Patented Dec. 18, 1951

2,578,725

UNITED STATES PATENT OFFICE

2,578,725

PROCESS OF PROTECTING METALS AGAINST CORROSION

Josef M. Michel and Karl F. Hager, Fort Bliss, Tex., assignors to the United States of America as represented by the Secretary of the Army

No Drawing. Application October 20, 1949, Serial No. 122,591

4 Claims. (Cl. 260—586)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

1

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

It is very well known that alcohols, ketones and their mixtures with water, such as methanol-water, ethanol-water, methanol-ethanol-water, acetone-water, glycol-water, phenol-water, sugar-water, etc., are corrosive to metals, especially iron, when stored for any length of time.

Such liquids are used, for example, as fuels for guided missiles, as anti-freezing liquids in radiators, as cooling liquids in deep freezing units and as pressure transfer medium in hydraulic systems.

Formation of iron oxides takes place as a result of such corrosive action, appearing in a muddy precipitate, sometimes in a more or less colloidal form. When using such contaminated fuels or liquids, difficulties may arise in the piping system occurring separately in the valves, pumps or nozzles, which lowers or disturbs the supply of the liquid in the cooling systems or varies the efficiency of the combustion and the thrust of a rocket.

Many proposals have been made to overcome these difficulties, for example, the addition of inorganic compounds such as chromates, silicates, phosphates and nitrites to act as inhibitor. The results have been considered good but the solubility, which is dependent upon the alcohol, ketone, mixing ratio and temperature, and the chemical reactions, such as the reduction of the six-valent Cr-ion to trivalent inactive compounds, show that such additions cannot be expected to be dependable.

In contrast to these proposals, it was found that a certain group of metal-active organic compounds, the "Mepasin"-sulfamido-(aliphatic or aromatic)-carboxylic-acids or their salts, which are either soluble in alcohol, ketone and their water mixtures or give emulsions with them, are able to prevent all corrosion. The protection is entirely independent of the fuel or liquid, even when the pH-value does not correspond to the neutral point (solutions with a pH-value below 7) or when sea-water is used as diluting agent with the alcohol or ketone water mixture, or of the metals and alloys to be used. This means that the protection is the same for heavy and light metals such as magnesium alloys. "Mepasin," in this connection, refers to a mixture of saturated hydrocarbons with a chain length between 12 and 18 carbon atoms

2

which was originated by the Fischer-Tropsch synthesis. The same effect can be obtained by using, instead of "Mepasin," the fraction of oil or gasoline of a corresponding chain length.

The compounds which are utilizable as corrosion inhibiting or corrosion preventing agents according to the present invention have the following general formula,

$$R_1—SO_2—NH—R_2—COOR_3$$

in which R_1 is a saturated hydrocarbon radical having a chain length of from 12 to 20 carbon atoms inclusive; R_2 is an aliphatic radical of the formula $—C_nH_{2n}—$, (n being a whole number), for example, $—CH_2—$, $—C_2H_4—$, $—C_3H_6—$, or an aryl or aromatic radical, for example, $—C_6H_4—$; and R_3 is a hydrogen atom, an alkali metal atom, an ammonium or substituted ammonium radical or other positive radical of a salt. The said compounds of the type defined should be either soluble in, or give emulsions with, the alcohols or ketones, or their mixtures with water, to which they are added for inhibiting or preventing corrosion. Compounds of the type defined above and their preparation are described in U. S. Patent No. 2,225,960, granted December 24, 1940.

The amount necessary for preventing any corrosion varies with the special conditions but does not necessarily exceed 1%. Generally, even 0.05 to 0.5% of the compounds in question will be sufficient to give results that guarantee corrosion-proof storage, transportation and handling in rockets, radiators, deep-cooling and hydraulic systems.

Other advantages are seen in the fact that those compounds are mostly of organic nature; for example as a rocket fuel, they will not influence or diminish the efficiency of the rocket motor; as a liquid in radiator systems, the hazard of generating inorganic salt-scale will be avoided; as inhibitor in anti-freezing liquids, they prevent every kind of hard scale for they act, in addition to preventing corrosion, as emulsifying agents.

Experiments have been carried out and the methods and results are given in the examples below:

Example 1

Ordinary iron strips, welded, 5 x 2.5 x 0.1 inches, were placed in closed containers at ambient temperature. These containers were then filled about one-half full with a mixture of 300 ccm. of methanol and 100 ccm. of distilled water. The pH-value of this solution was 6. To one of

the containers, an addition was made of 0.05% of the inhibitor, "Mepasin"-sulfamido-acetic-acid-sodium salt. After one day, corrosion took place on the iron strip in the pure mixture in the form of points and dots. Increasing more and more with the lapse of time, the corrosion turned badly on this plate. After the same time, the iron strip in the liquid containing the addition of a trace of the inhibitor, 0.05% "Mepasin"-sulfamido-acetic-acid-sodium salt, still has the same appearance as it had at the beginning of the test.

Example 2

Ordinary iron strips, welded, 5 x 2.5 x 0.1 inches, were tested in the same way as described in Example 1. A mixture, however, of 300 ccm. ethanol and 100 ccm. of distilled water containing 1% sodium chloride was used. The pH-value of this mixture was found to be 7. After a few hours, distinct corrosion symptoms appeared on the iron strip in the pure solution and after four days the appearance of the test sample indicated heavy corrosion symptoms on the entire surface of the sheet; the liquids showed a large amount of iron oxide scale. In contrast, the strip in the mixture of the same composition, but containing 0.6% "Mepasin"-sulfamido-butyric-acid-ammonium salt was entirely unchanged which is a much more important evidence for the high efficiency of this type of metal-active compound.

Example 3

Welded strips of magnesium alloy (6.5% Al, 1.0% Zn, 0.2% Mn, base Mg) 5 x 2.5 x 0.1 inches, were tested in a 50% ethylene-glycol-water solution; pH-value, 7.5. One of the containers was filled with the pure solution, to the other one 0.5% inhibitor, "Mepasin" - sulfamido - acetic-acid-cyclo-hexylamin salt was added. After a few days, heavy corrosion symptoms appeared on the light metal strip in the inhibitor-free solution, while the magnesium-alloy strip in the anti-corrosive 50% glycol had changed none from its original appearance. The corrosion in the pure solution progressed with the lapse of time; the situation in the 50% glycol containing the inhibitor remained the same as it was at the beginning of the test.

Example 4

Using the same test method as mentioned under Examples 1 and 2, but filling the containers with an 8% solution of phenol in water. The addition of 0.5% of the inhibitor "Mepasin"-sulfamido-acetic-acid-sodium salt to one of the containers resulted in the prevention of any corrosion on the iron strip in this solution. In comparison, the iron strip in the phenol-solution, without inhibitor, showed remarkable rust after one day, especially on the interphase between liquid and atmosphere.

Example 5

In the same test method, a 50% acetone-water mixture caused heavy corrosion on iron strips after a very few days. The same solution did not seem to influence the surface of the iron strips when containing 0.5% of the inhibitor mentioned in Example 4.

Example 6

A simple color reaction shows the protective action of the "Mepasin"-sulfamido-acetic-acid-sodium salt in a water-alcohol solution on iron surfaces. After putting iron strips in a 40% solution of pyrocatechin in water, immediately the known di-hydroxy-benzene-iron complex appears, indicated by a deep violet color of the solution. With the lapse of time, the solution contains a large scale of violet residue. If the same test is carried out with a 40% solution of pyrocatechin in water containing an addition of 0.5% of the inhibitor in question, the forming of the violet complex compound is greatly delayed and, over the same period of time, only a small portion of the violet scale is to be seen.

We claim:

1. The process of protecting metals against corrosion from contact with a material selected from the group consisting of alcohols, ketones and water mixtures thereof which comprises effecting said contact in the presence of a compound having the formula

$$R_1—SO_2—NH—R_2—COOR_3$$

in which R_1 is a saturated aliphatic hydrocarbon with a chain length of from 12 to 20 atoms, R_2 is a member of the group consisting of aryl radicals and alkylene radicals of the formula $—C_n H_{2n}—$ where n is a small positive integer and R_3 is a member of the group consisting of hydrogen, alkali metal and ammonium ions and substituted ammonium radicals, said compound forming a dispersion in said material.

2. The process of claim 1 in which the dispersion formed is a true solution.

3. The process of claim 1 in which the dispersion formed is colloidal.

4. The process of claim 1 in which the metal protected is magnesium.

JOSEF M. MICHEL.
KARL F. HAGER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,797,401	Calcott et al.	Mar. 24, 1931
1,810,946	Calcott et al.	June 23, 1931
2,225,960	Orthner et al.	Dec. 24, 1940