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(54) Titre : INHIBITEURS DE CORROSION A BASE DE NEO-ACID
(54) Title: NEOACID CORROSION INHIBITORS

(57) **Abrégé/Abstract:**

This invention relates to organic acid corrosion inhibitors for use in antifreeze coolant compositions. The corrosion inhibitors comprise a C₈ mono-carboxylic acid component, or isomers and/or salts thereof, and a neo-decanoic acid, or isomers and/or salts thereof. The corrosion inhibitors of this invention provide improved corrosion protection to metal surfaces as compared to conventional inhibitors and provide surprisingly improved corrosion protection as compared to inhibitors containing only a single mono-carboxylic acid component.



(57) Abstract

This invention relates to organic acid corrosion inhibitors for use in antifreeze coolant compositions. The corrosion inhibitors comprise a C₈ mono-carboxylic acid component, or isomers and/or salts thereof, and a neo-decanoic acid, or isomers and/or salts thereof. The corrosion inhibitors of this invention provide improved corrosion protection to metal surfaces as compared to conventional inhibitors and provide surprisingly improved corrosion protection as compared to inhibitors containing only a single mono-carboxylic acid component.

NEOACID CORROSION INHIBITORS

Field of the Invention

The present invention relates generally to organic acid corrosion inhibitors for antifreeze coolant formulations. More particularly, the present invention relates to C₈ mono-carboxylic acids, or isomers and/or salts thereof, and neo-decanoic acids, or isomers and/or salts thereof, for use in antifreeze coolant concentrates and compositions as corrosion inhibitors to provide prolonged corrosion protection to the metal surfaces in cooling and/or heating systems, such as those found in internal combustion engines.

Background of the Invention

Corrosion has long been a problem when certain metals or alloys are used in applications in which they come into contact with an aqueous medium. For example, in heat-transfer systems, such as those found in internal combustion engines, alcohol-based heat transfer fluids (i.e., antifreezes) can be very corrosive to the metal surfaces of the heat-transfer systems. Compounding this problem is that the corrosion is accelerated under normal engine operating conditions (i.e., high temperatures and pressures). Aluminum surfaces, are particularly susceptible to corrosion. See, Darden et al., "Monobasic/Diacid Combination as Corrosion Inhibitors in Antifreeze Formulations," Worldwide Trends in Engine Coolants, Cooling System Materials and Testing, SAE Int'l SP-811, Paper #900804, pp. 135-51 (1990) ("SAE SP-811").

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Corrosion inhibitors have been used to address these problems. For example, triazoles, thiazoles, borates, silicates, phosphates, benzoates, nitrates, nitrites and molybdates have been used in antifreeze formulations. See, e.g., United States patent No. 4,873,011; see also, SAE SP-811 at pp. 135-138, 145-146. However, such corrosion inhibitors have several problems, including toxicity (e.g., borates, nitrites, and molybdates), expense, and inadequate long-term protection. See United States patent No. 4,946,616, col. 1, lines 31-45; United States patent No. 4,588,513, col. 1, lines 55-64; SAE SP-811, pp. 137-138. Also, most of these inhibitors are metal-specific and as such, require multi-component formulations making them more difficult and more expensive to prepare commercially. See Canadian Patent No. 1,142,744, pp. 2-3.

Organic acids, such as mono- and/or di-carboxylic acids, have also been used as corrosion inhibitors. See, e.g., United States patent Nos. 4,382,008 (combination of C₇-C₁₃ di-carboxylic acid and conventional corrosion inhibitors); 4,448,702 (di-carboxylic acids having 3 or more carbons); 4,647,392 (combination of monobasic and dibasic acids); and 4,946,616 (combination of C₁₀ and C₁₂ diacids).

However, such organic acid formulations also suffer from a number of problems. For example, sebacic acid, which is used in several commercial antifreezes (e.g., Texaco's "Havoline"* Extended Life AntiFreeze/Coolant; General Motors' * Trade-mark

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"Dex-Cool"* Anti-Freeze/Coolant; Canadian Tire's "Motomaster"* Long Life and is currently used in the standard formulation set forth by the British Military (see Specification TS 10177, "Antifreeze, Inhibited Ethanediol, AL-39"), is more difficult to use commercially since it is commercially available as a solid, and as such requires heat to dissolve it in a heat transfer fluid. Also, sebacic acid is generally more expensive and difficult to obtain commercially since currently there is only one domestic industrial supplier (Union Camp Corporation). See SAE SP-811, pp. 141-142. Also, sebacic acid and higher di-carboxylic acids, tend to have poor solubility in antifreeze formulations using hard water. See United States patent No. 4,578,205, col. 1, lines 52-64.

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* Trade-mark

European patent publication No. 479,470 relates to corrosion inhibitors having at least one acid of the formula:



wherein the groups R_1 , R_2 and R_3 are the same or different C_1 - C_{10} alkyls or where one of R_1 , R_2 and R_3 is H, and the other two R groups are C_1 - C_{10} alkyls. However, this publication does not disclose any specific combination of mono-carboxylic acids nor does it teach or suggest which combinations would be useful. In fact, the only multi-acid combinations disclosed include sebacic acid, which as previously discussed has several disadvantages.

Corrosion inhibitors containing neo-decanoic acid (a mono-carboxylic organic acid) have also been suggested. United States patent No. 4,390,439 ("Schwartz et al.") relates to the use of neo-decanoic acid as a corrosion inhibitor in hydraulic fluids. However, Schwartz et al. does not teach or suggest other organic acids (except benzoic acid) used alone or in combination with neo-decanoic acid as a corrosion inhibitor.

SAE SP-811 also describes neo-decanoic acid as a possible corrosion inhibitor. However, SAE SP-811 relates to the use of combinations of mono-carboxylic acids and di-carboxylic acids, including sebacic acid, as corrosion inhibitors. Also, although SAE SP-811 suggests that neo-decanoic acid is effective as a corrosion inhibitor, SAE SP-811 teaches away from the use of neo-decanoic acid since it states that "[t]he use of neodecanoic acid is limited by solubility considerations ..." (p. 147).

Thus, it would be desirable to provide an effective corrosion inhibitor that is easy to prepare and uses readily available raw materials.

Summary of the Invention

It is an objective of this invention to provide improved organic acid corrosion inhibitors comprising a C_n mono-carboxylic acid component, or isomers

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and/or salts thereof, and a neo-decanoic acid, or isomers and/or salts thereof. The addition of relatively small amounts of neo-decanoic acid to a C₈ mono-carboxylic acid component results in surprisingly improved corrosion inhibiting properties as compared to conventional corrosion inhibitors, other organic acid corrosion inhibitors, and corrosion inhibitors comprising only the C₈ mono-carboxylic acid component or neo-decanoic acid alone. The C₈ mono-carboxylic acid component is preferably 2-ethylhexanoic acid or neo-octanoic acid, and more preferably 2-ethylhexanoic acid.

Optionally, these corrosion inhibitors may also comprise other organic acid corrosion inhibitors such as di-carboxylic acids, and conventional corrosion inhibitors such as triazoles, as well as other additives such as anti-foaming agents, dyes, pH buffers, scale inhibitors, sequestration and dispersion agents.

Another objective of this invention is to provide antifreeze coolant formulations comprising these corrosion inhibitors and methods of using the formulations for corrosion protection of metal surfaces in heating and/or cooling systems, primarily of internal combustion engines.

Brief Description of the Drawings

Figure 1A shows an example of a Type I pitting potential time-graph resulting from the formulation of Example 4.

Figure 1B shows an example of a Type I+ pitting

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potential time-graph resulting from the formulation of Example 3.

Figure 1C shows an example of a Type II pitting potential time-graph resulting from the formulation of Example 2.

Detailed Description of the Invention

In order that this invention may be more fully understood, the following detailed description is set forth.

According to one aspect of the present invention there is provided an antifreeze coolant concentrate comprising a water-soluble liquid alcohol freezing point depressant and a corrosion inhibitor composition for antifreeze formulations comprising a mixture of C₈ mono-carboxylic acids, or isomers and/or salts thereof, and a neo-decanoic acid, or isomers and/or salts thereof, wherein the corrosion inhibitor is present in an amount such that the total mono-carboxylic acid in the concentrate is from about 0.001% to about 5.0% (by weight) and is in excess of the total neo-decanoic acid in the concentrate (by weight).

According to a further aspect of the present invention there is provided an antifreeze coolant concentrate comprising a water-soluble liquid alcohol freezing point depressant and a corrosion inhibitor composition comprising a C₈ mono-carboxylic acid, or isomer and/or salt thereof, and a neo-decanoic acid, or isomer and/or salt thereof, wherein the corrosion inhibitor is present in an amount such that the total mono-carboxylic acid in the concentrate is from about 0.001% to about 5.0% (by weight) and is in excess of the total neo-decanoic acid in the concentrate (by weight).

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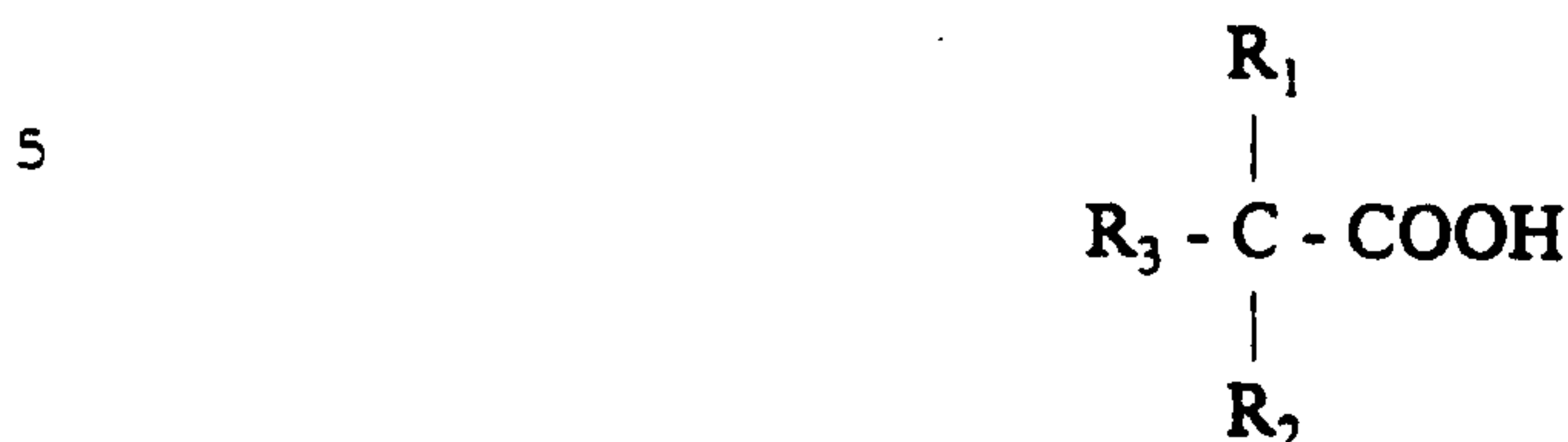
According to another aspect of the present invention there is provided an antifreeze coolant concentrate comprising: a) from about 90% to about 98% (by weight) of a liquid-alcohol freezing point depressant; b) from about 2.0% to about 5.0% (by weight) of a mixture of 2-ethylhexanoic acid, or isomer and/or salt thereof, and neo-decanoic acid, or isomer and/or salt thereof; c) from 0 to about 0.5% (by weight) of tolyltriazole; and d) an alkali metal hydroxide in an amount sufficient to adjust the pH of the concentrate to
10 between about 6.9 and about 9.6.

According to a still further aspect of the present invention there is provided a method for inhibiting corrosion of the metal components in internal combustion engines comprising the step of contacting the metals to be protected with the antifreeze coolant composition as defined above.

The corrosion inhibitors of this invention comprise a C₈ mono-carboxylic acid component (i.e., a single C₈ mono-carboxylic acid or mixtures of C₈ mono-carboxylic acids), or isomers and/or salts thereof, and a neo-decanoic acid

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component, or isomers and/or salts thereof. Neo-decanoic acid is a neoacid which is a type of mono-carboxylic acid. The term "neoacid" refers to trialkylacetic acids having the following general structure:



wherein the groups R_1 , R_2 and R_3 are alkyl groups. Neoacids such as neo-octanoic and neo-decanoic acids are readily available, for example, from Exxon Chemical Company.

The addition of a relatively small amount of neo-decanoic acid to a C_8 mono-carboxylic acid component results in surprisingly improved corrosion inhibiting properties as compared to corrosion inhibitors having conventional and/or organic acid components, as well as corrosion inhibitors comprising only the C_8 mono-carboxylic acid component or neo-decanoic acid alone.

Preferably, the corrosion inhibitors of this invention comprise either 2-ethylhexanoic acid ("2-EHA") or neo-octanoic acid, or isomers and/or salts thereof, and neo-decanoic acid, or isomers and/or salts thereof. As with neo-decanoic acid, 2-EHA and neo-octanoic acid are less expensive than sebacic acid and more readily available (2-EHA may be obtained from, for example, ALLCHEM Industries, Inc., ASHLAND Chemical Co., BASF Corp., Brook-Chem Inc., EASTMAN Chemical Group and Union Carbide Corp.; neo-octanoic acid is available from, for example, Exxon Chemical Company). Also, these mono-carboxylic acids are available as liquids rather than solids (as is sebacic acid) and as such, they are more easily used to prepare corrosion inhibitors on a commercial scale.

The acid components of the corrosion inhibitors of this invention may alternatively be in the form of an alkali metal salt, ammonium salt or amine salt. Preferred salts are the alkali metal salts, and most preferred are sodium or potassium salts of the mono-carboxylic acids.

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The corrosion inhibitors of this invention may also include one or more additional corrosion inhibitors, such as triazoles, thiazoles, di-carboxylic acids, phosphates, borates, silicates, benzoates, nitrates, nitrites, molybdates, or alkali metal salts thereof. The preferred corrosion inhibitors of this invention further comprise a triazole or thiazole, more preferably, an aromatic triazole or thiazole such as benzotriazole, mercaptobenzothiazole or tolyltriazole ("TTZ") and most preferably, TTZ.

10 Other additives may also be used depending on the application. Suitable additives include anti-foaming agents (e.g., "PM-5150" from Union Carbide Corp., "Pluronic L-61*" from BASF Corp., and "Patco* 492" or "Patco 415" from American Ingredients Company), dyes (e.g., "Alizarine Green*", "Uranine Yellow*" or "Green AGS-liquid*" from Abbey Color Inc., "Orange II*(Acid Orange 7)" or "Intracid Rhodamine* WT (Acid Red 388)" from Crompton & Knowles Corp.), pH buffers, scale inhibitors, and/or sequestration and dispersion agents (e.g., "Dequest"* from Monsanto Chemical Company, "Bayhibit"* from Miles Inc.,
20 "Nalco" or "NalPREP"* from Nalco Chemical Company).

It is contemplated that the corrosion inhibitors of this invention may be used in numerous applications where metal surfaces (e.g., aluminum, copper, iron, steel, brass, solder or other alloys) are in contact with an aqueous medium. For example, they may be used in conjunction with hydraulic fluids, aqueous cutting oils, paints, soluble oils, metal
* Trade-mark

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cutting fluids, aircraft deicers, and greases.

The corrosion inhibitors of this invention are particularly well-suited for use in antifreeze coolant formulations, such as antifreeze coolant concentrates and compositions, for internal combustion engines.

In antifreeze coolant concentrates, a minor amount of the corrosion inhibitor is added to a major amount of a water-soluble liquid alcohol freezing point depressant. The corrosion inhibitor may be added in an amount from about 0.001% to about 5.0% (total mono-carboxylic acid by weight in the concentrate), and preferably, from about 2.0% to about 5.0%. The corrosion inhibitor comprises a C₈ mono-carboxylic acid component, or isomers and/or salts thereof, and a relatively small amount of neo-decanoic acid, or isomers and/or salts thereof. The amount of

neo-decanoic acid used is that which is sufficient to result in a corrosion inhibitor exhibiting a synergistic effect as compared to the corrosion inhibiting effectiveness of the individual acid components. Preferably, the corrosion inhibitor comprises the C₈ mono-carboxylic acid component and neo-decanoic acid in the ratio from about 100:1 to about 1:1, and more preferably, about 3:1. In one preferred embodiment, the corrosion inhibitor comprises an amount sufficient of the C₈ mono-carboxylic acid component such that in the antifreeze coolant concentrate, this component is present from about 2.4% to about 3.3% (by weight), and more preferably about 3.1%. The neo-decanoic acid is present in an amount sufficient such that its concentration in the antifreeze coolant concentrate is from about 0.8% to about 1.1% (by weight), and more preferably about 1.0%.

The antifreeze coolant concentrate may also include one or more additional corrosion inhibitors, such as triazoles, thiazoles, di-carboxylic acids, phosphates, borates, silicates, benzoates, nitrates, nitrites, molybdates or alkali metal salts thereof. Such additional corrosion inhibitors may be added at concentrations of up to about 5.5% (by weight). Preferably, the antifreeze coolant concentrate comprises up to about 0.8% (by weight) of a triazole or thiazole, and more preferably, up to about 0.5%.

The major portion of the antifreeze coolant concentrate (i.e., 75%-99.999% (by weight), preferably 90%-99.999% (by weight)) comprises a liquid alcohol freezing point depressant. Suitable liquid alcohol freezing point depressants include any alcohol or heat transfer medium capable of use as a heat transfer fluid and preferably is at least one alcohol, selected from the group consisting of methanol, ethanol, propanol, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, glycerol, the monethylether of glycerol, the dimethylether of glycerol, alkoxy alkanols (such as methoxyethanol) and mixtures thereof. The preferred alcohol is selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol and mixtures thereof.

The antifreeze coolant concentrate may also comprise a sufficient amount of an alkali metal hydroxide to adjust the pH to between about 6.0 to about

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10.0, preferably to about 6.9 to about 9.6. Formulations having a pH less than about 6.0 or more than about 10.0 tend to be corrosive to metal surfaces. Other additives, as described above, may also be used depending on the application.

The antifreeze formulations most commonly used are antifreeze
5 coolant compositions. In these formulations, an antifreeze concentrate is usually diluted with water such that between 10% to about 90% (by weight) water is present in the composition, and preferably from about 25% to about 75% (by weight) water, with the balance being the antifreeze coolant concentrate.

It will be appreciated by one of skill in the art that the amount of
10 corrosion inhibitor (and its composition) used in a specific antifreeze coolant formulation may vary when minor adjustments are made to the other components of the formulations.

The present invention also provides methods for inhibiting corrosion of the metal components in internal combustion engines. Such methods comprise
15 the step of contacting the metals to be protected with the inventive corrosion inhibitors described above.

In order that this invention may be better understood, the following examples are set forth.

Examples

20 Twenty-six different antifreeze coolant concentrates were prepared (Examples 1-26). The components of these formulations are described in Tables 1-4 below. Each formulation contained ethylene glycol as the water-soluble liquid alcohol freezing point depressant, sodium hydroxide ("NaOH") to adjust the pH to about 9.0, sodium tolyltriazole ("NaTTZ"), and deionized water, in the specified
25 amounts.

Examples 1-4, as shown in Table 1 below, correspond to known antifreeze coolant concentrates and serve as control formulations. These Examples include a formulation comprising conventional corrosion inhibitors (Example 1), a formulation comprising an organic acid (mono-carboxylic acid based) corrosion
30 inhibitor (Example 2, contains primarily only organic acid corrosion inhibitors and a

small amount of NaTTZ), and formulations comprising conventional corrosion inhibitors as well as organic acid components (di-carboxylic acid based) (Examples 3 and 4).

Table 1
Control Formulations

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	Component (wt%)	Example No.			
		1	2	3	4
	Ethylene Glycol	93.76	94.3	95.7	95.6
	NaTTZ, 50% sol.	0.22	0.5	0.2	0.4
10	NaNO ₃ , 40% sol.	0.26	0	0.5	0.5
	Na ₂ MoO ₄ , 35% sol.	0.51	0	0.2	0
	Borax, 20% sol. in Ethylene Glycol	2.1	0	0	0
	Phosphoric Acid, 75% sol.	0.18	0	0	0
	Na-Mercaptobenzothiazole	0.55	0	0	0
15	Na-Silicate, Grade 40 sol.	0.33	0	0	0
	NaOH, 50% sol.	0.68	1.7	1.3	1.4
	Deionized Water	1.34*	0.1	0.1	0.1
	2-Ethylhexanoic Acid	0	3.2	0	0
	Sebacic Acid (solid)	0	0.2	0	2.0
20	Dodecanedioic Acid	0	0	2.0	0
	Neo-Heptanoic Acid	0	0	0	0
	Neo-Octanoic Acid	0	0	0	0
	Neo-Decanoic Acid	0	0	0	0
25	Galvanostatic Pitting Potential: Ep,mV (Type)	-270 (I)	1000 (II)	470 (I+)	150 (I)
	ASTM D-4340 (corrosion rate, mg/cm ² /week)	0.3	0.8	0.8	0.7

* Also includes antifoam, dye, and silicone

Examples 5-8 as shown in Table 2 below, are mono-carboxylic acid antifreeze concentrates each having only a single acid component: 2-EHA (Example 5), neo-heptanoic acid (Example 6), neo-octanoic acid (Example 7) and neo-decanoic acid (Example 8).

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Table 2
Formulations of One of 2-EHA, Neo-Heptanoic Acid
Neo-Octanoic Acid or Neo-Decanoic Acid

		Example No.			
Component (wt%)		5	6	7	8
10	Ethylene Glycol	94.7	94.7	94.6	94.7
	NaTTZ, 50% sol.	0.5	0.5	0.5	0.5
	NaNO ₃ , 40% sol.	0	0	0	0
	Na ₂ MoO ₄ , 35% sol.	0	0	0	0
	NaOH, 50% sol.	1.5	1.5	1.6	1.5
15	Deionized Water	0.1	0.1	0.1	0.1
	2-Ethylhexanoic Acid	3.2	0	0	0
	Sebacic Acid (solid)	0	0	0	0
	Dodecanedioic Acid	0	0	0	0
	Neo-Heptanoic Acid	0	3.2	0	0
20	Neo-Octanoic Acid	0	0	3.2	0
	Neo-Decanoic Acid	0	0	0	3.2
	Galvanostatic Pitting Potential: Ep,mV (Type)	1640 (II)	1445 (II)	2030 (II)	-112 (I)
25	ASTM D-4340 (corrosion rate, mg/cm ² /week)	0.8	0.6	0.6	0.7

Examples 9-14, as shown in Table 3 below, contain corrosion inhibitors comprising mixtures of 2-EHA and neo-decanoic acid (Examples 9-11) and neo-octanoic and neo-decanoic acids (Examples 12-14).

Table 3

Formulations of a Mixture of C₈ Mono-Carboxylic Acid and Neo-Decanoic Acid

Component (wt%)	Example No.													
	9	10	11	12	13	14								
Ethylene Glycol	94.8	94.8	94.8	94.7	94.7	94.7								
NaTTZ, 50% sol.	0.5	0.5	0.5	0.5	0.5	0.5								
NaNO ₃ , 40% sol.	0	0	0	0	0	0								
Na ₂ MoO ₄ , 35% sol.	0	0	0	0	0	0								
NaOH, 50% sol.	1.4	1.4	1.4	1.5	1.5	1.5								
Deionized Water	0.1	0.1	0.1	0.1	0.1	0.1								
2-Ethylhexanoic Acid	2.4	1.6	0.8	0	0	0								
Sebacic Acid (solid)	0	0	0	0	0	0								
Dodecanedioic Acid	0	0	0	0	0	0								
Neo-Heptanoic Acid	0	0	0	0	0	0								
Neo-Octanoic Acid	0	0	0	2.4	1.6	0.8								
Neo-Decanoic Acid	0.8	1.6	2.4	0.8	1.6	2.4								
Galvanostatic Pitting Potential: Ep,mV (Type)	2340 (II)	1715 (II)	110 (I+)	2620 (II)	1390 (II)	-61 (I+)								
ASTM D-4340 (corrosion rate, mg/cm ² /week)	0.4	1.1	1.2	0.8	0.5	0.7								

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The remaining antifreeze coolant concentrates, Examples 15-26, as shown in Table 4 below, contain comparative corrosion inhibitors. These formulations either contain mixtures of 2-EHA and neo-octanoic acid (Examples 15-17), or mixtures of neo-heptanoic acid with 2-EHA (Examples 18-20), neo-
5 octanoic acid (Examples 21-23) or neo-decanoic acid (Examples 24-26).

Table 4
Comparative Formulations

Example No.													
Component (wt%)	15	16	17	18	19	20	21	22	23	24	25	26	
Ethylene Glycol	94.6	94.6	94.6	94.7	94.7	94.7	94.6	94.6	94.6	94.6	94.6	94.6	94.6
NaTTZ, 50% sol.	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
NaNO ₃ , 40% sol.	0	0	0	0	0	0	0	0	0	0	0	0	0
Na ₂ MoO ₄ , 35% sol.	0	0	0	0	0	0	0	0	0	0	0	0	0
NaOH, 50% sol.	1.6	1.6	1.6	1.5	1.5	1.5	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Deionized Water	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
2-Ethylhexanoic Acid	2.4	1.6	0.8	2.4	1.6	0.8	0	0	0	0	0	0	0
Sebacic Acid (solid)	0	0	0	0	0	0	0	0	0	0	0	0	0
Dodecanedioic Acid	0	0	0	0	0	0	0	0	0	0	0	0	0
Neo-Heptanoic Acid	0	0	0	0.8	1.6	2.4	0.8	1.6	2.4	2.4	1.6	0.8	0.8
Neo-Octanoic Acid	0.8	1.6	2.4	0	0	0	2.4	1.6	0.8	0	0	0	0
Neo-Decanoic Acid	0	0	0	0	0	0	0	0	0	0.8	1.6	2.4	2.4
Galvanostatic Pitting Potential: Ep,mV (Type)	1765 (II)	1275 (II)	1315 (II)	875 (II)	552 (II)	880 (II)	1775 (II)	1188 (II)	1000 (II)	950 (II)	1305 (II)	648 (I+)	648
ASTM D-4340 (corrosion rate, mg/cm ² /week)	0.8	0.8	0.8	0.9	1.2	1.8	0.5	0.6	0.8	0.6	1.1	1.1	1.1

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Each of the formulations tested was prepared in a mixing vessel at room temperature (approximately 20°C) and at a pressure of 91-111 KPa. In each case, ethylene glycol was added first to the mixing vessel and while being agitated, the remaining components were added in the following order: acid components, 5 NaOH, NaTTZ, water, and other corrosion inhibitors, if any. All of the components were obtained commercially as follows: ethylene glycol from Union Carbide; NaTTZ, 50% solution, from PMC Specialties Group; NaNO₃, 40% solution, from Chilean Nitrate Sales Corp; Na₂MoO₄, 35% solution, from North Metal & Chemical Company; NaOH, 50% solution, from Occidental Petroleum; 10 2-EHA from ASHLAND Chemical Co.; Sebacic acid from Union Camp Corporation; dodecanedioic acid from DuPont; and the neo-acids were from Exxon Chemical Company.

After preparation, each of the formulations of the examples was subjected to the Ford Motor Company Laboratory Test Method BL 5-1, "A Rapid 15 Method to Predict the Effectiveness of Inhibited Coolants in Aluminum Heat Exchangers" (Galvanostatic Pitting Potential Test) and ASTM D-4340 "Standard Test Method for Corrosion of Cast Aluminum Alloys in Engine Coolants Under Heat-Rejecting Conditions" (Aluminum Hot Surface Test). These tests, described below, are well known analyses used to evaluate the effectiveness of corrosion 20 inhibitors in engine coolants.

Galvanostatic Pitting Potential

The Galvanostatic Pitting Potential Test is a standard electrochemical technique used to evaluate the effectiveness of corrosion inhibitors in the prevention of pitting corrosion. This test is used to predict the effectiveness 25 of engine coolants in preventing pitting and crevice formation on aluminum heat exchanger alloys. The test measures the pitting potential (Ep) of aluminum alloys in an engine coolant. See Ford Motor Company, BL 5-1, supra. The test procedure is well known. See, Wiggle et al., "The Effectiveness of Engine Coolant Inhibitors for Aluminum," Corrosion 80, National Association of Corrosion Engineering 30 Conference, Paper #69 and Wiggle et al., "A Rapid Method to Predict the Effectiveness of Inhibited Engine Coolants in Aluminum Heat Exchangers," SAE

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Paper #800800, Society of Automotive Engineers, Passenger Car Meeting, June 1980, Dearborn, Michigan.

This test provides a measure of how well the corrosion inhibitor prevents the breakdown of the protective oxide film and subsequent pit formation on the sample metal, and provides a measure of how well the inhibitor repassivates the surface once initial pit formation has begun. In general, the results from this test can be categorized in one of three types.

10 In the first (Type I) (as depicted in Figure 1A), upon polarization of the metal surface, the potential increases rapidly to some maximum level within the first few seconds. The passive film then ruptures followed by a rapid decrease in the potential. The pitting potential levels off once an equilibrium is reached between the potential, pit growth and pit repassivation. Figure 1A depicts the results of this test on the formulation of Example 4.

20 In the second (Types I+) (depicted in Figure 1B), the passive film rupture occurs almost immediately upon polarization. The potential initially decreases, but then begins to rise with time. This rise is indicative of the formation of a current inhibiting film on the metal surface. Figure 1B depicts the results of this test on the formulation of Example 3.

 In the third type (Type II) (depicted in Figure 1C), the potential does not decrease after rupture. Instead, the potential increases rapidly to a noble potential which

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remained constant or increased slightly throughout the test. Figure 1C depicts the results of this test on the formulation of Example 2.

Most commercial antifreeze formulations have a pitting potential ranging from -200 to +200 mV. Generally, the higher (more positive) the E_p value is at a fixed current density, the more effective the antifreeze formulation is in preventing pitting corrosion. See Ford Motor Company, BL 5-1, supra; Wiggle et al., Paper #69, supra, and SAE Paper #800800, supra; and SAE SP-811, supra, at p. 138, right col., line 44.

The results of the Galvanostatic Pitting Potential Corrosion Test for the formulations of Examples 1-26 are set forth in Tables 1-4, above. For each of the formulations, the pitting potential was determined using a current density of $100\mu\text{A}/\text{cm}^2$.

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As shown in Tables 1-4 above, corrosion inhibitors comprising a C₈ mono-carboxylic acid and neo-decanoic acid (Examples 9-14, Table 3) exhibit E_p values that are either above or within the acceptable range of -200 to +200 mV. Indeed, corrosion inhibitors comprising a C₈ mono-carboxylic acid and a relatively small amount of neo-decanoic acid (Examples 9 and 12, Table 3) exhibited the highest E_p values of all the formulations tested including those of the control group (Examples 1-4, Table 1).

Also, the corrosion inhibitors comprising a C₈ mono-carboxylic acid and a relatively small amount of neo-decanoic acid (Examples 9 and 12, Table 3) exhibited surprisingly higher E_p values than those expected from the E_p values exhibited by formulations containing only a single mono-carboxylic acid component. For example, a small amount of neo-decanoic acid added to 2-EHA (Example 9, Table 3) resulted in a synergistic E_p of 2340 mV as compared to the E_p values of the formulations that contained only 2-EHA (1640 mV, Example 5, Table 2) or neo-decanoic acid (-112 mV, Example 8, Table 2). Similarly, a small amount of neo-decanoic acid added to neo-octanoic acid (Example 12, Table 3) resulted in a synergistic E_p of 2620 mV as compared to the E_p values of the formulations that contained only neo-octanoic acid (2030 mV, Example 7, Table 2) or neo-decanoic acid (-112 mV, Example 8, Table 2).

The higher synergistic E_p values were not observed when using corrosion inhibitors comprising two C₈ mono-carboxylic acids without neo-decanoic acid (Examples 15-17, Table 4), or using corrosion inhibitors comprising neo-heptanoic acid and a C₈ mono-carboxylic acid (Examples 18-23, Table 4). Similarly, adding a small amount of neo-decanoic acid to neo-heptanoic acid (Examples 24-26, Table 4) did not result in a synergistic effect when compared to the formulations that contained only neo-heptanoic acid (Example 6, Table 2) or neo-decanoic acid (Example 8, Table 2).

ASTM D-4340 Aluminum Hot Surface Test

The Aluminum Hot Surface Test is another standard technique used to evaluate the effectiveness of corrosion inhibitors. This test measures the corrosion rate of a metal sample resulting from the corrosive properties of

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antifreeze formulations. According to ASTM D-3306, the maximum allowed corrosion rate resulting from a tested sample is 1.0 mg/cm²/week. The results for this test are also set forth in Tables 1-4 above. As shown in the Tables above, the antifreeze concentrates comprising a C₈ mono-carboxylic acid and a small amount
5 of neo-decanoic acid (Examples 9 and 12, Table 3) resulted in a corrosion rate of 0.8 and 0.4 mg/cm²/week, respectively, less than the ASTM D-3306 standard of 1.0 mg/cm²/week. This illustrates that the corrosion inhibitors of this invention not only protect aluminum from pitting corrosion, but also from cavitation erosion that occurs in aluminum cylinder heads.

10 One skilled in the art will appreciate that the present invention can be practiced by other than the above-described embodiments, which are presented herein for the purpose of illustration and not of limitation, and that the present invention is limited only by the claims that follow.

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CLAIMS:

1. An antifreeze coolant concentrate comprising a water-soluble liquid alcohol freezing point depressant and a corrosion inhibitor composition comprising: (1) a C₈ mono-
5 carboxylic acid, or isomer, or salt, or mixture thereof, and (2) a neo-decanoic acid, or isomer, or salt, or mixture thereof, wherein the corrosion inhibitor is present in an amount such that the total mono-carboxylic acid in the concentrate is from about 0.001% to about 5.0% (by weight) and
10 is in excess of the total neo-decanoic acid in the concentrate (by weight).
2. The antifreeze coolant concentrate of claim 1, wherein the C₈ mono-carboxylic acid in the corrosion inhibitor composition is selected from the group consisting of
15 2-ethylhexanoic acid and neo-octanoic acid.
3. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the mono-carboxylic acid components in the corrosion inhibitor composition are in the form of sodium or potassium salts.
- 20 4. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the corrosion inhibitor composition further comprises at least one additional corrosion inhibitor selected from the group consisting of triazoles, thiazoles, dicarboxylic acids, phosphates, borates, silicates, benzoates,
25 nitrates, nitrites, molybdates, and alkali metal salts thereof.
5. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the corrosion inhibitor composition further comprises an aromatic triazole or thiazole.

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6. The antifreeze coolant concentrate according to claim 5, wherein the corrosion inhibitor composition further comprises benzotriazole, mercaptobenzothiazole or tolyltriazole.

5 7. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the corrosion inhibitor is present in an amount such that the total mono-carboxylic acid concentration in the concentrate is from about 2.0% to about 5.0% (by weight).

10 8. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the corrosion inhibitor comprises the C₈ mono-carboxylic acid component, or isomer and/or salt thereof, and neo-decanoic acid, or isomer and/or salt thereof, in the weight ratio of from about 100:1 to about 1:1.

15 9. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the corrosion inhibitor comprises the C₈ mono-carboxylic acid component, or isomer and/or salt thereof, and neo-decanoic acid, or isomer and/or salt thereof, in the weight ratio of about 3:1.

20 10. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the corrosion inhibitor comprises from about 2.4% to about 3.3% (by weight) of the C₈ mono-carboxylic acid component, or isomer and/or salt thereof, and from about 0.8% (by weight) to about 1.1% (by weight) of neo-decanoic
25 acid, or isomer and/or salt thereof.

11. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the corrosion inhibitor comprises about 3.1% (by weight) of the C₈ mono-carboxylic acid component, or isomer and/or salt thereof, and about 1.0% (by weight) of neo-
30 decanoic acid, or isomer and/or salt thereof.

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12. The antifreeze coolant concentrate according to claim 1 or claim 2, wherein the water-soluble liquid alcohol freezing point depressant is selected from the group consisting of methanol, ethanol, propanol, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, glycerol, the monoethylether of glycerol, the dimethylether of glycerol, alkoxy alkanols, and mixtures thereof.

13. The antifreeze coolant concentrate according to claim 1 or claim 2, further comprising an alkali metal hydroxide in an amount sufficient to adjust the pH of the formulation to between about 6 to about 10.

14. An antifreeze coolant composition comprising the antifreeze coolant concentrate according to claim 1 or claim 2, and further comprising water in an amount sufficient such that the amount of water in the formulation is from about 10% to about 90% (by weight).

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