

1
2,704,264

PROCESS OF PROTECTING SURFACES OF METALS AGAINST CORROSION

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

No Drawing. Application July 16, 1951,
Serial No. 237,051

5 Claims. (Cl. 117-127)

(Granted under Title 35, U. S. Code (1952), sec. 266)

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

Different ways are known to protect metals and alloys against corrosion, e. g., oxide and phosphate coatings, paints, varnishes, plating, etc. The protection obtained by this means may be called permanent.

However, there are other conditions where corrosion, especially rust prevention has to be temporary only, like metal parts in storage or between processing steps. In this case, valuable agents are petroleum derivatives, suitably chosen fractions, which usually meet the requirements of the industries in question and may be able to give an adequate protection. However, it was found that they cannot provide completely satisfactory results when conditions encountered in practical use are too severe.

Therefore, it was important to search for compounds that, like inhibitors, prevent corrosion even when added in small amounts only to petroleum derivatives. It stands to reason that such additives must not change the favorable qualities of the base material like easy application, no cracking, peeling or slipping, no hardening, easy removal, lubricating properties, etc. The best way to reach this goal is to have a compound that is completely soluble in the agents in question.

It was found that the hydrocarbon-sulfamido-carboxylic acids as well as their inorganic and organic salts are highly effective corrosion preventives, even when added in small quantities to hydrocarbons or mixtures of such compounds with solvents, e. g., alcohols, ethers, ketones, aldehydes, mobile hydrocarbons and chlorinated hydrocarbons and other liquid non-aqueous solvents in which electrolytic dissociation does not occur. These solvents may be added to the petroleum derivatives in order to obtain solutions that can be handled easily, e. g., by dipping or spraying the metal parts even at low temperatures. Ethanol, benzene and acetone may be used as such solvents. Such solvents also act as thinning agents for the hydrocarbon oil.

In those instances where a film or coating of a lubricating oil upon the treated metal surface is unnecessary or undesired, the hydrocarbon-sulfamido-carboxylic acids may be dissolved in the solvents mentioned without the inclusion of any additional vehicle of the nature of petroleum derivatives or hydrocarbon lubricants. It is pointed out that in the practice of the invention the hydrocarbon-sulfamido-carboxylic acids, or the salts thereof, used according to the present invention are in real or true solution in the petroleum derivatives or hydrocarbon oils, and in the solvents referred to above, and in the mixtures of such solvents with the petroleum derivatives or lubricating oil. The practice of the invention results in the formation of a film or coating of these real or true solutions upon the surface of the metal to be protected against corrosion.

The said hydrocarbon-sulfamido-carboxylic acids can be designated by the chemical formula RSO_2NHR_1COOH , where R is an alkyl radical of from 5 to 20 carbon atoms, and R_1 an alkyl radical less one hydrogen atom. In other words, R_1 is a divalent saturated aliphatic radical, one valency bond of which is connected with the carbon atom of the carboxyl group and the other valency bond of which is connected with the nitrogen atom of the RSO_2NH group. Examples of hydrocarbon-sulfamido-

2

carboxylic acids, or the salts thereof, which may be used according to the invention are: octadecylsulfamido acetic acid ($C_{18}H_{37}SO_2NHCH_2COOH$), octylsulfamido butyric acid ($C_8H_{17}SO_2NHC_4H_7COOH$) and others given in the examples below. The hydrocarbon-sulfamido-carboxylic acids that are used in the practice of the invention may be regarded as derivatives of the lower fatty acids ($C_nH_{2n+1}O_2$), such as formic, acetic, propionic and butyric acids in which a hydrogen atom attached to a carbon atom has been replaced by the group $NHSO_2R$, where R is a univalent saturated hydrocarbon radical of from 5 to 20 carbon atoms in either a straight or branched chain, but preferably in a straight chain.

Examples of salts of hydrocarbon-sulfamido-carboxylic acids that may be used in practicing the invention are: inorganic salts such as sodium, potassium, and ammonium salts, and salts of ammonia derivatives such as hydroxylamine and hydrazine; and organic salts such as salts of cyclohexylamine, methylamine and ethylamine.

The hydrocarbon-sulfamido-carboxylic acids or the salts thereof, in accordance with the present invention, may be mixed with or dissolved in the hydrocarbon petroleum derivative, for example a hydrocarbon lubricating oil either as such or thinned or rendered more mobile by the admixture therein of solvents as above mentioned, in proportions varying over a wide range, for example from 0.1 percent to 50.0 percent. The composition so prepared is preferably used at a pH value of 7 or less. The pH value of the composition when the salts of the hydrocarbon-sulfamido-carboxylic acids are used is regulated to the pH value of 7 or less by incorporating into the composition a free hydrocarbon-sulfamido-carboxylic acid, preferably the free acid corresponding to the salt used. In those instances where the petroleum derivative or hydrocarbon oil is not mixed with the said solvents and the solvents alone are used to dissolve the said hydrocarbon-sulfamido-carboxylic acids, or salts thereof, the said acids and salts are also used in proportions of from 0.1 percent to 50.0 percent, with adjustment of the solutions of the salts to a pH value of 7 or less by the addition of a corresponding acid or acid of the same class.

The compositions described herein when used in practicing the invention are free of a separate phase of water or a separate phase of a water solution. While petroleum derivatives, such as lubricating oils, and solvents such as alcohols, ethers, ketones, etc. may contain a certain amount of dissolved water, such water is not associated with them as a separate or free phase, such as would exist for example in a dispersion or emulsion. The expression "substantially free of water" as used in the appended claim is intended to mean that water is not present in substantial amounts as a separate or free phase either as water as such, or as water solutions of some solutes, but the said expression is not intended to exclude water that may be present in dissolved condition in the petroleum derivative or solvents mentioned above or in mixtures of them.

Exposure, humidity and spraying tests showed excellent results insofar as even under these serious conditions, no formation of rust or other corrosion products was observed.

It is recommended that metal parts which are dirty or partially corroded be cleaned by proper treatment before the procedure is applied with lasting success. On the other hand, protected equipment can either be used as it is, because of the high lubricating power of the hydrocarbon-sulfamido-carboxylic acids and their salts or they can be cleaned easily, if necessary, as these compounds are also highly effective emulsifiers.

The following examples show the high protective power of different mixtures containing compounds of hydrocarbon-sulfamido-carboxylic acids and their salts:

Example #1

Iron specimens, $\frac{3}{4} \times 5 \times \frac{1}{8}$ " have been cleaned by sand blasting and washing with benzene. The dried samples are dipped for about 10 minutes into test tubes containing petrolatum, heavy liquid U. S. P., at ambient temperature. Test tube #1 contained nothing but this petrolatum; test tube #2 contained an additional ad-

mixture of 1% octadecylsulfamido acetic acid sodium salt; test tube #3 contained 10% of the same inhibitor. The samples were allowed to lose their adherent surplus oil while standing at ambient temperature. Then they were treated in a weather chamber for a longer period of time. After 3 hours' testing using tap water, the efficiency of the added inhibitor appeared clearly; specimen #1 treated with pure petrolatum was covered all over the surface with rust but specimens #2 and #3 stood unchanged completely.

Example #2

Iron specimens, same kind as in Example 1, have been dipped into the following preservatives:

- a. Lubricating oil, heavy.
- b. Lubricating oil, heavy, and 0.5% octylsulfamido butyric acid ammonium salt.
- c. Lubricating oil, heavy, and 5.0 octylsulfamido butyric acid ammonium salt.

Temperatures of about 70° C. and a dipping period between 2 and 5 minutes were used. After testing in the weather chamber the same remarkable difference was observed: on specimen (a) first corrosion phenomena appeared after 30 minutes while the other samples (b) and (c) containing 0.5 and 5.0% inhibitor remained unchanged even after several hours of testing.

Example #3

Dow Metal M (containing 98.5% Mg, 1.5% Mn) specimens, $\frac{3}{4} \times 5 \times \frac{1}{16}$ inches, wet scrubbed with pumice, rinsed with water containing 0.1% sodium bichromate, were dried and dipped in the following solutions at ambient temperature for about 10 minutes:

- a. 50% petrolatum, 50% benzene.
- b. Same as (a) with 4% R-sulfamido acetic acid, where R=a mixture of aliphatic hydrocarbons with a chain length between 12 and 18 carbon atoms.

After one day storage under normal conditions in the laboratory, the samples were tested in a chamber by repeated spraying with 1% sodium chloride solution.

The difference as to corrosion resistance is distinctly seen. While samples (a) showed severe corrosion after one hour treatment, specimens treated with inhibitor containing solution described under (b) remained unchanged even after several hours' treatment of the same kind.

Example #4

Different parts of a fuel pump (cast iron) cleaned and derusted by a cathodic treatment in a 15% NaOH solution at a temperature between 50–60° C., rinsed and dried afterwards, were protected against corrosion by spraying with the solutions as follows:

- a. Oil fraction consisting of hydrocarbons with a chain length between 10 and 16 carbon atoms.
- b. Same fraction as mentioned under (a) with addition of 15% dodecylsulfamido sodium propionate—5% dodecylsulfamido propionic acid.

After two days' storage at ambient temperature, the different metal parts were tested in a humidity chamber at elevated temperature (70–80° C.) for 36 hours. While the specimens treated with solution (a) showed severe corrosion, the other ones protected by the oil containing inhibitors named under (b) were entirely unchanged.

These examples show precisely that this special group of highly metal active inhibitors are fully effective already after a few minutes treatment. Therefore, if they are allowed to react even for a much longer time during storage this protection will become better and better with the lapse of time.

We claim:

1. The process of protecting a metal surface against corrosion which comprises applying to said surface a solution comprising a major proportion of a liquid hydrocarbon and a minor proportion of octadecyl sulfamido acetic acid sodium salt.

2. The process of protecting a metal surface against corrosion which comprises applying to said surface a solution comprising a major proportion of a liquid hydrocarbon and a minor proportion of octylsulfamido butyric acid ammonium salt.

3. The process of protecting a metal surface against corrosion which comprises applying to said surface a solution comprising a major proportion of liquid hydrocarbon and a minor proportion of a mixture of compounds having the formula RSO_2NHCH_2COOH in which R is an alkyl chain of 12 to 18 carbon atoms.

4. The process of protecting a metal surface against corrosion which comprises applying to said surface a solution comprising a major proportion of a liquid hydrocarbon and a minor proportion of a mixture of dodecylsulfamido sodium propionate and dodecylsulfamido propionic acid.

5. The process of protecting a metal surface against corrosion which comprises applying to said surface a coating of a solution, selected from the group consisting of petrolatum and lubricating oil and containing from 0.1 to 50.0 percent of a compound having the formula $RSO_2NHR_1COOR_2$ in which R is an alkyl radical of from 5 to 20 carbon atoms, R_1 an alkyl radical in which one of the hydrogen atoms has been replaced by the RSO_2NH -group of said compound, and R_2 is selected from the group consisting of a hydrogen atom, an alkali metal atom, an ammonium radical and an organic salt radical, said solution being substantially free of water.

References Cited in the file of this patent

UNITED STATES PATENTS

2,225,960	Orthner et al. -----	Dec. 24, 1940
2,520,356	Bishop -----	Aug. 29, 1950
2,578,725	Michel et al. -----	Dec. 18, 1951
2,602,760	Michel et al. -----	July 8, 1952