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NONCORROSIVE LIQUID

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This invention relates to non-corrosive liquids suitable for use in heat exchange devices and the like and particularly to non-corrosive aqueous solutions of alcohols particularly adapted for use in heat exchange devices containing iron and solder.

Heat exchange devices, and particularly the cooling systems of internal combustion engines, are generally composed of iron and copper with parts joined together by means of solder. Water is the cooling liquid most commonly employed. However, in cold weather it is usual to employ aqueous solutions of non-electrolyte freezing point depressants. The water soluble alcohols, such as methanol, ethanol, ethylene, glycol, glycerol and the like, are generally employed as the freezing point depressant, particularly in internal combustion engines. It is well known that water alone is quite corrosive to the metals of the heat exchange devices. Aqueous solutions of the water soluble alcohols are known to be even more corrosive than water alone. In order to overcome this difficulty, it has become common practice to add to the cooling liquid various materials for inhibiting corrosion of the metals of the heat exchange devices by the cooling liquid.

Sodium nitrite has been recognized as a very effective corrosion inhibitor for ferrous metals, such as iron and steel, but I have found that it tends to increase the corrosion of solder and copper in the cooling system. Clarkson and Pedersen, in Patent 2,054,282, have disclosed that the corrosion of copper, in heat exchange systems employing water or aqueous solutions of alcohols and various metal nitrites, may be inhibited by incorporating in the cooling liquid a mercapto-aryl-thiazole, a hydrocarbon mercaptan or a disulfide thereof.

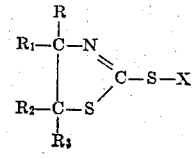
It is an object of the present invention to provide an aqueous heat exchange liquid which is non-corrosive or substantially non-corrosive to the metals of a heat exchange device, and particularly iron and solder. A further object is to provide an antifreeze liquid, employing a non-electrolyte freezing point depressant, which liquid is substantially non-corrosive to the heat exchanger as a whole and particularly is substantially non-corrosive to iron and solder. A still further object is to provide a non-electrolyte freezing point depressant which is non-corrosive or substantially non-corrosive to metal containers in which it may be transported and marketed. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with my invention which comprises incorporating in water, in an aqueous solution of a non-electrolyte freezing point depressant or in a non-electrolyte freezing point depressant, and in the absence of substantial amounts of electrolyte, at least 0.03% of a nitrite of a metal above aluminum in the electromotive series together with a small proportion of a water soluble member of the group of 2-mercapto-thiazolines devoid of non-hydrocarbon substituents, organic acyl derivatives of such 2-mercapto-thiazolines and salts of such 2-mercapto-thiazolines. I have found that such aqueous liquids are substantially non-corrosive to the metals of the usual heat exchange devices, particularly those employed in the cooling systems of internal combustion engines, and do not materially affect the heat transfer coefficient of the devices. Also, the concentrated non-electrolyte freezing point depressants, containing such nitrites and 2-mercapto-thiazoline compounds, are substantially non-corrosive to metal containers of the type ordinarily employed for transporting and marketing them. The 2-mercapto-thiazolines, their acyl derivatives and their salts, inhibit the corrosion of solder, particularly that ordinarily taking place in the presence of the nitrite, and do not prevent the nitrite from materially inhibiting the corrosion of iron.

By "a metal above aluminum in the electromotive series," I mean the metals on the sodium side of the series. Among the nitrites, the most desirable are those of sodium, potassium, barium, strontium, calcium and magnesium, and particularly those of the alkali metals, such as sodium and potassium.

By the term "non-electrolyte freezing point depressant," I means the water soluble mono and polyhydric aliphatic alcohols which decrease the freezing point of water when dissolved therein. By the term "substantial proportions of electrolytes," I means proportions of over 5% by weight of the solution.

The 2-mercapto-thiazolines, their acyl derivatives and their salts, which may be employed in accordance with my invention, are the water soluble compounds represented by the following structural formula:



wherein each of R, R_1, R_2 and R_3 represent hydrogen or an alkyl, aralkyl, aryl or alkaryl radical, and X represents hydrogen, an organic acyl radical or a basic salt forming element or group. Of the thiazoline compounds of my invention, it will generally be preferred to employ the 2-mercapto-thiazolines devoid of non-hydrocarbon substituents and particularly 2-mercapto-thiazoline itself. The next preferred class of compounds is the water soluble organic acyl derivatives of the 2-mercapto-thiazolines devoid of non-hydrocarbon substituents, particularly the organic acyl derivatives of 2-mercapto-thiazoline itself and specifically benzoyl thiazolinyl sulfide.

The amount of the thiazoline compound employed may be varied from a mere trace up to about 0.5% by weight of the heat exchange liquid. Larger amounts may be employed but without advantage. About 0.01% of the thiazoline compound will be sufficient for cooling liquids employed for most automobile radiators.

In order to illustrate the advantages of my invention, the data of some tests are given in Table I.

These experimental data were obtained by immersing freshly cleaned metal test strips in contact with 500 cc. of a 35% solution of a commercially denatured ethyl alcohol, contained in a 1 liter flask, maintained at 80° C. and saturated with air. The metal pieces were submitted to two separate 100 hour periods of exposure. At the end of each period, the test strips were cleaned in water by rubbing with a rubber stopper, dried and weighed. Hard, adherent scale or film, formed on the metal pieces, was not removed by abrasion or chemical means, since it is practically impossible to remove such a coating without taking some of the metal with it. It seems better to record positive gains in weight, rather than questionable losses obtained by a too rigorous method of cleaning. In general, an increase or a decrease in weight of the test strips indicates some form of corrosion. An increase, however, does not necessarily mean destructive corrosion since the metal may acquire a weighable film which serves to protect it from further attack. On the other hand, a significant loss in weight shows actual corrosion.

TABLE I

Corrosion of steel and solder in 35% aqueous ethyl alcohol

No.	Conc. $NaNO_2$	Inhibitor	Conc.	Corrosion: Gain (+) or loss (−) in mg./square inch			
				Steel		Solder	
				1st 100 hrs.	2nd 100 hrs.	1st 100 hrs.	2nd 100 hrs
	Wt. percent		*Wt. percent*				
1	0.0	None		−11.7	−14.1	−0.9	−0.6
2	0.088	do		+1.2	−.08	−13.6	−14.5
3	0.088	2-mercapto-thiazoline.	0.009	−3.5	−1.5	+3.9	+0.4
4	0.088	Benzoyl thiazolinyl sulfide.	0.009	−3.6	−2.1	−0.3	−0.6

It will be observed that the corrosion of steel, in uninhibited aqueous alcohol, is high while that of solder is slight (No. 1). The addition of 0.088% of sodium nitrite greatly reduces the corrosion of steel but increases that of solder (No. 2). The further addition of 0.009% of either 2-mercapto-thiazoline or benzoyl thiazolinyl sulfide, although decreasing slightly the protection of steel by sodium nitrite, greatly reduces the attack on solder by sodium nitrite (Nos. 3 and 4). The combination of sodium nitrite and 2-mercapto-thiazoline or benzoyl thiazolinyl sulfide is, therefore, much better than sodium nitrite alone.

It will be understood that the above tests and data are given for illustrative purposes only, and that my invention is not to be limited to the specific embodiments disclosed therein. Many variations and modifications which may be made without departing from the spirit or scope of my invention will be readily apparent to those skilled in the art. Accordingly, I intend to claim my invention broadly as in the appended claims.

Amongst the variations and modifications which may be made in accordance with my invention would comprise substituting one or more of the nitrites of the metals above aluminum in the electromotive series for the sodium nitrite or to employ two or more nitrites of the metals above aluminum in the electromotive series. Amounts up to about 1% by weight of the nitrites will generally be employed in practice. However, larger amounts may be employed if desired.

Also, other thiazoline compounds may be substituted for those employed in the tests. For example, one or more of R, R_1, R_2 and R_3, in the formula previously given, may represent hydrocarbon radicals such as methyl, ethyl, isopropyl, butyl, isobutyl, phenyl, tolyl, benzyl, phenylethyl and the like. Representative acyl derivatives are those in which X represents acetyl, propionyl, benzoyl, isopropylbenzoyl, methoxybenzoyl, chlorobenzoyl, nitrobenzoyl, phthaloyl and furoyl. Representative salts are those in which X represents sodium, potassium, trimethylammonium, diethanolammonium and tetraethylammonium.

Furthermore, my inhibitors will be found to be equally as effective in water alone and in aqueous solutions of other water soluble aliphatic alcohols, such as methanol, ethylene glycol and glycerol. Also, when my inhibitors are incorporated in the concentrated alcohol, they will inhibit corrosion of the metal containers in which such alcohols are ordinarily packaged for storage, shipment and marketing.

The 2-mercapto-thiazoline compounds of my invention have advantages over the 2-mercapto aryl thiazole compounds of Clarkson and Pedersen, in Patent 2,054,282, of being more soluble and more stable, that is, they are more resistant to oxidation on storage and under the conditions to which they are subject in automobile radiators. Also, my corrosion inhibitors may be employed in compositions such as those disclosed by Spiegler and Pedersen, in Patent 2,087,098, and Downing and Pedersen, in Patent 2,087,103. In fact, my corrosion inhibitors are particularly de-

signed to be substituted for the corrosion inhibitors employed in compositions of the type disclosed in Patent 2,087,103.

I claim:

1. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water having incorporated therein at least 0.03% of a nitrite of a metal above aluminum in the electromotive series and a small proportion of a water-soluble member of the group consisting of 2-mercapto-thiazolines devoid of non-hydrocarbon substituents, organic acyl derivatives of such 2-mercapto-thiazolines and salts of such 2-mercapto-thiazolines, in the absence of substantial proportions of electrolytes.

2. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water having incorporated therein at least 0.03% of a nitrite of a metal above aluminum in the electromotive series and a small proportion of a water-soluble 2-mercapto-thiazoline devoid of non-hydrocarbon substituents, in the absence of substantial proportions of electrolytes.

3. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water having incorporated therein at least 0.03% of a nitrite of a metal above aluminum in the electromotive series and a small proportion of 2-mercapto-thiazoline, in the absence of substantial proportions of electrolytes.

4. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water having incorporated therein at least 0.03% of a nitrite of a metal above aluminum in the electromotive series and a small proportion of a water-soluble organic acyl derivative of a 2-mercapto-thiazoline devoid of non-hydrocarbon substituents, in the absence of substantial proportions of electrolytes.

5. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water having incorporated therein at least 0.03% of a nitrite of a metal above aluminum in the electromotive series and a small proportion of a water-soluble aromatic acyl derivative of 2-mercapto-thiazoline, in the absence of substantial proportions of electrolytes.

6. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water having incorporated therein at least 0.03% of a nitrite of a metal above aluminum in the electromotive series and a small proportion of benzoyl thiazolinyl sulfide, in the absence of substantial proportions of electrolytes.

7. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water and a water-soluble aliphatic alcohol having incorporated therein at least 0.03% of an alkali metal nitrite and a small proportion of a water-soluble member of the group consisting of 2-mercapto-thiazolines devoid of non-hydrocarbon substituents, organic acyl derivatives of such 2-mercapto-thiazolines and salts of such 2-mercapto-thiazolines, in the absence of substantial proportions of electrolytes.

8. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water and a water-soluble aliphatic alcohol having incorporated therein at least 0.03% of an alkali metal nitrite and a small proportion of a water-soluble 2-mercapto-thiazoline devoid of non-hydrocarbon substituents, in the absence of substantial proportions of electrolytes.

9. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water and a water-soluble aliphatic alcohol having incorporated therein at least 0.03% of an alkali metal nitrite and a small proportion of 2-mercapto-thiazoline, in the absence of substantial proportions of electrolytes.

10. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water and a water-soluble aliphatic alcohol having incorporated therein at least 0.03% of an alkali metal nitrite and a small proportion of a water-soluble organic acyl derivative of a 2-mercapto-thiazoline devoid of non-hydrocarbon substituents, in the absence of substantial proportions of electrolytes.

11. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water and a water-soluble aliphatic alcohol having incorporated therein at least 0.03% of an alkali metal nitrite and a small proportion of a water-soluble aromatic acyl derivative of a 2-mercapto-thiazoline devoid of non-hydrocarbon substituents, in the absence of substantial proportions of electrolytes.

12. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water and a water-soluble aliphatic alcohol having incorporated therein at least 0.03% of an alkali metal nitrite and a small proportion of benzoyl thiazolinyl sulfide, in the absence of substantial proportions of electrolytes.

13. A water-soluble aliphatic alcohol having incorporated therein a small proportion of a nitrite of a metal above aluminum in the electromotive series sufficient to inhibit corrosion of ferrous metals by the alcohol and a small proportion of a water-soluble member of the group consisting of 2-mercapto-thiazoline devoid of non-hydrocarbon substituents, organic acyl derivatives of such 2-mercapto-thiazolines and salts of such 2-mercapto-thiazolines, in the absence of substantial proportions of electrolytes.

14. A water-soluble aliphatic alcohol having incorporated therein a small proportion of a nitrite of a metal above aluminum in the electromotive series sufficient to inhibit corrosion of ferrous metals by the alcohol and a small proportion of a water-soluble 2-mercapto-thiazoline devoid of non-hydrocarbon substituents, in the absence of substantial proportions of electrolytes.

15. A water-soluble aliphatic alcohol having incorporated therein a small proportion of a nitrite of a metal above aluminum in the electromotive series sufficient to inhibit corrosion of ferrous metals by the alcohol and a small proportion of 2-mercapto-thiazoline, in the absence of substantial proportions of electrolytes.

16. A water-soluble aliphatic alcohol having incorporated therein a small proportion of a nitrite of a metal above aluminum in the electromotive series sufficient to inhibit corrosion of ferrous metals by the alcohol and a small proportion of a water-soluble organic acyl derivative of a 2-mercapto-thiazoline devoid of non-hydrocarbon

substituents, in the absence of substantial proportions of electrolytes.

17. A water-soluble aliphatic alcohol having incorporated therein a small proportion of a nitrite of a metal above aluminum in the electromotive series sufficient to inhibit corrosion of ferrous metals by the alcohol and a small proportion of benzoyl thiazolinyl sulfide, in the absence of substantial proportions of electrolytes.

18. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water having incorporated therein at least 0.03% of sodium nitrite and a small proportion of 2-mercapto-thiazoline, in the absence of substantial proportions of electrolytes.

19. A non-corrosive liquid, suitable for use in heat exchange devices and the like containing iron and solder, which comprises water and a water-soluble aliphatic alcohol having incorporated therein at least 0.03% of sodium nitrite and a small proportion of 2-mercapto-thiazoline, in the absence of substantial proportions of electrolytes.

20. A water-soluble aliphatic alcohol having incorporated therein a small proportion of sodium nitrite sufficient to inhibit corrosion of ferrous metals by the alcohol and a small proportion of 2-mercapto-thiazoline, in the absence of substantial proportions of electrolytes.

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