the metal being cleaned. Moreover, this is accomplished without interfering with cleaning functions of the acid.

The acid inhibitors of this invention will find use in the wide variety of acid cleaning and pickling solutions that are used to clean metal surfaces of unwanted oxide scales and other undesirable corrosion products. Examples of such cleaning solutions are those containing acids, such as for example, hydrochloric acid, phosphoric acid, sulphamic acid, sulphonic acid, sulphuric acid, acetic acid, citric acid, formic acid, glycolic acid and oxalic acid.

The amine compounds described herein can be utilized to particularly good advantage in applications involving strip line and batch hydrochloric acid pickling of stainless steel and iron surfaces, that is in applications wherein iron tends to build up in the cleaning solution. However, the amine compounds and amine salts described herein can also be utilized in other types of cleaning and pickling solutions, for example in sulfuric acid pickling solutions. The amines of the invention will thus find use in any of the wide variety of cleaning and pickling solutions which are available for cleaning metal surfaces.

The preferred acid inhibitors of this invention are those of Examples IV to VIII, inclusive. It has been found that the amines of these examples exhibit particularly good acid inhibition properties when incorporated in acidic cleaning or pickling solutions.

In general, the acid inhibitors of this invention can be incorporated in the acidic cleaning solution in any amount effective to reduce the tendency of the acid to attack and corrode the metal without interfering with the cleaning operation performed by the acid. The most effective amount of acid inhibitor will vary depending on a number of factors, including the particular amine compound utilized, the specific cleaning solution utilized and the type of metal being treated.

In general, it has been found that good results can be obtained when the acid inhibitors of this invention are present in the acidic cleaning or pickling solution in amounts ranging from about 0.005 to about 0.1 percent by volume. Larger amounts can be used; however, for most applications this will be unnecessary and, for the sake of economy, it will be generally advantageous to avoid the use of larger amounts.

Particularly good results have been obtained when the acid inhibitors are utilized in amounts ranging from about 0.0125 to about 0.0625 percent by volume. This range encompasses the preferred amounts.

Generally, cleaning and pickling solutions containing the compounds of this invention can be utilized to treat any of a wide variety of metals. Examples of metal surfaces that can be treated are aluminum, magnesium, zinc, titanium, iron, steel and other metal surfaces.

The acid inhibitors of this invention can be utilized in acidic pickling or cleaning solutions which also contain non-ionic or cationic surfactants. Examples of surfactants include the nonylphenol/ethylene oxide condensation products, ethoxylated amines and ethoxylated alcohols, used in conventional amounts.

The acid inhibitors of this invention may also be utilized in conjunction with other known acid inhibitors, examples of which include aryl mercapto acetic acids, hexamethylene tetra-amine, propargyl alcohol, thiourea and urea.

In order to demonstrate the improvement in acid inhibition effect of the compounds of this invention, even in the presence of a high content of iron, there are reported below the results of a number of evaluations.

Aqueous test solutions were prepared to consist of 11.3 grams/100 ml. of hydrochloric acid without iron and with 14 grams/100 mls. of iron (expressed as Fe^{++}). The aqueous test solutions also contained, as an inhibitor, one of the amine starting materials or the reaction products of each of Examples I to VI herein. Into these test solutions containing amine compounds, there was immersed a 1010 hot rolled steel panel of 3 square inch total surface area for 25 minutes at 180° F. and the weight loss was noted. This weight loss was compared to the weight loss of a control panel immersed under the same conditions in an inhibitor-free acidic solution, that is one that contains no amide compound or other inhibitor. The results of the tests are expressed in the follow-

ing table as "percent inhibition" which was calculated according to the formula

$$\frac{A-B}{A}\times 100$$

wherein A is loss in weight of the control panel, that is the panel immersed in the inhibitor-free acidic solution, and B is loss in weight of the test panel immersed in the test solution containing an acid inhibitor in the inhibition test solution. It is noted that the higher the percentage inhibition value, the more effective the acid inhibitor.

Inhibitor type	Iron, Fe^{++} g./100 ml.	Percent inhibition at the following conc. of inhibitor, percent vol.*				
		0.0125	0.0250	0.0375	0.0500	0.0625
Example I:						
Starting material	No	6.80	8.93	13.07	17.48	11.68
Reaction product	No	41.35	73.33	85.07	88.70	90.93
Starting material	14	0.57	0.71	0.48	0.15	1.31
Reaction product	14	30.04	46.00	66.93	75.06	84.11
Example II:						
Starting material	No	50.17	86.14	88.41	89.80	89.82
Reaction product	No	93.23	94.25	95.98	96.54	96.89
Starting material	14	46.19	76.03	80.08	81.63	82.49
Reaction product	14	91.06	95.03	96.68	97.26	97.49
Example III:						
Starting material	No	16.18	24.02	33.18	52.49	37.18
Reaction product	No	85.39	90.43	92.31	93.84	94.35
Starting material	14	0.96	1.31	1.34	1.52	2.07
Reaction product	14	73.39	85.04	90.49	93.02	95.71
Example IV:						
Starting material	No	87.34	88.89	89.53	90.43	89.39
Reaction product	No	96.06	96.67	97.83	98.43	98.72
Starting material	14	0.09	0.57	0.58	2.16	2.83
Reaction product	14	73.02	93.38	96.29	96.82	97.86
Example V:						
Starting material	No	21.94	95.58	93.11	96.35	96.51
Reaction product	No	96.90	97.47	97.35	97.47	98.10
Starting material	14	13.79	70.34	80.12	91.10	90.42
Reaction product	14	56.32	88.47	95.46	94.63	96.84
Example VI:						
Starting material	No	87.21	88.57	90.06	89.99	91.48
Reaction product	No	94.43	96.99	97.67	98.18	98.29
Starting material	14	6.55	13.31	19.09	18.23	26.54
Reaction product	14	91.60	95.72	97.04	97.32	97.67

*The concentrations refer to the active amine materials only, not the actual residues referred to in the foregoing Examples I to VI.

It will be seen from the results shown in the foregoing table that improved acid inhibition was obtained using the compounds of this invention. The degree of improvement varied from compound to compound but as a general rule a significant improvement was noted in each case, even when the compound was tested for acid inhibition in the presence of relatively high concentration of iron.

The same general pattern of effectiveness of the acid inhibitors of this invention, as shown in the above table, will be obtained when the inhibitors are utilized in cleaning solutions containing other types of cleaning acids.

We claim:

1. An acidic aqueous solution for cleaning or pickling metal surfaces, the aqueous solution comprising an acid having metal cleaning properties and being present in an amount effective to clean the metal surface and in an amount sufficient to reduce the tendency of the acid of said solution from attacking the metal surface, the amine product formed by the Mannich reaction in the presence of acid, of formaldehyde, with a ketone having at least one reactive hydrogen, and an amine starting material of the formula

$$CH_3(CH_2)_n-\underset{\displaystyle HN-Z}{\overset{\displaystyle |}{CH}}-R$$

wherein n is an integer ranging from about 2 to about 20, R is selected from the group consisting of hydrogen and $CH_3(CH_2)_{m-1}$, wherein m is an integer ranging from 1 to about 21, and Z is selected from the group consisting of hydrogen and the propylamine radical, said acid being present in an amount sufficient to maintain the pH of the reaction below 7 and wherein for each mole of said amine starting material there is utilized at least 1 mole of formaldehyde and 1 mole of ketone for amine starting material.

2. An acidic aqueous solution according to claim 1 wherein there is utilized in said reaction a 10 to 20 molar percent excess of formaldehyde and a 1 to 2 mole excess of ketone.

3. A solution according to claim 1 wherein the amount of said amine product in said solution is within the range of about 0.005 to about 0.1% by volume.

4. A solution according to claim 1 wherein the amount of said amine product in said solution is within the range of about 0.0125 to about 0.0625% by volume.

5. In the process for cleaning or pickling a metal surface utilizing an acidic aqueous solution which contains an acid inhibitor in an amount effective to reduce the tendency of the solution to attack the metal surface, the improvement comprising utilizing the amine product formed by the Mannick reaction, in the presence of acid, of formaldehyde, with a ketone having at least one reactive hydrogen, and an amine starting material of the formula

$$CH_3(CH_2)_n-\underset{\displaystyle HN-Z}{\overset{\displaystyle |}{CH}}-R$$

wherein n is an integer ranging from about 2 to about 20, R is selected from the group consisting of hydrogen and $CH_3(CH_2)_{m-1}$, wherein m is an integer ranging from 1 to about 21, and Z is selected from the group consisting of hydrogen and the propylamine radical, said acid being present in an amount sufficient to maintain the pH of the reaction below 7 and wherein for each mole of said amine starting material there is utilized at least 1 mole of formaldehyde and 1 mole of ketone for each hydrogen atom attached to a nitrogen atom in the amine starting material.

6. The process according to claim 5 wherein said ketone is acetone, wherein in the formula of said amine starting material n is 10 and R and Z are each hydrogen and wherein the acid in said reaction is hydrochloric acid.

7. The process according to claim 5 wherein said ketone is acetone, wherein in the formula of said amine starting material n is 8, R is $CH_3(CH_2)_8$ and Z is hydrogen and wherein the acid in said reaction is sulfuric acid.

8. The process according to claim 5 wherein said ketone acetone, wherein in the formula of said amine starting material n is 10, R is hydrogen and Z is propylamine and wherein the acid in said reaction is hydrochloric acid.

9. The process according to claim 5 wherein said ketone is acetophenone, wherein in the formula of said amine starting material n is 12, R and Z are each hydrogen and wherein the acid in said reaction is acetic acid.

10. The process according to claim 5 wherein said ketone is acetone, wherein in the formula of said amine starting material n is 12, R is methyl and Z is hydrogen and wherein the acid in said reaction is hydrochloric acid.

11. A process according to claim 2 wherein there is utilized in said reaction a 10 to 20 molar percent excess of formaldehyde and a 1 to 2 mole excess of ketone.

12. An acidic aqueous solution for cleaning or pickling an iron or steel surface comprising hydrochloric acid in an amount effective to clean said surface and in an amount effective to reduce the tendency of the solution to attack the surface, the amine product formed by the Mannich reaction, in the presence of acid, of formaldehyde, with a ketone having at least one reactive hydrogen, and an amine starting material of the formula

$$CH_3(CH_2)_n-\underset{\displaystyle HN-Z}{\overset{\displaystyle |}{CH}}-R$$

wherein n is an integer ranging from about 2 to about 20, R is selected from the group consisting of hydrogen and $CH_3(CH_2)_{m-1}$, wherein m is an integer ranging from 1 to about 21, and Z is selected from the group consisting of hydrogen and the propylamine radical, said acid being present in an amount sufficient to maintain the pH of the reaction below 7 and wherein for each mole of said amine starting material there is utilized at least 1 mole of

formaldehyde and 1 mole of ketone for each hydrogen atom attached to a nitrogen atom in the amine starting material.

13. An acidic aqueous solution according to claim **12** wherein said ketone is acetone, wherein in the formula of said amine starting material *n* is 10 and R and Z are each hydrogen and wherein the acid in said reaction is hydrochloric acid.

14. An acidic aqueous solution according to claim **12** wherein said ketone is acetone, wherein in the formula of said amine starting material *n* is 8, R is $CH_3(CH_2)_8$ and Z is hydrogen and wherein the acid in said reaction is sulfuric acid.

15. An acidic aqueous solution according to claim **12** wherein said ketone is acetone, wherein in the formula of said amine starting material *n* is 10, R is hydrogen and Z is propylamine and wherein the acid in said reaction is hydrochloric acid.

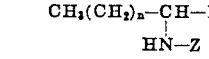
16. An acidic aqueous solution according to claim **12** wherein said ketone is acetophenone, wherein in the formula of said amine starting material *n* is 12, R and Z are each hydrogen and wherein the acid in said reaction is acetic acid.

17. An acidic aqueous solution according to claim **12** wherein said ketone is acetone, wherein in the formula of said amine starting material *n* is 12, R is methyl and Z is hydrogen and wherein the acid in said reaction is hydrochloric acid.

18. An acidic aqueous solution according to claim **12** wherein there is utilized in said reaction a 10 to 20 molar percent excess of formaldehyde and a 1 to 2 mole excess of ketone.

19. An acidic aqueous solution according to claim **12** containing about 0.005 to about 0.1% by volume of said amine product.

20. A process for cleaning a stainless steel or iron surface comprising contacting the surface with an aqueous acidic pickling solution comprising hydrochloric acid and in an amount at least effective to reduce the tendency of the solution from attacking the surface, the amine product formed by the Mannich reaction, in the presence of acid, of formaldehyde, with a ketone having at least one reactive hydrogen, and an amine starting material of the formula



wherein *n* is an integer ranging from about 2 to about 20, R is selected from the group consisting of hydrogen and $CH_3(CH_2)_{m-1}$, wherein *m* is an integer ranging from 1 to about 21, and Z is selected from the group consisting of hydrogen and the propylamine radical, said acid being present in an amount sufficient to maintain the pH of the reaction below 7 and wherein for each mole of said amine starting material there is utilized at least 1 mole of formaldehyde and 1 mole of ketone for each hydrogen atom attached to a nitrogen atom in the amine starting material.

21. A process according to claim **20** wherein there is utilized in said reaction a 10 to 20 molar percent excess of formaldehyde and a 1 to 2 mole excess of ketone.

22. The process according to claim **20** wherein the amount of said amine product in said solution is within the range of about 0.005 to about 0.1% by volume.

23. The process according to claim **20** wherein the amount of said amine product in said solution is within the range of from about 0.0125 to about 0.0625% by volume.

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CERTIFICATE OF CORRECTION

Patent No. 3,630,933 Dated December 28, 1971

Inventor(s) Walter R. Dudlik and George S. Gardner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE SPECIFICATION

Column 2, last line, "Formulla" should read --Formula 1--.

IN THE CLAIMS

Claim 1, last line, before "amine", read--each hydrogen atom attached to a nitrogen atom in the--.

Claim 11, first line, for "2", read --5--.

Signed and sealed this 4th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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