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CORROSION INHIBITOR

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The present invention relates to corrosion inhibitors for the protection of metals such as iron, steel, copper and brass, and it has particular relation to inhibitors adapted to prevent the formation of iron oxide or rust in containers for alcohol, cooling systems of internal combustion engines and the like.

The main objects of the invention are to provide a corrosion inhibitor for protecting containers of alcohol, cooling systems of internal combustion engines and the like from corrosion which is relatively simple and economical to prepare; which exerts a very strong retarding action against the agencies of corrosion over a relatively long period of time; which is highly effective as a corrosion inhibitor even at relatively low concentration; which does not tend to clog up or otherwise foul the restricted passages of the cooling systems of internal combustion engines.

These and other objects will be apparent from consideration of the following specification and the appended claims.

It has heretofore been observed that alcohol such as common ethyl alcohol, methyl alcohol, butyl alcohol, and polyhydroxy alcohol such as glycol and glycerol exerted a pronounced corrosive action upon iron, steel, copper, and the like. This corrosion is increased with elevation of temperature and in case the alcohols are employed either in substantially pure form or diluted with water, as antifreeze solutions in the cooling systems of internal combustion engines, the corrosive action became so pronounced as to result in the formation of such substantial amounts of iron oxide or other insoluble forms of iron as in some cases to result in the partial or complete clogging of the restricted passages and channels of the cooling systems. It has heretofore been proposed to reduce this corroding action by incorporating into non-freezing media certain inhibiting substances. Among the materials suggested for the purpose may be included ordinary caustic which doubtless tended to neutralize free acids contained in the corrosive fluids. Borax, soap, triethanolamine and mixtures of triethanolamine with soap have also been suggested. These substances when incorporated in adequate amounts into anti-freeze cooling media were found materially to reduce the tendency of the solutions to corrode metal parts over a period of time. However, after protracted use the inhibiting action was either weakened to such an extent that the corroding action became appreciable, or a material degree of corrosion occurred

by reason of slow action permitted by the low protective action of the inhibitor.

The present invention is based upon the discovery that cyclohexylamines, such as cyclohexylamine, C-methyl cyclohexylamine, dicyclohexylamine, etc. (amines which may be obtained by hydrogenation of aniline and its homologues) are highly effective inhibitors of corrosion in solutions of alcohol and that this protective action may be greatly increased by incorporating into alcohol or solutions of alcohol along with the cyclohexylamine a suitable proportion of soap. The protective action exerted by mixtures of cyclohexylamine and an ordinary soap is not merely due to the independent additive action of the two components, but is so much stronger than can be accounted for by reason of the independent action of each of the two materials that it must be assumed that it is in some way due to some mutual interaction (chemical or physical) between the two components.

Various soaps may be employed in combination with cyclohexylamine to produce corrosion inhibitors for alcohol solutions, of which sodium stearate may be considered an example. However, the sodium or potassium stearates, palmitates, oleates, laurates, and mixtures of any two or more of these may likewise be employed with cyclohexylamine. Soaps of the above indicated fatty acids and ammonia or with organic bases such as triethanolamine, ethyl amine, cyclohexylamine, and the like are also contemplated. The soap forming fatty acid and the base may be added separately to the alcohol and then added to alcohol containing cyclohexylamine.

Cyclohexylamine and soaps may be combined to form good inhibitors for alcohol solutions over a relatively wide range of proportions, for example, they may be combined in the ratio of one part by weight of soap to three parts of cyclohexylamine, or they may be combined in the ratio of equal parts of the two ingredients. However, optimum results seem to be produced by incorporating approximately three parts by weight of soap with one part by weight of cyclohexylamine.

Comparative tests were conducted to determine the relative merit of cyclohexylamine and various mixtures of cyclohexylamine with common soap as compared with various inhibitors heretofore suggested for use in alcohol solutions. The most sensitive and reliable test for this purpose involves boiling the desired alcohol or solution of the alcohol with water under a reflux condenser and in the presence of steel wool, which is substantially free from rust and other corrosion products until

rust appears thereupon. The following table shows the results of a series of such tests.

Test No.	Amount of inhibitor per 100 gallons of alcohol	First rust formed
1	4.2 lbs. soap	11 days.
2	5.9 lbs. borax	9 days.
3	2.5 lbs. soap and 2.5 lbs. $C_6H_{11}NH_2$	36 days.
4	5 lbs. cyclohexylamine	Over 13 days.
5	5 lbs. triethanolamine	8 days.
6	0.83 lb. soap and 2.5 lbs. $C_6H_{11}NH_2$	19 days.
7	3.32 lbs. soap and 1.66 lbs. $C_6H_{11}NH_2$	Over 46 days.
8	1.66 lbs. soap and 1.66 lbs. $C_6H_{11}NH_2$	31 days.
9	1.66 lbs. soap and 0.83 lb. $C_6H_{11}NH_2$	12 days.
10	2.5 lbs. soap and 0.83 lb. $C_6H_{11}NH_2$	46 days.
11	2.5 lbs. soap and 2.5 lbs. $C_6H_{11}NH_2$	36 days.
12	2.5 lbs. oleic acid and 2.5 lbs. $C_6H_{11}NH_2$	18 days.

The first, second and fifth tests are of soap, borax and triethanolamine, respectively, which have been used commercially as inhibitors. The fourth test discloses that as compared with the heretofore available inhibitors cyclohexylamine is quite satisfactory and the remainder of the tests disclose that mixtures of cyclohexylamine in various proportions exert an inhibiting action against corrosion in alcohol solutions far superior to that of either of the component ingredients of the inhibitor mixture.

In preparing a solution of alcohol and soap, cyclohexylamine mixture, various methods are applicable. However, the following constitute specific examples of methods which have by practical tests been found to be satisfactory.

I. In case the available alcohol is 190 proof or over and alcohol of 188 proof is desired, 92.6 pounds of soap may be dissolved in 100 gallons of warm alcohol of a concentration of 60 to 80%. The addition should be accompanied by vigorous agitation. The time and temperature required for solution may vary over considerable range. Specific examples of satisfactory values for alcohol of 60, 70, and 80% are given in the following table:

Conditions necessary for dissolving 10 grams soap flakes in 90 cc. of 60, 70, or 80% alcohol (92.6 lbs. in 100 gallons)

Percent alcohol	Time required to dissolve at various temperatures			
	33° C.	36° C.	40° C.	45° C.
	Minutes	Minutes	Minutes	Minutes
60	45	10		
70		45	20	
80				30

The concentrated solution is incorporated into 3600 gallons of 95% alcohol containing 31 lbs. of cyclohexylamine. As a result of the addition there is a slight reduction in the strength of the alcohol which, if 60% alcohol is used in making up the initial concentrated solution of soap and cyclohexylamine amounts to 1.1%, and if 80% alcohol is used amounts to .5%. If a further dilution of the final alcohol-inhibitor solution is desired in order to make alcohol of 188 or lower proof, water, of course, may be added. In event that it is preferred to start with alcohol of the desired proof, (for example 188 proof) and to maintain this concentration in the final product the following procedure may be followed:

Dissolve 123 pounds of soap in 400 gallons of warm 188 proof alcohol and then add this solution to 4500 gallons of 188 proof alcohol containing 41 pounds of cyclohexylamine. In case the

addition of the concentrated soap solution is made at relatively low temperature it may be preferable to add 123 pounds of soap to 800 gallons of warm 188 proof alcohol and then to add this to 4100 gallons of 188 proof alcohol containing 41 pounds of cyclohexylamine. Where the soap is added to 400 gallons of alcohol, solution takes place within a period of 10 minutes at 70° C. or 30 minutes at 60° C. In case the soap is added initially to 800 gallons of alcohol the solution takes place within a period of 20 minutes at 60° C. In the first case a gel tends to form at temperatures below 44° C. while in the second case gelling does not occur until the temperature has passed below 31° C.

The solutions prepared as above described may be stored and shipped in ordinary metal containers without any appreciable tendency to produce corrosion of the walls thereof. The solutions may be diluted with water to substantially any desired degree in order to form solutions suitable for use in the cooling systems of such internal combustion engines as are employed in motor boats, airplanes, automobiles, and the like. The concentration of the solution in the cooling system, of course, will depend upon the temperature to which the solution is to be subjected. The lower the temperature, the more concentrated will be the solution employed. The concentration of the solution required to reduce the desired lowering of the freezing point of the cooling fluid, of course, is well understood by those skilled in the art and does not constitute a part of the present invention. For most purposes a solution of approximately 40% alcohol is quite satisfactory.

The foregoing description has been directed more particularly to the application of cyclohexylamine and mixtures of cyclohexylamine with soap to use as an inhibitor for corrosion in solutions of ordinary ethyl alcohol. However, it is to be understood that it may also be employed with excellent results in any of the other common alcohols such as propyl alcohol, butyl alcohol, ethylene glycol, glycerol, and the like, or mixtures of any two or more of these.

Cyclohexylamine may be replaced by derivatives such as C-methyl cyclohexylamine and di-cyclohexylamine already alluded to.

The use of the new inhibitor in water in cooling systems containing no alcohol or other freezing point depressant is also contemplated as being within the purview of the invention.

The cyclohexylamine employed as an inhibitor is itself comparatively inexpensive to obtain, and from the foregoing description, it will be apparent that it can be combined with a relatively large amount of inexpensive soap to produce an inhibitor of unusual effectiveness. For this reason its use does not constitute a material expense in the preparation of the anti-freeze solutions. The material is substantially free of odors and toxicity, and it also does not tend to form undesirable deposits when employed. For the foregoing reasons it is highly desirable for commercial application.

Although only the preferred forms of the invention have been described in the foregoing description, it will be apparent to those skilled in the art that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

What I claim is:

1. A corrosion inhibitor for liquids corrosive to

metals comprising a mixture of cyclohexylamine and soap.

2. As a cooling medium for internal combustion engines, water-alcohol solution containing cyclohexylamine.

3. A solution as defined in claim 2 to which soap has been added.

4. As a new composition of matter a mixture of cyclohexylamine and soap.

5. As a new composition of matter a mixture of cyclohexylamine, soap and alcohol.

6. As a new composition of matter a mixture of ethyl alcohol, cyclohexylamine and soap.

7. An anti-freeze solution comprising a mixture of an alcohol, cyclohexylamine and soap.

8. An anti-freeze solution comprising a mixture of a polyhydric alcohol, soap and cyclohexylamine.

9. A method of preparing a non-corrosive alcohol mixture which comprises dissolving soap in a warm mixture of water and alcohol and then incorporating the solution into a solution of a cyclohexylamine in alcohol.

10. A method as defined in claim 9 in which the alcohol of the second solution is of higher concentration than that of the first.

11. A non-corrosive alcohol solution containing a soap and a cyclohexylamine.

12. A solution as defined in claim 11 in which the soap is an oleic acid soap.

13. A solution as defined in claim 11 in which the soap is potassium oleate.

14. A corrosion inhibitor for alcohols, comprising a mixture of dicyclohexylamine and soap.

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