Patented July 8, 1952 **2,602,760**

UNITED STATES PATENT OFFICE

2,602,760

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 July 18, 1950,
Serial No. 174,566

3 Claims. (Cl. 117—127)

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

The present invention relates to the protection of metallic parts against corrosion and more particularly to obtaining such protection by means of coatings applied to the parts.

Different methods are known for preserving metal parts against corrosion. The procedure applied depends on the condition of the objects, their structural composition and material qualities. Usually machined parts can only be treated immediately by such simple methods as dipping or spraying with corrosion inhibiting oils. Mostly, however, a cleaning operation has to be applied first, either by sand-blasting or treatment with acids, alkalies or organic solvents according to the particular state and structure of the metal parts in question.

Phosphate coatings are mostly used and are applicable not only to iron but are also suitable for zinc and aluminum. The technical procedure, usually, consists of the following six steps: spray cleaning, rinsing, treatment with a proper acid phosphate solution, forming a phosphate coating on the metal surface, rinsing with water, after treatment of the phosphate coating, and drying.

It is evident that the phosphatizing process is cumbersome in nature. A simpler method for protecting or inhibiting against corrosion is obviously desirable. Accordingly, the primary object of our invention is development of corrosion inhibiting or preventing coatings which afford protection equal to or more reliable than that offered by phosphate coatings but which are more easily applied than are the latter. Other objects of the invention will be evident hereinafter.

We have discovered that water emulsions, adjusted to a pH value numerically less than 7, of hydrocarbon (alkyl)-sulfamido-carboxylic acids, or of their inorganic or organic salts, when applied to metal surfaces form molecular films thereon that are firmly bonded on the metal surfaces and that such so bonded molecular films provide excellent protection against corrosion. The molecular films generated by the alkyl-sulfamido carboxylic acids or their salts are formed faster and are more effective in preventing corrosion when the pH values of their emulsions are kept in the acid range than when they are kept within the alkaline range. The present invention involves, therefore, adjusting such emulsions to a pH value numerically less than 7 and when so adjusted applying them upon the metal surfaces to be protected against corrosion.

The alkyl-sulfamido-carboxylic acids referred to above may be prepared by reacting an alkyl sulphonamid of the general formula RSO_2NH_2, in

which R is an alkyl radical, with a monochlor aliphatic acid, such as acetic acid, propionic acid and butyric acid. This reaction is known, and involves the liberation of hydrogen chloride by the union of a hydrogen atom of the amino group of the alkyl sulphonamid with a chlorine atom attached to a carbon atom of the monochlor aliphatic acid, whereby said carbon atom becomes attached to the mono-valent group $—NHSO_2R$. R in the present invention may be an alkyl group having its carbon atoms either in straight or branched chain arrangement. Therefore, the said alkyl-sulfamido-carboxylic acids can be correctly designated as aliphatic acid in which a hydrogen atom attached to a carbon atom has been replaced by the mono-valent group $—NHSO_2R$. It follows, therefore, that the corresponding alkyl-sulfamido-carboxylic acids for formic acid, acetic acid, propionic acid and butyric acid, which are utilizable according to the present invention, have the following chemical formulas $RSO_2NHCOOH$, RSO_2NHCH_2COOH, $RSO_2NHC_2H_4COOH$, and $RSO_2NHC_3H_6COOH$, respectively. The alkyl radical R in the compounds used in the present invention contains at least five carbon atoms, and the number of these carbon atoms may be as high as twenty. Preferably R contains from eight to sixteen carbon atoms.

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

The pre-claimed or pickled metal parts are put into the above described emulsions containing 0.1% or more of the alkyl-sulfamido-carboxylic acid or salt thereof. The procedure may take place at ambient or elevated temperature, and according to these conditions the treatment will be performed in different periods of time. It is self-evident that also the type of metal and alloy influences the special conditions of the procedure and therefore this point has to be watched carefully in order to get a good reliable protection.

The adjustment of the pH value of the emulsion is advantageously made by the addition of phosphoric acid to the emulsion because phosphoric acid is not only a very satisfactory agent for this purpose, but it also gives an additional positive effect of corrosion protection, while other acids like hydrochloric or sulphuric acid do not show such advantages.

It is desirable to check the quality of the water used for the preparation of the emulsion in advance, in order to avoid a too high salt content, especially of scale forming compounds like calcium carbonate, calcium bicarbonate, calcium sulphate, magnesium sulfate, magnesium chloride, etc. which deteriorate the emulsion or at least makes it inefficient ahead of time by formation of insoluble calcium or magnesium salts with the hydrocarbon-sulfamido-carboxylic acids or their salts. In order to avoid this, it is preferable to use ion-exchanging equipment to treat the water prior to its use in preparing the emulsions.

The procedure described above operates not only on iron, iron alloys, zinc and zinc alloys, but also on light metals like aluminum and magnesium and their alloys.

From the foregoing it may be easily understood that this treatment according to the present invention is also highly suitable for the after-treatment of phosphate coatings mentioned above. Weathering as well as humidity and salt spray tests have proved the reliability and efficiency of this procedure.

The following examples illustrate the practice of the invention on different metals and alloys under varying procedure and test conditions.

Example #1

Freshly machined parts consisting of low carbon steel were stored for several days before assembly. Half of these pieces received no after-treatment after leaving the lathe; the other half of the pieces obtained the following surface protection: 10 parts of octodecylsulfamido acetic acid sodium salt were diluted under constant stirring with 90 parts of tap water; enough phosphoric acid was added to the emulsion to obtain a pH value of 5.5. The second part of the freshly machined pieces was put into this emulsion for several hours and then stored as was the first part. During the storage period, the untreated pieces showed remarkable corrosion, especially to finger prints; the after-treated parts did not change in appearance during the same time.

Example #2

Normal iron sheets, size 10 x 5 x ⅛'' were sand-blasted to remove rust picked up during transport and storage. Without further treatment, these samples started rusting again in a few days. Some of the pieces were treated directly after sand-blasting in an emulsion prepared in the following way: 5 parts of hexadecylsulfamido butyric acid were neutralized by an insufficient amount of 5% KOH solution and diluted to 100 mls. with water, so that the pH value of the emulsion was about 5. The liquid was heated up to 75° C. under agitation and the test pieces were treated with this emulsion for 30 minutes. After this time, the pieces were rinsed with water and allowed to dry. No rust appeared on the treated pieces for quite some time when stored under the same conditions as the untreated pieces.

Example #3

A rocket motor, made from iron alloy of the composition: C, 0.24–0.30; Si, less than 0.4; Mn, 1.0–1.3; Cr, 0.6–0.9; V, 0.1–0.2; P, 0.25; S, 0.20, became badly corroded during a storage time of several years. A mechanical treatment such as sand-blasting and painting could not be used because of the double-wall construction. Moreover, many nozzles made from brass and built in

the combustion chamber made any usual treatment inadvisable. The large piece of equipment was treated for 8 hours in 20% phosphoric acid at ambient temperature until the surface became rust free. After a short rinsing period with water, the combustion chamber was put immediately into a container filled with the following emulsion: 5 parts of hydrocarbon $(C_{12}—C_{18})$-sulfamido acetic acid sodium salt were slowly diluted with 95 parts of tap water under constant mixing, using a centrifugal pump. The emulsion was given a pH value of 4.5 to 5.5 by adding phosphoric acid. At ambient temperature, the rocket combustion chamber was allowed to stay for 12 hours in this emulsion which was constantly pumped for a good circulation. After this period, the combustion chamber was lifted out of the emulsion and allowed to dry. The rocket combustion chamber surface was returned to its former condition of storage and withstood corrision for many months. Test samples, cut out of the rocket combustion chamber after the acid pickling and after the emulsion treatment were exposed to a weather test in a weather chamber. The samples, pickled but not treated with the emulsion, started rusting after 10 minutes exposure to the weather test, the samples taken off the treated combustion chamber did not show any rust even after 2 hours of the same weather treatment.

Example #4

Test pieces made from low carbon steel, size 5 x 1½ x ⅛'' were derusted by boiling in 10% aqueous NaOH solution, rinsed with water and put in a Parkerizing phosphating solution at about 90° C. After half an hour of this Parkerizing treatment, the test samples were divided into two groups. The first group was treated for another half hour in a Parkerizing solution at 90° C., then taken out, rinsed with water and allowed to dry. The second group was treated for the next half hour in a Parkerizing solution at 90° C. containing an addition of 5% octodecyl-sulfamido acetic acid, under agitation. After this treatment was completed, the samples were rinsed with water, and dried at ambient temperature. Both test groups were exposed in a weather-chamber and resulted in a corrosion of the first group in a much shorter test time than the second group which possessed the additional surface protection applied in a bath together with Parkerizing.

Example #5

Metal sheets, size 4.0 x 1.0 x 0.05'', which were a magnesium alloy (6% Al, 3% Zn, 0.5% Si, 0.1% Mn, rest Mg) were dipped in a water solution containing about 20% nitric acid and 15% sodium dichromate for one minute at ambient temperature.

One set was rinsed with tap water and dried, the other set obtained an additional treatment of alternating rinsing and drying with an 8.5% emulsion of tetradecylsulfamido propionic acid ammonium salt. This procedure took about 10 minutes and was performed at temperatures between 50–60° C. During this time, the pH value of the emulsion was kept between 5.5 and 6.5 by adding corresponding amounts of diluted phosphoric acid to the emulsion.

Corrosion tests carried out in a 0.5% solution of sodium chloride showed a significant difference. The test pieces coated by a molecular film of the tetradecylsulfamido propionic acid ammonium salt did not change their appearance, while generation of hydrogen followed by formation of spots and dots all over the surface of the metal sheets started on the other samples at once.

Example #6

Different metal parts consisting of a zinc die-casting alloy (4.0% Al, 1.0% Cr, 0.1% Fe, rest Zn) were cleaned in a water solution containing 6–7% NaOH, rinsed afterwards and finally dipped in a 0.1% aqueous solution of chromic acid in tap water for 1–2 minutes. While one half of the test samples was allowed to dry at room temperature, the others, in addition, were treated in an acid water emulsion containing 20% of a mixture consisting of 70% octylsulfamido butyric acid potassium salt and 30% dodecylsulfamido acetic acid. The procedure was performed at ambient temperature and took about one hour. During this time, the emulsion was kept moving by means of stirring equipment. Finally, the metal parts were taken out of the emulsion and allowed to dry. Corrosion tests carried out in a spray chamber using tap water and a diluted aqueous solution of sodium chloride (0.5–1.0% NaCl) showed a characteristic difference between the different samples. While all the parts which had a protective coating resulting from the emulsion treatment did not change after several sprayings, corrosion started after the second spray test on the samples which had not been treated with the emulsion.

Example #7

The same behavior was observed on different aluminum sheets (commercial 2S type, 99% Al, rest mostly silicon, copper and iron), size 2.5 x 1.0 x 0.05″, that were cleaned and treated in the same way as mentioned for the zinc die-castings in Example 6.

All the samples protected by treatment according to the manner of practicing the invention described in this example were definitely superior and did not show any corrosion phenomena even after a long period of indoor and outdoor storage.

Example #8

Iron sheets (low carbon steel), size 2″ x 5″ x 0.05″, were derusted in inhibited 10% hydrochloric acid, rinsed first with water and finally with a 0.05% solution of sodium bichromate. After this treatment, the samples were put in an emulsion containing 5% dodecylsulfamido acetic acid sodium salt and monobutyl acid orthophosphate in sufficient amount to keep the solution in the pH range from 6 to 6.5 during the treatment (temperature, 75° C.; duration of immersion, 35 minutes). After drying, the specimens were sprayed with tap water in a weather chamber. These specimens showed during this corrosion test a definite improvement in comparison with samples that were coated in emulsions where the pH value was regulated by phosphoric acid, for example.

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

We claim:

1. The process of protecting a metal surface against corrosion which comprises forming a film on said surface by applying thereto a water emulsion adjusted to a pH value numerically less than 7 containing at least 0.1% of a material selected from the group consisting of alkyl-sulfamido-carboxylic acids, inorganic salts of such acids and organic salts of such acids, the alkyl radical of said acids having at least five carbon atoms.

2. The process of protecting a metal surface against corrosion which comprises forming a film on said surface by applying thereto and subsequently drying a mixture adjusted to a pH value numerically less than 7 comprising water and at least 0.1% of a material selected from the group consisting of alkyl-sulfamido-carboxylic acids, and inorganic and organic salts of said acids, the alkyl radical of said acids having at least five carbon atoms.

3. The process of protecting a metal surface against corrosion which comprises forming a film on said surface by applying thereto and subsequently drying a mixture, adjusted to a pH value numerically less than 7, comprising water and at least 0.1% of a material selected from the group consisting of alkyl-sulfamido-carboxylic acids and the salts of such acids, the alkyl radical of said acids having from eight to sixteen carbon atoms.

JOSEF M. MICHEL.
KARL F. HAGER.

No references cited.