

1

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CORROSION INHIBITORS

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4 Claims. (Cl. 21—2.5)

This invention relates to inhibiting the corrosion of metals and metal surfaces and more particularly it relates to corrosion inhibitors which are effective on a variety of metals and which are easily applied.

There are many pieces of mechanical equipment containing intricate metal parts which are used only intermittently. Engines, including gasoline, diesel, jet etc., farm and marine equipment, machine tools, containers, bins, etc., are illustrative of items which have intermittent periods of use. It is desirable to have a rapid and easy method for protecting metal surfaces forming a part of these items. Since many of them contain parts which because of their location or intricacy are inaccessible to the common methods of applying an anti-corrosion coating (such as painting, spraying or dipping) it is essential to provide a corrosion inhibitor which may be carried into and around these intricate or inaccessible parts by means of a gas or easily introduced liquid.

The pieces of mechanical equipment to be protected are not only intricate in construction but they also are composed of parts made of a wide variety of metals, including steel, magnesium, aluminum, bronze, brass and bearing materials. This is particularly true of internal combustion engines and also of jet engines. It is well known that corrosion inhibitors which are basic in character protect steel but attack magnesium and aluminum while those corrosion inhibitors which contain nitrous salts of amines protect steel and magnesium and aluminum but attack copper-containing alloys. Thus, it is desirable to find a corrosion inhibitor which is easily applied and which protects a wide variety of metals and their alloys.

Internal combustion engines and jet motors are very often exposed to sea water spray, atmospheres of exceedingly high humidities, and the ordinary products of combination, including those from leaded fuels, which remain in the engine or jet motor after shutdowns. The corrosion inhibitors of this invention are particularly well suited to protect metal surfaces from these corrosive agents.

There are a number of methods known for protecting metal surfaces against moisture and corrosive vapors, but many of them either deposit a permanent coating on the surface or use materials, such as heavy greases which require a great deal of time to remove. The coating deposited by the corrosion inhibitors of this invention on the other hand, is neither permanent nor does it have to be removed before operations can be continued.

The use of corrosion inhibitors such as dicyclohexylamine nitrite which may be vaporized for more convenient deposition on the metal surface to be protected is known in the art. However, as pointed out above, such vapor-phase corrosion inhibitors do not protect all types of metals. In fact, it has often been necessary to protect one type of metallic surface to the detriment of another type or types of metal. A more desirable corrosion inhibitor would, therefore, be one which can be easily applied in its vapor state, in solution or in the form of an aerosol-type dispersion and which will be effective in protecting a wide range of metal surfaces without having any adverse effects. This in effect involves finding a

2

corrosion inhibitor which is a good compromise in its ability to protect many different metal surfaces.

An object of this invention is to furnish a volatilizable inhibitor capable of protecting a wide variety of metal surfaces including steel, aluminum, magnesium, brass, bronze and bearing metals. Another object is to furnish corrosion inhibitors which may be readily applied and which do not require a special operation for their removal. A further object of this invention is to protect metal surfaces not only against corrosion due to contact with air, water and sea spray but also against that due to the products of combustion encountered in engines and jet motors. An additional object is to provide corrosion inhibitors which are hydrophobic in character. These and other objects will appear in the following discussion.

The improved corrosion inhibitors of this invention are organic sulfides of the general formula



where n has the value of one or two and R' is either



or



in which R is an alkyl radical, being unsubstituted or substituted with hydrocarbon radicals.

It will be noted that the corrosion inhibitors of this invention as defined by the above formula are neutral compounds and do not have the amino group. Thus, the deleterious effects on aluminum and magnesium caused by alkaline compounds and the adverse effects of the amino group on copper and copper-containing metals are all eliminated.

The sulfide linkage of these corrosion inhibitors may be introduced either by way of the alcohol or by way of the acid as indicated in the two possible general forms for R' . The preparation of typical representatives of this class of compounds may be found in J. Chem. Soc. 1950, 3061 (1950), for thiodiglycol diacetate; J. Am. Chem. Soc. 69, 241 (1947) for di-(2-ethylhexyl)thiodipropionate; and Berichte 63, 2393 (1930) and Fihnel and Carmack "Organic Syntheses," vol. 30, p. 65 (1950), for dimethyl thiodipropionate.

The esters of thiodiacetic acid and of 3,3'-thiodipropionic acid, and more particularly di-(2-ethylhexyl)thiodipropionate and di-(2-ethylhexyl)thiodiacetate, have been found to be especially effective in preventing corrosion in internal combustion engines and jet motors.

The mechanism of corrosion inhibition is not too well understood but it is generally assumed that the inhibiting agent or its vapor reacts with, or is somehow attracted to, the exposed surface molecules of the metal to be protected.

In the case of the esters of this invention it appears that two effects, both contributing to the protection of the metal, are present. The first of these is the effect of the —S— (sulfide) linkage, while the second appears to be an effect of the remaining portion of the molecule. A reasonable explanation would seem to be that the —S— linkage reacts or is in some manner attracted to the surface molecules of the metal to be protected to form a surface coating which is less reactive with the corroding agents such as water vapor, combustion gases and sea spray.

The fact that a compound such as an alkyl mercaptan containing the sulfide linkage, but not two alkyl chains, does not prevent corrosion (see Bul. soc. chim. 1954,

650 (1954)), is strong indication that the additional alkyl radical also contributes to the overall corrosion inhibiting effect. One possible explanation is that the alkyl radical gives the corrosion inhibitors of this invention a paraffinic character and hence accounts for the hydrophobic character which they exhibit on the protected metal surfaces. Such a hydrophobic character is particularly important for corrosion inhibitors designed to protect metal surfaces from atmospheres of very high humidities.

A bench test was devised to test the effectiveness of the corrosion inhibitors of this invention and to compare them with corrosion inhibitors now in use. In this bench test the metal specimen, supported from the top of a 250-ml. wide mouth Erlenmeyer flask by a nylon thread, was exposed to water vapor and the inhibitor in the flask. These tests were run at room temperature and at 150° F. The polished samples were graded on the basis of zero to four, where zero represented no corrosion and four represented complete attack on the specimen surface.

Typical results from these bench tests are given in Table I.

TABLE I

Effectiveness of corrosion inhibitors used on different metals found in an internal combustion engine

Corrosion Inhibitor	Hours run	Lead-Indium Bearing	Bronze Bushing	Bronze Valve Guide	Al Piston	Al Pump Housing	Steel Cylinder	Average
None	85	1.5	0.5	1.5	2.0	0.5	4.0	1.8
Dicyclohexylamine nitrite	89	3.5	0.0	1.0	---	1.0	---	1.4
Di-(2-ethylhexyl) thiodipropionate	139	0.0	1.5	0.0	0.5	0.5	0.5	0.5
Thiodiglycol diacetate	41	0.0	2.0	1.5	0.5	0.0	3.0	1.1

¹ Typical commercial inhibitor.

NOTE.—Graded on basis of 0 to 4. 0=no corrosion; 4=complete attack on surface.

Another series of tests were run in which the metal sample was first exposed to the vaporized inhibitor and then sprayed with a fine mist of sea water and subsequently stored for 65 hours over sea water in a closed container so that the sample was in an atmosphere of 100% relative humidity. This meant that there was substantially no evaporation of the sea water on the specimen. Such conditions are sufficient to attack stainless steel. The results of these tests are shown in Table II.

TABLE II

Effectiveness of corrosion inhibitors used on steel, aluminum and magnesium

Corrosion Inhibitor	Stainless Steel	Aluminum	Magnesium	Average
None	1.0	1.0	3.0	1.7
Dicyclohexylamine nitrite (proprietary composition)	2.0	1.0	3.0	2.0
Di-(2-ethylhexyl)thiodipropionate	0.0	1.0	2.0	1.0
Di-(2-ethylhexyl)thiodiacetate	0.0	0.0	1.0	0.3
Dimethyl thiodipropionate	0.0	0.0	3.0	1.0
Di-isopropyl thiodipropionate	0.0	1.0	3.0	1.3
Thiodiglycol diacetate	1.0	1.0	3.0	1.7
	0.0	1.0	3.0	1.3

NOTE.—Graded on basis of 0 to 4. 0=no corrosion; 4=complete attack on surface.

The improved protection offered by the corrosion inhibitors of this invention is shown in terms of not only less corrosion measured for each individual type of metal sample but also for the overall average for all the metals included. The protection given under the severe conditions of salt atmospheres of 100% relative humidity is particularly marked as shown by the data of Table II.

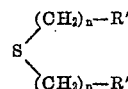
Although the corrosion inhibitors of this invention are conveniently applied to metal surfaces by condensation

from the vapor phase as is conventionally done for vapor-phase corrosion inhibition, other means of application are equally well suited. Such other means include, but are not limited to, brushing or spraying on solutions made up with acetone or other suitable solvents, suspending finely divided particles in the form of an aerosol (i.e., as a colloidal system in a gas), or entraining them in a current of hot air. In addition, since the corrosion inhibitors of this invention are soluble in lubricating oils they may be dissolved in them and taken into an engine in the oil run through the engine or motor when it is shut down. Methods of application which involve vaporization or carrying finely divided particles in air or as aerosols are also suitable for applying the corrosion inhibitors to the internal parts of engines and jets. If it is desirable to protect small individual parts the corrosion inhibitors may be used to treat wrapping paper (as by impregnation followed by drying) which in turn may be used to wrap about the parts or to be put in a closed container along with the metal surfaces to be protected.

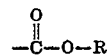
I claim:

1. Process for inhibiting the corrosion of the internal

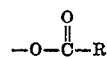
parts of an engine which comprises introducing a corrosion inhibitor as a vapor into the engine intake, said corrosion inhibitor comprising a compound of the general formula



where n is an integer selected from one and two and R' is a radical selected from the group consisting of

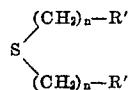


and

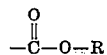


wherein R is an alkyl radical having from one to eight carbon atoms.

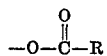
2. An anti-corrosion wrapping paper suitable for protecting metallic objects, said wrapping paper being impregnated with a corrosion inhibitor, said corrosion inhibitor comprising a compound of the formula



where n is an integer selected from one and two and R' is a radical selected from the group consisting of



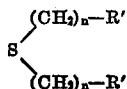
and



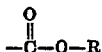
wherein R is an alkyl radical having from one to eight carbon atoms.

5

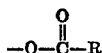
3. Process for inhibiting the corrosion of a metal surface normally corrodible by high humidities which comprises at least partially enclosing said metal surface in a wrapping paper impregnated with a corrosion-inhibiting amount of a corrosion inhibitor, said corrosion inhibitor comprising a compound of the formula



where n is an integer selected from one and two and R' is a radical selected from the group consisting of



and

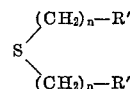


wherein R is an alkyl radical having from one to eight carbon atoms.

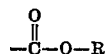
4. The combination comprising a metal article normally corrodible by high humidities and a wrapping paper at least partially enclosing said metal article, said wrapping paper impregnated with a corrosion-inhibiting

6

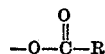
amount of a corrosion inhibitor, said corrosion inhibitor comprising a compound of the formula



where n is an integer selected from one and two and R' is a radical selected from the group consisting of



and



wherein R is an alkyl radical having from one to eight carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

2,262,686	Kyrides	Nov. 11, 1941
2,331,270	George	Oct. 5, 1943
2,475,186	Kamlet	July 5, 1949
2,481,372	Fuchs	Sept. 6, 1949
2,649,416	Richter et al.	Aug. 18, 1953
2,653,854	Schaar	Sept. 29, 1953
2,717,196	Wachter	Sept. 6, 1955