Patented June 11, 1946 2,401,733

UNITED STATES PATENT OFFICE

2,401,733

CORROSION INHIBITOR

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No Drawing. Application January 26, 1945, Serial No. 574,819

7 Claims. (Cl. 252—77)

1

The present invention relates to a corrosion inhibitor for use in anti-freeze mixtures used in the cooling systems of liquid-cooled internal combustion engines particularly those employed to propel automobiles and airplanes. The present application is a continuation-in-part of my prior application Serial No. 433,463 filed March 5, 1943.

It is well known that the metal parts in the cooling system of internal combustion engines comprise iron, copper, brass, solder and aluminum, in addition these metals are in electrical contact and consequently local electric cells are formed. Corrosion of these metal parts has occurred and attempts have been made to inhibit or to lessen the corrosion of the metallic parts of such cooling systems by the use of corrosion inhibitors in the liquid employed as a cooling medium. The prior art has suggested the use of many types of corrosion inhibitors among which may be mentioned borax, ethanolamine, particularly triethanolamine, sulfonated oils, resinates, sodium nitrite either alone or mixed with other inhibitors, such as small amounts of maleic acid, picric acid, molybdates, tungstates, urea, naphthenates, etc. In German Patent No. 485,012 there is disclosed an anti-freeze mixture containing 25 parts glycol, 75 parts water and 0.2 part sodium hydroxide. It is suggested in this German patent that guanidine can be substituted for the sodium hydroxide, but as herein subsequently pointed out, guanidine as shown by actual test results does not produce a corrosion inhibiting action which is at all comparable to that of the corrosion inhibitor of my present invention. However, so far as I am aware, none of the prior art corrosion inhibitors or combinations of corrosion inhibitors have been wholly satisfactory.

In the search for a satisfactory corrosion inhibitor or erosion inhibitor it must be borne in mind that the inhibitor must be efficient not only at ordinary temperatures, such as those below 100° F. (37.7° C.) but also at elevated such as those at which the internal combustion engine operates most efficiently, for example, 160 to 180° F. (60–82.2° C.). The inhibitor must prevent corrosion whether due to the corrosion of the metals of the cooling system, whether this corrosion is due simply to the cooling medium itself or to the electrolytic effects or local couples that occur between the different metals of the cooling system, or by the necessary rapid circulation of the cooling medium in order to bring about prompt and ready heat transfer from

2

the engine to the cooling medium. Anti-freeze solutions such as alcohols or glycols when used in internal combustion engine cooling systems without the addition of a satisfactory corrosion inhibitor cause severe corrosion of the metals comprising the system, particularly the iron and aluminum portions thereof.

It is the object of this invention to provide a corrosion inhibitor which will retain its inhibitory effect in suppressing or preventing corrosion throughout the normal life of the cooling liquor.

It is a further object of this invention to provide a corrosion inhibitor which will not be materially changed in effectiveness by air over the normal life of the cooling liquid.

It is a further object of my invention to provide a corrosion inhibitor which is soluble in concentrated alcoholic solutions such as glycols or methanol and thus facilitating the compounding of the anti-freeze material for storage and shipment.

Broadly stated, the corrosion inhibitor described hereinafter may be employed in any cooling system which is constructed of metal. The novel corrosion inhibitor may be employed in conjunction with the cooling medium used in the cooling systems of automobile and airplane engines, for example, and in the latter systems, less water or perhaps no water at all is employed in the cooling medium. The novel corrosion inhibitor may be used with any type of anti-freeze, such as methanol, ethanol, glycerol, ethylene glycol, propylene glycol, or a mixture of glycols. It has been found that guanidine carbonate is a highly effective and satisfactory corrosion inhibitor for use in the cooling systems of internal combustion engines. When guanidine carbonate is added to one of the anti-freeze materials and diluted with water it has been shown that corrosion is prevented whether due to the corrosion of the metals of the cooling system as a result of the corrosive effect of the cooling medium, the electrolytic effects that occur between the different metals or the necessary rapid circulation of the cooling medium.

The guanidine carbonate may be used in quantities of about 0.05% to about 2.0% of the weight of the concentrated anti-freeze component such as glycol. As a result of the presence of the guanidine carbonate the anti-freeze solution has an alkaline reaction of about pH 8 to pH 11. This provides an alkaline reserve should acidity develop during prolonged usage of the cooling medium.

When desired the amount of guanidine carbonate may be decreased and other alkaline inorganic compounds such as disodium phosphate, or sodium carbonate or the like, may be added in small but effective amounts to provide additional or a less expensive alkaline reserve to the anti-freeze solution.

Likewise, when desired small quantities of oils such as a mineral oil, may be added, without affecting the corrosion inhibiting properties of the inhibitor, to prevent or materially lower any tendency to foam under strong agitation as often occurs in the cooling systems.

The improved corrosion inhibiting properties of guanidine carbonate are all the more unusual and unexpected when compared with the corresponding properties of a quite similar chemical compound, namely guanidine. In Table I, corrosion test results are set forth, wherein anti-freeze solutions were made up containing 350 g. per liter of a mixture of 2 mols of ethylene glycol and 1 mol of propylene glycol, the balance being 650 g. of water. Test solutions were made up on the basis of this mixture, each test solution containing guanidine carbonate, guanidine carbonate and disodium phosphate, and guanidine, respectively, and in the amounts as noted in Table I. Sets of metal test strips, including steel and aluminum which were assembled together in electrical contact and including other metals, namely brass, copper and solder, were then immersed in the continually stirred test solutions for a period of 1440 hours or 60 days and the amount of corrosion determined by the weight loss of the metal strips. The test period of 60 days corresponds to about 2 seasons' use of a commercial vehicle or six seasons' use of a private pleasure car. The results of these corrosion tests on aluminum were as follows:

TABLE I

Corrosion test results of mixed glycol-water solutions on aluminum in electrical contact with steel

Inhibitor	Weight loss (60 days at 69° C.)	Percent increase over guanidine carbonate
	Mg./cm.[2]	
Guanidine carbonate (5 g. p. l.)	0.67	
Guanidine carbonate (5 g. p. l.) and disodium phosphate (2.5 g. p. l.)	0.91	35
Guanidine (5 g. p. l.) [1]	2.12	216
Guanidine (5 g. p. l.) 60 days at 21° C.[1]	2.64	294

[1] Mixed glycol solution containing 5 g. p. l. guanidine immediately attacked aluminum when it was immersed in solution under the above conditions, as evidenced by formation of bubbles and bubbling action.

The corrosion tests of the 35% mixed glycol solutions on steel followed the same general pattern as in the foregoing table, with the exception that the solution containing 5 g. per liter of guanidine carbonate together with 2.5 g. per liter of disodium phosphate showed better results than the solution containing the guanidine carbonate alone. For the purpose of comparison, the weight loss of the steel in the guanidine glycol mixture solution was 89% greater than the solution containing guanidine carbonate, and 154% greater than the solution containing guanidine carbonate and disodium phosphate. All of the latter tests were, of course, run for the same period of time, viz.: 60 days at 69° C.

Illustrative examples of anti-freeze compositions employing the novel guanidine carbonate corrosion inhibitor are as follows:

EXAMPLE 1

	Parts by weight
Mixed ethylene and propylene glycol (in the proportion of 2 mols. to 1 mol.)	350
Water	650
Guanidine carbonate	5

EXAMPLE 2

	Parts by weight
Denatured ethyl alcohol	400
Water	600
Guanidine carbonate	5
Disodium hydrogen phosphate	2.5

EXAMPLE 3

	Parts by weight
Mixed ethylene and propylene glycol (in the proportion of 2 mols. to 1 mol.)	350
Water	650
Guanidine carbonate	3
Disodium hydrogen phosphate	2.5

The effectiveness of this new corrosion inhibitor is shown by results in which parallel tests were run using commerical anti-freeze compositions containing well-known types of prior art inhibiting agents. The following table sets forth corrosion tests results upon the formulations of Examples 1 and 3 above, as well as two commercial anti-freeze compositions containing inhibiting agents. In this case, the metal strip sets were made up of iron, brass, aluminum and solder bolted together with brass bolts and nuts with brass spacer washers between the metal strips; and the size of strips, i. e. their respective surface areas, were in approximate proportion to that in which these metals would be present in an internal combustion engine cooling system. It suffices to say that the iron or soft steel strip was present in substantial excess over that of the remaining strips. The results of the corrosion tests so conducted as measured in the weight loss of the soft steel strips, were as follows:

TABLE II

Corrosion test results of mixed glycol solution containing guanidine carbonate, and of commercially available glycol solutions containing other inhibiting agents

Anti-freeze solution	Weight loss of soft steel (after 60 days at 60–65° C.)
	Mg./cm.[2]
Formulation of Example 1	.07
Formulation of Example 3	1.024
Commercial anti-freeze solution #1	.81
Commercial anti-freeze solution #2	.26

[1] Weight gain: #1–35% glycol solution containing borate type inhibitor; #2–35% glycol solution containing tri-ethanolamine inhibitor.

As shown in Table II, commercial anti-freezes #1 and #2 produced 1060% and 270% increase of corrosion of steel respectively, over that of guanidine carbonate inhibitor according to formulation of Example 1.

Although the present invention has been described in conjunction with certain preferred embodiments, it is to be understood that variations and modifications thereof can be made as those skilled in the art will readily understand. Such variations and modifications are to be considered within the purview of the specification and the scope of the appended claims. Thus the

term "anti-freeze mixture" as used hereinbefore and in the claims is to be understood as including not only the anti-freeze mixture when used in conjunction with water in cooling systems but also when the anti-freeze mixture is used per se as the cooling medium.

Equivalent modes of practicing my invention may be followed provided that they are within the scope and purview of the appended claims.

I, therefore, distinctly claim and particularly point out as my invention:

1. As a new article of manufacture, an anti-freeze mixture for use in cooling systems of liquid-cooled internal combustion engines in the presence of metals subject to electrolytic corrosion, said anti-freeze mixture consisting of water an organic water-soluble freezing point depressant and a small but effective amount of guanidine carbonate, said anti-freeze mixture having a pH value of about 8 to about 11.

2. As a new article of manufacture, an anti-freeze mixture for use in cooling systems of liquid-cooled internal combustion engines in the presence of metals subject to electrolytic corrosion, said anti-freeze mixture consisting of water an organic water-soluble freezing point depressant and .05% to 2.0% by weight of guanidine carbonate on the basis of said organic freezing point depressant present.

3. As a new article of manufacture, an anti-freeze mixture containing a corrosion inhibitor capable of reducing substantially the corrosion of different metals in electrical contact forming at least a part of cooling systems of liquid-cooled internal combustion engines, said anti-freeze mixture consisting of about 350 parts by weight of ethylene and propylene glycols in the proportion of 2 mols. to 1 mol., about 650 parts by weight of water, about 3 parts by weight of guanidine carbonate and about 2 parts by weight of disodium hydrogen phosphate.

4. As a new article of manufacture, an anti-freeze mixture containing a corrosion inhibitor capable of reducing substantially the corrosion

of different metals in electrical contact forming at least a part of cooling systems of liquid-cooled internal combustion engines, said anti-freeze mixture consisting of about 400 parts by weight ethyl alcohol, about 600 parts by weight water, about 5 parts by weight guanidine carbonate and about 2.5 parts by weight disodium hydrogen phosphate.

5. As a new article of manufacture, an anti-freeze mixture containing a corrosion inhibitor capable of reducing substantially the corrosion of aluminum and ferrous metals in electrical contact with each other forming at least a part of cooling systems of liquid-cooled internal combustion engines, said anti-freeze mixture consisting of a mixture of ethylene and propylene glycol water and a small but effective amount of guanidine carbonate, said anti-freeze mixture having a pH value of about 8 to about 11.

6. As a new article of manufacture, an anti-freeze mixture containing a corrosion inhibitor capable of reducing substantially the corrosion of aluminum and ferrous metals in electrical contact with each other forming at least a part of cooling systems of liquid-cooled internal combustion engines, said anti-freeze mixture consisting of a mixture of ethylene and propylene glycol water and .05% to 2.0% by weight of guanidine carbonate on the basis of said ethylene and propylene glycols present.

7. As a new article of manufacture, an anti-freeze mixture containing a corrosion inhibitor capable of reducing substantially the corrosion of aluminum and ferrous metals in electrical contact with each other forming at least a part of cooling systems of liquid-cooled internal combustion engines, said anti-freeze mixture consisting of about 350 parts by weight of ethylene and propylene glycols in the proportion of 2 mols. to 1 mol., about 650 parts by weight of water, about 3 parts by weight of guanidine carbonate and about 2 parts by weight of disodium hydrogen phosphate.

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