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INHIBITOR IN ACID PICKLING

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This invention relates to the acid pickling of metals and more particularly to materials for inhibiting the corrosive effects of the acid upon the metal itself.

To properly prepare the surface of iron and steel and alloys thereof for galvanizing, tinning, electroplating, painting, and other after treatments, it is necessary to remove the scale that is formed in hot working operations or the rust formed on unprotected surfaces during storage time. The usual methods for scale and rust removal are sandblasting and acid pickling. Sandblasting is limited to open surfaces only, but acid pickling can be used in all cases, even when double walled equipment has to be treated. The acid to be used attacks not only the scale and rust but the pure metal as well. Inhibitors, including those of organic composition, have been quite universally used to decrease the acid attack on the basic metal without appreciably altering the rate of scale removal. It is therefore an object of the present invention to provide a novel and useful inhibitor to reduce or prevent acid attack upon the metal during a metal pickling operation.

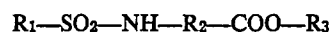
It is well known that the freshly pickled surface of iron and its alloys shows a high reactivity towards oxygen. As a result there is an extremely rapid rate of re-rusting of freshly pickled ferrous surfaces while the residual pickling liquor is drying on them. This re-rusting is normally reduced at present by use of a rinse and after treatment bath immediately following the pickling operation, air drying of the metal stock before the rinse being carefully avoided. The production line necessitated by such treatments must be a cumbersome continuous series of baths avoiding any intermediate contact with the air. Chemicals are known which will prevent air corrosion of metals but they have not been applied to pickling baths. It is accordingly a second object of this invention to provide an inhibitor useful to prevent corrosion of metal stock upon exposure to air between steps in a metal pickling process.

The inhibitors used to prevent excess etching of the metal during a pickling process are not themselves generally effective to prevent air corrosion of the same stock. Obviously an inhibitor capable of serving the dual purpose of preventing acid attack or etching of metal during a rust removal step and air corrosion of the same metal wet with the pickling liquor would simplify pickling procedures. A third object of our invention is consequently provision of a pickling inhibitor effective to prevent attack of a metal by a pickling acid and by air when the metal is wet with pickling acid. Other objects of the invention will be evident hereinafter.

We have found that hydrocarbon-sulfamido-carboxylic acids and their salts, both organic and inorganic, are highly effective inhibitors in preventing etching of a metal by an acid pickling bath and in preventing corrosion of the same metal, still wet with pickling liquor, by exposure to air. The class of chemicals named are well known organic compounds, their preparation being described for example in Patent 2,193,824 to Lockwood

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and Richmond and in Patent 2,225,960 to Orthner and Balle. For the purpose of this invention they may be represented by the formula



in which R_1 stands for an alkyl radical of from 10 to 18 carbon atoms which radical is sometimes referred to as Mepasin, which is defined in applicants earlier Patent No. 2,578,725 as "a mixture of saturated hydrocarbons with a chain length between 12 and 18 carbon atoms which was originated by the Fischer-Tropsch synthesis" R_2 for an alkyl or aryl radical, that is, a hydrocarbon less two hydrogen atoms for which are substituted the other parts of the molecular chain, and R_3 for a hydrogen atom, or a basic radical such as ammonium, cyclohexylamine, sodium, potassium or the like. The alkyl radical is essential an alkylene radical. Examples of hydrocarbon-sulfamido-carboxylic acids, or the salts thereof, which may be used according to the invention are: octadecylsulfamido acetic acid



octylsulfamido butyric acid ($C_8H_{17}SO_2NHC_3H_7COOH$) and others given in the examples below. The hydrocarbon-sulfamido-carboxylic acids used in the practice of this invention may be regarded as derivatives of the lower carboxylic acids ($C_nH_{2n+1}COOH$) such as formic, acetic, propionic and butyric in which a hydrogen atom attached to a carbon atom has been replaced by the group



R here representing a univalent saturated hydrocarbon radical of from around 5 to 20 carbon atoms in either a straight or branched chain, but preferably in a straight chain. The compounds are usually obtained as mixtures.

The inhibiting and rust preventing properties of the compounds described above show up even in concentrations as low as 0.01% or lower. Consequently the procedure of adding these compounds to a pickling bath allows an interruption after the metal is immersed in the bath without any danger of corrosion of the fresh surface. In some cases the use of the compounds permits omission of one container completely and utilization of the preservation container alternately as a rinsing bath. Intermediate drying and contact with air during a draining and refilling operation does not start any re-rusting on the pickled material.

By way of illustration of our invention the following examples are given:

Example 1.—Mild steel pieces, size 3" x 3/4" x 1/16", were immersed in 500 ml. of 4.19% sulfuric acid with agitation. Another piece of the same kind was immersed in 500 ml. 4.9% sulfuric acid containing 0.01% of the sodium salt of alkyl ($C_{12}-C_{18}$)-sulfamidoacetic acid. The latter substance is sometimes called Mepasin-sulfamido-acetic acid. After 26 hours treatment at ambient temperature, the iron sheet in the uninhibited acid showed a loss of 22.6% of weight; the test pieces in the acid with the inhibitor showed a loss of only 0.7% of weight. The retardation by the inhibitor was thus about 96%. After a water rinse, test piece #1 started rusting upon contact with air. Test piece #2 kept its original color after a rinse and showed no signs of re-rusting even when observed with the microscope.

Example 2.—Iron pieces of the same size as those of Example 1 were tested under parallel conditions to those used before. However 0.1% of the "Mepasin" inhibitor mentioned in Example 1 was used and agitation was omitted. The retardation obtained was 94% while the rust prevention results were identical with those obtained above.

Example 3.—Two pieces of mild steel, S. A. E. 1010, each having a surface area of 20 cm.² were totally im-

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mersed in a 5% nitric acid pickling bath at ambient temperature.

The control piece was inserted into 400 ml. of uninhibited nitric acid. The test piece was inserted into 400 ml. of the 5% nitric acid to which 0.1% of "Mepasin"-sulfamido-acid sodium salt was added.

The following observations of the volume of gas evolution were made over a 4 hour period:

Table I

Hours	cc. gas generation per cm. ² area of the control piece	cc. gas generation per cm. ² area of the test piece
1.....	0.210	less than 0.003.
2.....	0.75	0.005.
3.....	1.83	0.020.
4.....	3.5	0.027.

The above table shows that the inhibitor possess about a 99% etching retardation effect. Another significant fact noted was that after a very short time, the uninhibited acid turned a brown color because of the reduction of the nitric acid by the iron. The inhibited acid however even after 12 hours contact with the test piece was not discolored to the slightest degree.

The corrosive retardation in this case was the same as that previously observed.

Example 4.—The rate of acid attack and its retardation by the addition of 0.1% "Mepasin"-sulfamido-carboxylic acid sodium salt were again repeated as in Example 3 except that 10% oxalic acid was substituted for the nitric as the pickling acid.

The following observations were made:

Table II

Hours	cc. gas generation per cm. ² area of the control piece	cc. gas generation per cm. ² area of the test piece
1.....	0.03	0.0035
2.....	0.048	0.017
3.....	0.071	0.026
4.....	0.088	0.034

These figures show that even in the case of an organic acid, the rate of etching attack is decreased and more than 60% retardation effect is obtained when using the inhibitor. The same air corrosion results were obtained in this case as in Examples 1-3.

Example 5.—Sheet steel pieces (SAE 1010) having an area of 29 square centimeters and a thickness of 0.035 inch were polished, cleaned and weighed. They were immersed in 1 normal sulfuric acid contained in 800 ml. glass beakers at 23° C. Two beakers contained uninhibited acid, two contained 0.01 percent of the sodium salt of alkyl (C₁₂-18) sulfamidocetic acid added as inhibitor, two of the beakers contained 0.01 percent by weight of the ammonium salt of this alkylsulfamido-acetic acid added as inhibitor; two beakers contained 0.01 percent by weight of the cyclohexylamine salt of this acid added, and the final two beakers contained 0.01 percent by weight of the potassium salt of the above acid added as an inhibitor.

The table below presents the results observed:

Table III

Time in Hrs.	Control Samples	0.01% Na Salt Added	0.01% NH ₄ Salt Added	0.01% K Salt Added	0.01% Cyclohexylamine salt added
1.....	2.03	0.178	0.181	0.203	0.185
3.....	3.71	0.398	0.390	0.432	0.409
6.....	5.45	0.688	0.677	0.746	0.710
22.....	17.8	2.14	2.125	2.30	2.22
48.....	34.3	3.25	3.13	3.51	3.38

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Example 6.—A group of sheet steel pieces, type 8617, heat treat S3121, spec. AN-QQS-676 (composition: C=0.165%; Mn=0.85%; P=0.018%; Si=0.21%; S=0.034%; Ni=0.62%; Cr=0.50%; Mo=0.16%) was immersed in 1 N sulfuric acid in 800 ml. beakers at 62-65° C. One beaker contained a control uninhibited acid and one beaker contained 0.1% of the sodium salt of alkyl (C₂₀) sulfamidocarboxylic acid. The results observed were tabulated below.

Table IV

Time in mins.	Weight loss in mg./cm. ²		Percent Retardation, 0.1% Inhibitor
	Control	0.1% Inhibitor	
15.....	4.89	0.37	92.3
30.....	10.25	0.722	92.8
45.....	16.21	1.006	93.8
60.....	22.45	1.227	94.5
120.....	76.3	2.19	97.2

Example 7.—A group of polished SAE 1010 stainless steel pieces was immersed in 5% and 15% nitric acid and 5% and 15% hydrochloric acid at ambient temperatures (approximately 23° C.) for periods up to 1320 minutes. The ammonium and sodium salts of the alkyl (C₁₂-18) sulfamidocarboxylic acid in 0.1% concentrations were used as the inhibitor and compared to the controls. In all cases, the inhibition was 95% or greater. The steel pieces pickled in the inhibited acids did not rerust after being dipped in water and allowed to dry in the air, whereas the pieces pickled in uninhibited acid rerusted shortly after rinsing and being allowed to dry in the air.

Example 8.—Uniformly rusted steel pieces were carefully cut and pickled in uninhibited 1 N sulfuric acid and in acid inhibited with 0.01%, 0.1% and 0.5% sodium, ammonium, potassium and cyclohexylamine salts of the alkyl sulfamidocetic acid. The rate of rust removal was not affected by the addition of the inhibitors to the pickling acid. The pieces pickled in inhibited acid did not rerust upon drying in the air after removal from the pickling bath and dipping in distilled water.

This case is a continuation-in-part of our application Serial No. 248,101 filed September 24, 1951, now abandoned.

The foregoing examples are intended merely as illustrations of our invention. Since modifications in the examples will occur to those skilled in the art, we wish to be limited, not by the scope of the specific examples, but solely by the appended claims.

What we claim is:

1. An acid bath for pickling ferrous metals containing as an inhibitor to repress its etching and air-corrosive properties towards said metals between about 0.01 and 0.1% of its weight of a compound having the formula R₁-SO₂-NH-R₂-COOR₃ in which R₁ is a saturated aliphatic radical with a chain length of from 12 to 18 carbon atoms, R₂ is a member of the group consisting of aryl radicals and alkyl radicals of the formula -C_nH_{2n}- where n is a small positive integer and R₃ is a member of the group consisting of hydrogen, alkali metal, ammonium and cyclohexylamine ions.

2. The acid pickling bath of claim 1 in which the inhibitor is the sodium salt of an alkyl-sulfamido-acetic acid, wherein said alkyl radical has a chain length of 12 to 18 carbon atoms.

3. The acid pickling bath of claim 1 in which the inhibitor is the ammonium salt of an alkyl-sulfamido-acetic acid, wherein said alkyl radical has a chain length of 12 to 18 carbon atoms.

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4. The acid pickling bath of claim 1 in which the inhibitor is the potassium salt of an alkyl-sulfamido-acetic acid, wherein said alkyl radical has a chain length of 12 to 18 carbon atoms.

5. The acid pickling bath of claim 1 in which the inhibitor is the cyclohexylamine salt of an alkyl-sulfamido-acetic acid, wherein said alkyl radical has a chain length of 12 to 18 carbon atoms.

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