

1

3,466,192

CORROSION PREVENTION PROCESS

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4 Claims

ABSTRACT OF THE DISCLOSURE

Oxidizing acid attack on basis metal surfaces is reduced by use of an oxidizing acid solution containing nitrate, ferric ion or hydrogen peroxide along with soluble methylol thiourea compounds in the acid solution. Copper ion is added to enhance corrosion prevention by the acid solutions.

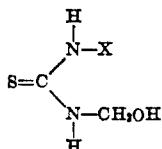
The present invention relates to a method of inhibiting the corrosion of metal surfaces and more particularly is concerned with the utilization of inhibited oxidizing acid systems for treating metal surfaces.

It is known in the art that oxidizing acid systems, while capable of producing the desired treatment of metal surfaces, have not found wide use in the metal treating industry for the reason that these oxidizing acid systems are too active with respect to the basis metal, dissolving large quantities thereof in short periods of time. Attempts to inhibit the attack of such oxidizing acids on basis metal surfaces have not been successful from a commercial viewpoint.

It is also well known in the art that certain non-oxidizing acid systems can be used to treat metal surfaces provided certain organic nitrogen bases or other compounds are employed in the acid system as corrosion inhibiting agents. These latter systems have found extensive commercial use as may be illustrated by reference to U.S. Patents 2,403,153; 2,485,529; 2,799,648; 3,047,510; and 3,277,011 which teach the use of certain thiourea compounds either alone or in combination with other agents as corrosion inhibitors in non-oxidizing acid systems. For example U.S. Patent 2,485,529 teaches the use of thioureas along with thiocyanate compounds for purposes of inhibiting acid attack on basis metal, whereas U.S. Patent 2,403,153 teaches the use of thiourea in conjunction with certain organic coal tar bases for inhibiting acid attack on basis metal. As good as these thiourea compounds are in conventional non-oxidizing acid systems, they are ineffective for retarding or eliminating acid attack in oxidizing acid solutions.

With the foregoing in mind the principal object of the present invention may be said to reside in the provision of a process for inhibiting the attack of oxidizing acids upon basis metal surfaces.

The present invention is based upon the surprising discovery that if at least 0.35 gram/liter of a soluble methylol thiourea derivative of the formula:



wherein X is selected from the group consisting of hydrogen and CH₂OH is added to an aqueous oxidizing acid solution containing an agent selected from the class consisting of nitrate ion, ferric ion and hydrogen peroxide, there will result an improved acid treating solution having a reduced rate of corrosive attack on basis metal surfaces.

2

Typical examples of aqueous oxidizing acid system which contain an agent from the class consisting of nitrate ion, ferric ion and hydrogen peroxide, and which are suitable for use in accordance with the process of this invention include:

- 5 Nitric acid.
- Nitric acid + hydrochloric acid.
- Nitric acid + sulfuric acid.
- Nitric acid, sulfuric acid + ferric sulfate.
- 10 Nitric acid + hydrofluoric acid.
- Hydrochloric acid + ferric chloride.
- Hydrochloric acid, ferric chloride + citric acid.
- Sulfuric acid + ferric sulfate.
- Acetic acid + ferric nitrate.
- 15 Glycolic and formic acids + ferric nitrate.
- Hydrogen peroxide and hydrofluoric acid.
- Hydrogen peroxide, hydrochloric acid and acetic or nitric acids.

The concentration of the respective components in each of these examples of oxidizing acid systems will vary depending upon the type of metal being treated and the temperature of treatment as is well known to those skilled in the art of pickling and cleaning of metal surfaces. Accordingly, it is only necessary that sufficient of each component be used to achieve the desired result in any given instance.

In addition to the inclusion of an agent selected from the class consisting of nitrate ion, ferric ion and hydrogen peroxide in the oxidizing acid solution of the present invention, it is also essential, as noted hereinabove, that such oxidizing acid solutions also contain at least 0.35 g./l. of a soluble methylol thiourea compound of the above formula. Where the amount of methylol thiourea compound used is less than 0.35 g./l. the rate of attack of the oxidizing acid system upon the basis metal being treated will be too great to permit commercial utilization of the oxidizing system. So far as an upper limit of methylol thiourea is concerned, this will depend largely upon the type of oxidizing acid system employed. For example, methylol thiourea has greater or less solubility in different oxidizing acid systems over different temperature ranges. The same observations have been made with respect to the dimethylol thiourea compound, so that the primary consideration is solubility of the methylol thiourea compound in the particular oxidizing acid system employed.

It is within the scope of this invention to employ, in addition to the methylol thiourea compound, other corrosion inhibiting agents. For example, it is well known that certain types of organic nitrogen-base corrosion inhibitors, such as those derived from aromatic and heterocyclic coal tar bases, provide enhanced corrosion resistance in acid treating systems. Typical examples of such inhibitors are pyridine, α -picoline, γ -picoline, 2-n-amylypyridine, 4-n-amylypyridine, 2-hexylpyridine, as well as various substituted lutidines, collidines, quinolines, lipidines, and quinaldines. The well known rosin amine based inhibitors are also suitable for use in this respect. The concentration or amount of the corrosion inhibitor depends upon its effectiveness in the particular oxidizing acid solution employed and at the temperature at which it is used. Generally, the amount effective to inhibit or reduce the corrosive effect of the oxidizing acid is in the range of 0.1 to 1.0% based on the weight of the acid in the treating solution.

In order to illustrate the excellent results achieved in accordance with the teachings of this invention, there are presented below a series of results which are presented herewith solely by way of illustration and which are not intended in any way to be construed as a limitation of this invention.

3

Example 1

Aqueous solutions were prepared containing, per 100 mls., 10 mls., of 70% nitric acid. Various amounts of a 3.3 molar solution of methylol thiourea (MTU) were added to these solutions. Uniformly sized hot-rolled steel strip, SAE 1010, which had been previously cleaned to remove mill scale, were subjected to the action of the oxidizing acid solution for a 4-hour period at 160° F. The weight loss, in mg., from these tests in comparison with control tests, is shown in the following table.

TABLE 1

Bath No.	Thiourea Compound		Loss in Weight, mg.
	Type	Grams	
1.....	None		4,947
2.....	0.71		470
3.....	0.76		428

Example 2

Acidic solutions containing, per 100 mls., 20 mls. of 7.0% nitric acid and 80 mls. of 5% hydrochloric acid were used to treat uniformly sized hot-rolled steel strips (SAE 1010) which had previously been cleaned in hydrochloric acid to remove mill scale. All treatments were of one hour duration at a temperature of 160° F. Varying amounts of methylol thiourea (MTU) were added to these solutions and the results are shown in the following table.

TABLE 2

Bath No.	Thiourea Compound		Loss in weight, mg.
	Type	Grams	
1.....	None		811
2.....	0.71		64
3.....	1.42		54
4.....	2.84		39

Example 3

Uniformly sized stainless steel test strips (type SAE 304) were treated in aqueous solutions containing, per 240 mls., 190 mls. of 7.0% nitric acid and 10 mls. of 49% hydrofluoric acid. All treatments were continued for a period of 17 hours and were carried out at 70° F. Varying amounts of methylolthiourea (MTU) were added to these solutions and the weight loss results are shown in the following table.

TABLE 3

Bath No.	Thiourea Compound		Loss in weight, mg.
	Type	Grams	
1.....	None		503
2.....	3.53		3
3.....	7.06		1

Example 4

Hot-rolled steel specimens of uniform size were subjected to the action of aqueous solutions containing 90 mls. of 5% hydrochloric acid and 5 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ per 120 mls. of solution. The treatments were conducted at 160° F. for one hour. Varying amounts of methylol thiourea (MTU) or of thiourea (TU) were added to these solutions for comparison and the loss in weight, due to acid attack, was determined and is shown in the following table. Each test solution also contained 0.1% by volume of a rosin amine based inhibitor of the type disclosed in U.S. Patent No. 2,758,970.

TABLE 4

Bath No.	Thiourea Compound		Loss in Weight, mg.
	Type	Grams	
1.....	Control		393
2.....	MTU	0.71	235
3.....	MTU	1.42	135
4.....	MTU	2.84	44
5.....	TU	2.0	437

Example 5

Uniformly sized hot-rolled steel test strips were sub-

4

jected to the action of aqueous acid solutions containing, per 120 ml., 90 mls. of 5% hydrochloric acid, 5 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5 grams of citric acid. Varying amounts of methylol thiourea (MTU), thiourea (TU) or diethylthiourea (DETU) were added to these solutions and the treatments were continued for a 4-hour period at 160° F. Results are shown below.

TABLE 5

Bath No.	Thiourea Compound		Loss in Weight, mg.
	Type	Grams	
1.....	Control		1,588
2.....	MTU	2.13	124
3.....	TU	2.0	143
4.....	DETU	2.0	224

Example 6

Uniformly sized hot-rolled steel strips (SAE 1010) were subjected to the action of aqueous acid solutions containing, per 125 ml., 90 ml. of 10% sulfuric acid and 5 grams of $\text{Fe}_2(\text{SO}_4)_3$. Varying amounts of methylol thiourea (MTU) or of thiourea (TU) were added to these solutions. Treatments were continued at 160° F. for one hour. Results appear in Table 6.

TABLE 6

Bath No.	Thiourea Compound		Weight Loss, mg.
	Type	Grams	
1.....	Control		850
2.....	MTU	1.76	57
3.....	MTU	3.53	36
4.....	TU	2.0	376

Example 7

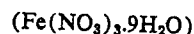
Uniformly sized hot-rolled steel strips (SAE 1010) were subjected to the action of aqueous solutions containing, per 125 mls., 5 grams of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 100 mls. of 10% acetic acid. Varying amounts of methylol thiourea (MTU) and of thiourea (TU) were added to these solutions. All treatments were continued for a period of 1 hour at 160° F. Weight loss data is shown in the following table.

TABLE 7

Bath No.	Thiourea Compound		Weight Loss, mg.
	Type	Grams	
1.....	Control		688
2.....	MTU	1.76	17
3.....	MTU	3.53	9
4.....	TU	2.0	134

Example 8

Uniformly sized hot-rolled steel and copper strips were subjected to the action of an aqueous solution containing, per 130 ml., 2 ml. of 70% glycolic acid, 1 ml. of 90% formic acid and 5 grams of ferric nitrate



Varying amounts of thiourea (TU) and of methylol thiourea were added to these solutions. All treatments were continued for a period of 3 hours at 160° F. Weight loss data for both the steel and the copper strips is shown in the following table.

TABLE 8

Bath No.	Thiourea Compound		Weight Loss, mg.	
	Type	Grams	Steel	Copper
1.....	Control		1,283	-----
2.....	TU	2.0	246	-----
3.....	MTU	1.76	41	-----
4.....	MTU	3.53	23	-----
5.....	Control		894	-----
6.....	MTU	1.76	68	-----
7.....	MTU	3.53	15	-----

Example 9

Inhibition of acid attack on hot-rolled steel (SAE 1010) strips was determined on acid solutions contain-

ing hydrogen peroxide. Three different acids were used as described in the following table. All test solutions were 130 ml. in volume, and all contained, in addition to the acid noted below, 1 ml. of 30% hydrogen peroxide, and thiourea (TU) or methylol thiourea (MTU) in amounts indicated. Each test was conducted at 160° F. for one hour. Weight loss data for these tests is reported in the following table.

TABLE 9

Bath No.	Acid Used -		Thiourea Compound		Weight Loss, mg.
	Type	Ml.	Type	Grams	
1.....	HCl (5%).....	100	Control		411
2.....	HCl (5%).....	100	TU	2.0	508
3.....	HCl (5%).....	100	MTU	3.5	54
4.....	Acetic (glacial).....	5	Control		125
5.....	do.....	5	TU	2.0	32
6.....	do.....	5	MTU	3.5	6
7.....	HNO ₃ (7%).....	50	Control		1,353
8.....	HNO ₃ (7%).....	50	TU	2.0	374
9.....	HNO ₃ (7%).....	50	MTU	3.5	36

It has also been surprisingly discovered that if copper ion is added to the oxidizing acid solutions of this invention which contain an agent selected from the class consisting of nitrate ion, ferric ion and hydrogen peroxide a further reduction in acid attack upon basis metal will result.

The amount of copper ion which is required to effect this enhanced result depends upon the particular type of acid system being used, and also upon the concentration of the acidic components. Generally, as a guide for copper utilization, it can be stated that the amount of copper ion should be at least 5 milligrams of copper, calculated as Cu ion, per 100 ml. of acid solution.

So far as concerns an upper limit of copper ion, it has been found that no apparent maximum limitation exists. For example, amounts of copper ion, calculated as Cu, of up to 2000 mg. per 100 ml. of acid solution have resulted in decreased attack upon basis metal as compared to similar solutions which do not contain copper ion. The only practical consideration in the utilization of copper arises in the level of copper used as compared with the utilization of thiourea compound. As is known from U.S. Patent 3,074,825, thiourea compounds as disclosed therein are capable of chelating copper ion so as to prevent its deposition onto metal surfaces in acid solution. Accordingly, the level of copper ion should not be such as to exceed the chelating power of the particular thiourea compound employed so as to prevent copper plating from such acid solutions.

In order to illustrate the enhancing effect of copper ion in the prevention or inhibition of oxidizing acid attack on basis metal surfaces there are presented below various results of tests conducted utilizing different acid systems in accordance with the teachings of this invention. These results are presented herewith solely by way of illustration, and they are not to be construed as in any way limiting this invention except as it is defined in the appended claims.

In the table which follows the following abbreviations are used:

TU=thiourea

MTU=methylolthiourea

DMTU=dimethylolthiourea

All tests were run using uniformly sized hot-rolled steel strips (SAE 1010).

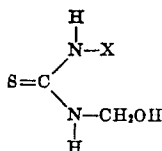
Example No.	Bath Vol., ml.	Acid Used		Thiourea Compound		Cu Ion, mg.	Test Conditions		Weight Loss, mg.
		Type	Amount	Type	Grams		° F.	Hours	
10.....	125	HNO ₃ (70%).....	10 mls.....	None		None	160	4	4,947
11.....	125	HNO ₃ (70%).....	10 mls.....	MTU	1.76	None	160	4	470
12.....	125	HNO ₃ (70%).....	10 mls.....	MTU	1.76	50	160	4	28
13.....	120	HCl (5%).....	80 mls.....	None		None	160	1	811
14.....	120	HNO ₃ (7.0%).....	20 mls.....	MTU	0.71	None	160	1	64
		HCl (5%).....	80 mls.....						
15.....	120	HNO ₃ (7.0%).....	20 mls.....	MTU	0.71	20	160	1	3
		HCl (5%).....	80 mls.....						
16.....	120	HNO ₃ (7.0%).....	20 mls.....	None		None	160	1	394
		HCl (5%).....	90 mls.....						
17.....	120	FeCl ₃ .6 H ₂ O.....	5 g.....	MTU	2.84	None	160	1	44
		HCl (5%).....	90 mls.....						
18.....	120	FeCl ₃ .6 H ₂ O.....	5 g.....	MTU	2.84	20	160	1	3
		HCl (5%).....	90 mls.....						
19.....	125	HNO ₃ (7.0%).....	100 mls.....	None		None	160	1	2,889
		FeCl ₃ .6 H ₂ O.....	5 g.....						
20.....	125	HNO ₃ (7.0%).....	100 mls.....	None		100	160	1	4,270
		FeCl ₃ .6 H ₂ O.....	5 g.....						
21.....	125	HNO ₃ (7.0%).....	100 mls.....	TU	2.0	100	160	1	(1)
		FeCl ₃ .6 H ₂ O.....	5 g.....						
22.....	125	HNO ₃ (7.0%).....	100 mls.....	MTU	3.53	100	160	1	51
		FeCl ₃ .6 H ₂ O.....	5 g.....						
23.....	140	HCl (5%).....	100 mls.....	None		None	160	1	1,745
		HNO ₃ (7.0%).....	20 mls.....						
24.....	140	FeCl ₃ .6 H ₂ O.....	5 g.....	MTU	2.53	None	160	1	47
		HCl (5%).....	100 mls.....						
25.....	140	HNO ₃ (7.0%).....	20 mls.....	MTU	3.53	20	160	1	11
		FeCl ₃ .6 H ₂ O.....	5 g.....						
26.....	125	H ₂ SO ₄ (10%).....	90 mls.....	None		None	160	1	850
		Fe ₂ (SO ₄) ₃	5 g.....						
27.....	125	H ₂ SO ₄ (10%).....	90 mls.....	MTU	3.53	None	160	1	36
		Fe ₂ (SO ₄) ₃	5 g.....						
28.....	125	H ₂ SO ₄ (10%).....	90 mls.....	MTU	3.53	20	160	1	6
		Fe ₂ (SO ₄) ₃	5 g.....						
29.....	125	HNO ₃ (7.0%).....	30 mls.....	None		None	160	1	4,011
		Fe ₂ (SO ₄) ₃	5 g.....						
30.....	125	H ₂ SO ₄ (10%).....	70 mls.....	MTU	3.53	None	160	1	442
		HNO ₃ (7.0%).....	30 mls.....						
31.....	125	Fe ₂ (SO ₄) ₃	5 g.....	MTU	3.53	60	160	1	11
		HNO ₃ (7.0%).....	30 mls.....						
32.....	125	HNO ₃ (7.0%).....	100 mls.....	None		None	160	1	2,815
		Fe(NO ₃) ₃ .9 H ₂ O.....	5 g.....						
33.....	125	HNO ₃ (7.0%).....	100 mls.....	TU	2	None	160	1	(1)
		Fe(NO ₃) ₃ .9 H ₂ O.....	5 g.....						
34.....	125	HNO ₃ (7.0%).....	100 mls.....	TU	2	100	160	1	(1)
		Fe(NO ₃) ₃ .9 H ₂ O.....	5 g.....						
35.....	125	HNO ₃ (7.0%).....	100 mls.....	DMTU	3.53	None	160	1	546
		Fe(NO ₃) ₃ .9 H ₂ O.....	5 g.....						
36.....	125	HNO ₃ (7.0%).....	100 mls.....	DMTM	3.53	100	160	1	162
		Fe(NO ₃) ₃ .9 H ₂ O.....	5 g.....						

¹ Test strip completely disintegrated in 5 min.

From all of the foregoing results it is readily apparent that the attack of oxidizing solutions on basis metal surfaces can be inhibited through utilization of nitrate or ferric ion or hydrogen peroxide added to an acid system which also contains at least 0.35 g./l. of a soluble methylolthiourea compound of the formula indicated above.

I claim:

1. A method of inhibiting the attack of oxidizing acid solutions on basis metal surfaces which comprises adding at least 0.35 gram per liter of a soluble thiourea derivative having the formula:



wherein X is selected from the group consisting of hydrogen and CH_2OH , to an aqueous oxidizing acid solution containing an agent selected from the group consisting of nitrate ion, ferric ion and hydrogen peroxide.

2. The method of claim 1 wherein the acid solution also contains at least 5 mg. of dissolved copper ion per 100 ml. of solution.

3. The method of claim 1 wherein the acid solution contains an amount of an organic nitrogen-base in addition to the methylolthiourea which organic nitrogen-base

is capable of inhibiting the corrosive action of the acid on metal surfaces.

4. The method of claim 2 wherein the acid solution contains an amount of an organic nitrogen-base in addition to the methylolthiourea, which organic nitrogen-base is capable of inhibiting the corrosive action of the acid on metal surfaces.

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U.S. Cl. X.R.

21—2.7; 252—149; 134—41

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,466,192

September 9, 1969

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:

Column 2, line 69, "arep resented" should read -- are represented --. Column 3, Table 1, "0.76" should read -- 1.76 --. In the table spanning columns 5 and 6, in Example 24 under the heading "Grams", "2.53" should read -- 3.53 --; and in Example 36 under the heading "Type", second occurrence, "DMTM" should read -- DMTU --.

Signed and sealed this 24th day of February 1970.

(SEAL)

Attest:

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Attesting Officer

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Commissioner of Patents