

TITLE OF THE INVENTION

STABILIZED CHLOROFLUOROETHYLENES

FIELD

[0001] The present application provides compositions comprising one or more chlorofluoroethylenes and one or more stabilizer components, which are useful, for example, for use in refrigeration, air conditioning, chiller, or heat pump systems and for reducing oxidation byproducts of the chlorofluoroethylenes.

BACKGROUND

[0002] Chlorofluoroethylenes are stable molecules under normal refrigeration usage conditions. However, in the presence of trace air, chlorofluoroethylenes can be oxidized. The oxidation product will produce HCl and HF upon contact with moisture, which can have a negative impact on systems using the chlorofluoroethylene.

[0003] The industry is in need of stable refrigerants that meet the evolving regulatory landscape. The regulatory landscape for refrigerants is continuously evolving, taking into consideration properties beyond just ozone depletion potential (ODP) and global warming potential (GWP), which have been the focus of late. More particularly, there is a need for refrigerant compositions that not only meet low ODP standards and have low global warming potentials, but that also provide superior performance in a variety of applications, and which meet the standards of evolving regulations.

[0004] The present invention solves certain problems associated with conventional refrigerants and provides refrigerants containing stabilized chlorofluoroethylenes, which meet the evolving regulatory landscape.

SUMMARY

[0005] The present application provides, *inter alia*, compositions comprising one or more chlorofluoroethylenes and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.

[0006] The present application further provides processes for producing cooling, comprising condensing a composition provided herein and thereafter evaporating said composition in the vicinity of a body to be cooled.

[0007] The present application further provides processes for producing heating, comprising evaporating a composition provided herein and thereafter condensing said composition in the vicinity of a body to be heated.

[0008] The present application further provides air conditioning systems, heat pump systems, chiller systems, and refrigeration systems comprising a composition provided herein.

[0009] The present application further provides methods of replacing an incumbent refrigerant in a refrigeration, air conditioning, or heat pump system, with a replacement composition provided herein (e.g., a replacement composition comprising one or more chlorofluoroethylenes as provided herein) comprising providing a composition provided herein as replacement for said incumbent refrigerant.

[0010] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Methods and materials are described herein for use in the present invention; other, suitable methods and materials known in the art can also be used. The materials, methods, and examples are illustrative only and not intended to be limiting. All publications, patent applications, patents, sequences, database entries, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control.

DETAILED DESCRIPTION

[0011] There is a need to provide alternative compositions to reduce decomposition byproducts resulting, e.g., from the oxidation of chlorofluoroethylenes (e.g., one or more chlorofluoroethylenes as provided herein). Accordingly, the present disclosure provides compositions (e.g., heat transfer composition and/or refrigerant compositions) comprising one or more chlorofluoroethylenes and one or more stabilizer components. The compositions provided herein may reduce

undesirable degradation byproducts, such as chloride (*e.g.*, hydrogen chloride), fluoride (*e.g.*, hydrogen fluoride), and/or phosgene, resulting decomposition (*e.g.*, oxidation) of the one or more chlorofluoroethylenes provided herein.

[0012] In some embodiments, the one or more chlorofluoroethylenes are each independently selected from:

trichlorofluoroethylene;
1,1,-dichloro-2,2-difluoroethylene (CFO-1112a);
Chlorotrifluoroethylene (CFO-1113);
1-chloro-2,2-difluoroethylene (HCFO-1122);
E-1-chloro-1,2-difluoroethylene (E-HCFO-1122a);
Z-1-chloro-1,2-difluoroethylene (Z-HCFO-1122a);
E-1-chloro-2-fluoroethylene (E-HCFO-1131);
Z-1-chloro-2-fluoroethylene Z-HCFO-1131);
1-chloro-1-fluoroethylene (HCFO-1131a);
1,2-dichloro-1-fluoroethylene (HCFO-1121); and
1,1-dichloro-2-fluoroethylene (HCFO-1121a).

[0013] In some embodiments, the chlorofluoroethylene provided herein is not E-1,2-dichloro-1,2-difluoroethylene, Z-1,2-dichloro-1,2-difluoroethylene, or a mixture thereof. In some embodiments, the chlorofluoroethylene provided herein is not E-1,2-dichloro-1,2-difluoroethylene. In some embodiments, the chlorofluoroethylene provided herein is not Z-1,2-dichloro-1,2-difluoroethylene. In some embodiments, the chlorofluoroethylene provided herein is not a mixture of E-1,2-dichloro-1,2-difluoroethylene and Z-1,2-dichloro-1,2-difluoroethylene.

[0014] In some embodiments, the composition comprises one chlorofluoroethylene provided herein. In some embodiments, the composition comprises two chlorofluoroethylenes provided herein. In some embodiments, the composition comprises three chlorofluoroethylenes provided herein. In some embodiments, the composition comprises four chlorofluoroethylenes provided herein.

[0015] In some embodiments, the chlorofluoroethylene is selected from the group consisting of 1-chloro-2,2-difluoroethylene and 1-chloro-1,2-difluoroethylene.

[0016] In some embodiments, the chlorofluoroethylene is trichlorofluoroethylene. In some embodiments, the chlorofluoroethylene is 1,1,-dichloro-2,2-difluoroethylene. In some embodiments, the chlorofluoroethylene is chlorotrifluoroethylene. In some embodiments, the chlorofluoroethylene is 1-chloro-2,2-difluoroethylene. In some embodiments, the chlorofluoroethylene is 1-chloro-1,2-difluoroethylene. In some embodiments, the chlorofluoroethylene is E-1-chloro-1,2-difluoroethylene. In some embodiments, the chlorofluoroethylene is Z-1-chloro-1,2-difluoroethylene. In some embodiments, the chlorofluoroethylene is E-1-chloro-2-fluoroethylene. In some embodiments, the chlorofluoroethylene is Z-1-chloro-2-fluoroethylene. In some embodiments, the chlorofluoroethylene is 1-chloro-1-fluoroethylene. In some embodiments, the chlorofluoroethylene is 1,2-dichloro-1-fluoroethylene. In some embodiments, the chlorofluoroethylene is 1,1-dichloro-2-fluoroethylene.

[0017] In some embodiments, the one or more stabilizer components are each selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.

[0018] In some embodiments, the one or more stabilizer components are present in small amounts relative to the overall composition. In some embodiments, the amount of the one or more stabilizer components in the disclosed compositions is from less than about 0.1 weight percent to as much as about 5 weight percent of the total composition. In some embodiments of the present invention, the additives are present in the disclosed compositions in an amount between about 0.1 weight percent to about 5 weight percent of the total composition or in an amount between about 0.1 weight percent to about 3.5 weight percent. The one or more stabilizer components selected for the disclosed composition is selected on the basis of the utility and/or individual equipment components or the system requirements.

[0019] In some embodiments, each stabilizer component is independently present in the composition at a concentration of from about 0.5 ppm to about 1500 ppm, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, about 1500 ppm or in a range extending between any of the aforementioned concentrations. In some

embodiments, each stabilizer component is independently present in the composition at a concentration of from about 500 ppm to about 1000 ppm. In some embodiments, each stabilizer component is independently present in the composition at a concentration of about 500 ppm or about 1000 ppm. In some embodiments, each stabilizer component is independently present in the composition at a concentration of about 1000 ppm.

[0020] In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein and an antioxidant. In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein and an antioxidant. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene and an antioxidant. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene and an antioxidant. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene and an antioxidant. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene and an antioxidant.

[0021] In some embodiments, the antioxidant is selected from a terpene, butylated hydroxytoluene, butylated hydroxyanisole, *tert*-butylhydroquinone, propyl 3,4,5-trihydroxybenzoate, 2-phenyl-2-propanol, 1-(2,4,5-trihydroxyphenyl)-1-butanone, 4-methoxyphenol, bisphenol methane derivatives, 2,2'-methylene bis (4-methyl-6-*t*-butyl phenol, and 2-isopropyl-5-methylphenol. In some embodiments, the antioxidant is selected from meta-xylene, ortho-xylene, para-xylene, thymol, limonene (in particular, d-limonene), and pinene.

[0022] In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein and an acid scavenger. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene and an acid scavenger. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene and an acid scavenger. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene and an acid scavenger. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene and an acid scavenger.

[0023] In some embodiments, the acid scavenger is selected from an epoxide and an amine. In some embodiments, the acid scavenger is an epoxide. In some

embodiments, the acid scavenger is epoxybutane. In some embodiments, the epoxybutane is 1,2-epoxybutane.

[0024] In some embodiments, the composition comprises one or more chlorofluoroethylenes and a metal stabilizer. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene and a metal stabilizer. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene and a metal stabilizer. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene and a metal stabilizer. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene and a metal stabilizer.

[0025] In some embodiments, the metal stabilizer is selected from N,N'-bis(salicylidene)-1,2-propanediamine and benzotriazole. In some embodiments, the metal stabilizer is N,N'-bis(salicylidene)-1,2-propanediamine. In some embodiments, the metal stabilizer is benzotriazole.

[0026] In some embodiments, the composition comprises one or more chlorofluoroethylenes, an antioxidant, and an acid scavenger. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, an antioxidant, and an acid scavenger. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, an antioxidant, and an acid scavenger. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, an antioxidant, and an acid scavenger. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, an antioxidant, and an acid scavenger.

[0027] In some embodiments, the composition comprises one or more chlorofluoroethylenes, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene. In

some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene.

[0028] In some embodiments, the composition comprises one or more chlorofluoroethylenes, meta-xylene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, meta-xylene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, meta-xylene, and epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, meta-xylene, and epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, meta-xylene, and epoxybutane.

[0029] In some embodiments, the composition comprises one or more chlorofluoroethylenes, meta-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, meta-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, meta-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, meta-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, meta-xylene, and 1,2-epoxybutane.

[0030] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), meta-xylene, and 1,2-epoxybutane comprises about 0.5 ppm to about 1500 ppm of the meta-xylene, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, about 1500 ppm of the meta-xylene or in range extending between any of the aforementioned concentrations. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the meta-xylene. In some embodiments, the composition comprises about 1000 ppm of the meta-xylene.

[0031] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), meta-xylene, and 1,2-epoxybutane comprises about 0.5 ppm to about 1500 ppm of the 1,2-epoxybutane, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the 1,2-epoxybutane or in a range extending between any of the aforementioned concentrations. In some embodiments, the composition comprises about 1000 ppm of the meta-xylene and about 1000 ppm of the 1,2-epoxybutane.

[0032] In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein, ortho-xylene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, ortho-xylene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, ortho-xylene, and epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, ortho-xylene, and epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, ortho-xylene, and epoxybutane.

[0033] In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein, ortho-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises one or more chlorofluoroethylenes, ortho-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, ortho-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, ortho-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, ortho-xylene, and epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, ortho-xylene, and 1,2-epoxybutane.

[0034] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-

1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), ortho-xylene, and 1,2-epoxybutane comprises 0.5 ppm to about 1500 ppm of the ortho-xylene, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the ortho-xylene or in a range extending between any of the aforementioned concentrations. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the ortho-xylene. In some embodiments, the composition comprises about 1000 ppm of the ortho-xylene.

[0035] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), ortho-xylene, and 1,2-epoxybutane comprises about 500 ppm to about 1500 ppm of the 1,2-epoxybutane, for example, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the 1,2-epoxybutane. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the 1,2-epoxybutane. In some embodiments, the composition comprises about 1000 ppm of the 1,2-epoxybutane.

[0036] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), ortho-xylene, and 1,2-epoxybutane comprises about 1000 ppm of the ortho-xylene and about 1000 ppm of the 1,2-epoxybutane.

[0037] In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein, para-xylene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, para-xylene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, para-xylene, and epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, para-xylene, and

epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, para-xylene, and epoxybutane.

[0038] In some embodiments, the composition comprises one or more chlorofluoroethylenes, para-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, para-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, para-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, para-xylene, and 1,2-epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, para-xylene, and 1,2-epoxybutane.

[0039] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), para-xylene, and 1,2-epoxybutane comprises about 0.5 ppm to about 1500 ppm of the para-xylene, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the para-xylene or in a range extending between any of the aforementioned concentrations. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the para-xylene. In some embodiments, the composition comprises about 1000 ppm of the para-xylene.

[0040] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), para-xylene, and 1,2-epoxybutane comprises about 500 ppm to about 1500 ppm of the 1,2-epoxybutane, for example, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the 1,2-epoxybutane. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the 1,2-epoxybutane. In some embodiments, the composition comprises about 1000 ppm of the 1,2-epoxybutane.

[0041] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), para-xylene, and 1,2-epoxybutane comprises about 1000 ppm of the para-xylene and about 1000 ppm of the 1,2-epoxybutane.

[0042] In some embodiments, the composition comprises one or more chlorofluoroethylenes, thymol, and epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, thymol, and epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, thymol, and epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, thymol, and epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, thymol, and epoxybutane.

[0043] In some embodiments, the composition comprises one or more chlorofluoroethylenes, thymol, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, thymol, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, thymol, and 1,2-epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, thymol, and 1,2-epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, thymol, and 1,2-epoxybutane.

[0044] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), thymol, and 1,2-epoxybutane comprises about 100 ppm to about 1000 ppm of the thymol, for example, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, or about 1000 ppm of the thymol. In some embodiments, the composition comprises about 400 ppm to about 600 ppm of the thymol. In some embodiments, the composition comprises about 500 ppm of the thymol.

[0045] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-

difluoroethylene), thymol, and 1,2-epoxybutane comprises about 0.5 ppm to about 1500 ppm of the 1,2-epoxybutane, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the 1,2-epoxybutane or in a range extending between any of the aforementioned concentrations. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the 1,2-epoxybutane. In some embodiments, the composition comprises about 1000 ppm of the 1,2-epoxybutane.

[0046] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), thymol, and 1,2-epoxybutane comprises about 500 ppm of the thymol and about 1000 ppm of the 1,2-epoxybutane.

[0047] In some embodiments, the composition comprises one or more chlorofluoroethylenes, pinene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, pinene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, pinene, and epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, pinene, and epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, pinene, and epoxybutane.

[0048] In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein, pinene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, pinene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, pinene, and 1,2-epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, pinene, and 1,2-epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, pinene, and 1,2-epoxybutane.

[0049] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-

1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), pinene, and 1,2-epoxybutane comprises about 100 ppm to about 1000 ppm of the pinene, for example, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, or about 1000 ppm of the pinene. In some embodiments, the composition comprises about 400 ppm to about 600 ppm of the pinene. In some embodiments, the composition comprises about 500 ppm of the pinene.

[0050] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), pinene, and 1,2-epoxybutane comprises about 0.5 ppm to about 1500 ppm of the 1,2-epoxybutane, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the 1,2-epoxybutane or in a range extending between any of the aforementioned concentrations. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the 1,2-epoxybutane. In some embodiments, the composition comprises about 1000 ppm of the 1,2-epoxybutane.

[0051] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), pinene, and 1,2-epoxybutane comprises about 500 ppm of the pinene and about 1000 ppm of the 1,2-epoxybutane.

[0052] In some embodiments, the composition comprises one or more chlorofluoroethylenes, d-limonene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, d-limonene, and epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, d-limonene, and epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, d-limonene, and epoxybutane. In some embodiments,

the composition comprises (Z)-1-chloro-1,2-difluoroethylene, d-limonene, and epoxybutane.

[0053] In some embodiments, the composition comprises one or more chlorofluoroethylenes provided herein, d-limonene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-2,2-difluoroethylene, d-limonene, and 1,2-epoxybutane. In some embodiments, the composition comprises 1-chloro-1,2-difluoroethylene, d-limonene, and 1,2-epoxybutane. In some embodiments, the composition comprises (E)-1-chloro-1,2-difluoroethylene, d-limonene, and 1,2-epoxybutane. In some embodiments, the composition comprises (Z)-1-chloro-1,2-difluoroethylene, d-limonene, and 1,2-epoxybutane.

[0054] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), d-limonene, and 1,2-epoxybutane comprises about 100 ppm to about 1000 ppm of the d-limonene, for example, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, or about 1000 ppm of the d-limonene. In some embodiments, the composition comprises about 400 ppm to about 600 ppm of the d-limonene. In some embodiments, the composition comprises about 500 ppm of the d-limonene.

[0055] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), d-limonene, and 1,2-epoxybutane comprises about 0.5 ppm to about 1500 ppm of the 1,2-epoxybutane, for example, about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm of the 1,2-epoxybutane or in a range extending between any of the aforementioned concentrations. In some embodiments, the composition comprises about 900 ppm to about 1100 ppm of the 1,2-epoxybutane.

In some embodiments, the composition comprises about 1000 ppm of the 1,2-epoxybutane.

[0056] In some embodiments, the composition comprising one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), d-limonene, and 1,2-epoxybutane comprises about 500 ppm of the d-limonene and about 1000 ppm of the 1,2-epoxybutane. In some embodiments, the composition provided herein comprising one or more additional compounds selected from:

(E)-1-chloro-1,2-difluoroethene (E-1122a);
(Z)-1-chloro-1,2-difluoroethene (Z-1122a);
1,2-dichloro-1,1-difluoroethane (R-132b);
2-chloro-1,1,1-trifluoroethane (R-133a); and
1-chloro-1,2,2,2-tetrafluoroethane (R-124).

[0057] In some embodiments, the composition provided herein comprising one or more additional compounds selected from:

(1-chloro-2,2-difluoroethylene (1122);
(E)-1,2-dichloro-1,2-difluoroethylene (E-1112);
(Z)-1,2-dichloro-1,2-difluoroethylene (Z-1112);
1-chloro-1,2,2-trifluoroethane (R-133);
chlorotrifluoroethylene (R-1113); and
1-chloro-2,2,2-trifluoroethane (R-133a).

[0058] In some embodiments, the composition provided herein consists essentially of the one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.

[0059] In some embodiments, the composition provided herein consists of the one or more chlorofluoroethylenes provided herein (*e.g.*, 1-chloro-2,2-difluoroethylene, 1-

chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.

[0060] In some embodiments, the composition provided herein consists essentially of the one or more chlorofluoroethylenes provided herein (e.g., 1-chloro-2,2-difluoroethylene, 1-chloro-1,2-difluoroethylene, (E)-1-chloro-1,2-difluoroethylene, or (Z)-1-chloro-1,2-difluoroethylene), and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof; and one or more additional compounds.

[0061] In some embodiments, the composition provided herein consists essentially of 1-chloro-2,2-difluoroethylene and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof; and one or more additional compounds selected from:

(E)-1-chloro-1,2-difluoroethene (E-1122a);
(Z)-1-chloro-1,2-difluoroethene (Z-1122a);
1,2-dichloro-1,1-difluoroethane (R-132b);
2-chloro-1,1,1-trifluoroethane (R-133a); and
1-chloro-1,2,2,2-tetrafluoroethane (R-124).

[0062] In some embodiments, the composition provided herein consists essentially of 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene; and one or more additional compounds selected from:

(E)-1-chloro-1,2-difluoroethene (E-1122a);
(Z)-1-chloro-1,2-difluoroethene (Z-1122a);
1,2-dichloro-1,1-difluoroethane (R-132b);
2-chloro-1,1,1-trifluoroethane (R-133a); and
1-chloro-1,2,2,2-tetrafluoroethane (R-124).

[0063] In some embodiments, the composition provided herein consists of the one or more chlorofluoroethylenes provided herein and one or more stabilizer

components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof; and one or more additional compounds.

[0064] In some embodiments, the composition provided herein consists of 1-chloro-2,2-difluoroethylene and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof; and one or more additional compounds selected from:

(E)-1-chloro-1,2-difluoroethene (E-1122a);
(Z)-1-chloro-1,2-difluoroethene (Z-1122a);
1,2-dichloro-1,1-difluoroethane (R-132b);
2-chloro-1,1,1-trifluoroethane (R-133a); and
1-chloro-1,2,2,2-tetrafluoroethane (R-124).

[0065] In some embodiments, the composition provided herein consists of 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene; and one or more additional compounds selected from:

(E)-1-chloro-1,2-difluoroethene (E-1122a);
(Z)-1-chloro-1,2-difluoroethene (Z-1122a);
1,2-dichloro-1,1-difluoroethane (R-132b);
2-chloro-1,1,1-trifluoroethane (R-133a); and
1-chloro-1,2,2,2-tetrafluoroethane (R-124).

[0066] In some embodiments, the composition provided herein consists of 1-chloro-1,2-difluoroethylene and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof; and one or more additional compounds selected from:

1-chloro-2,2-difluoroethylene (1122);
(E)-1,2-dichloro-1,2-difluoroethylene (E-1112);
(Z)-1,2-dichloro-1,2-difluoroethylene (Z-1112);
1-chloro-1,2,2-trifluoroethane (R-133);
chlorotrifluoroethylene (R-1113); and

1-chloro-2,2,2-trifluoroethane (R-133a).

[0067] In some embodiments, the composition provided herein consists of 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene; and one or more additional compounds selected from:

1-chloro-2,2-difluoroethylene (1122);
(E)-1,2-dichloro-1,2-difluoroethylene (E-1112);
(Z)-1,2-dichloro-1,2-difluoroethylene (Z-1112);
1-chloro-1,2,2-trifluoroethane (R-133);
chlorotrifluoroethylene (R-1113); and
1-chloro-2,2,2-trifluoroethane (R-133a).

[0068] In some embodiments, the compositions of the present invention are found to be free of or substantially free of Group A Fluorinated Substances, and degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.

[0069] In one embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that (i) contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it); and (ii) meets the criterion for persistence in soil/sediment and water established in Annex XIII (Section 1.1.1) of the European Union's REACH Regulation (<https://reachonline.eu/reach/en/annex-xiii-1-1.1-1.1.1.html> as accessed on May 2, 2023) and referenced in the Annex XV Restriction Report dated March 22, 2023, the disclosure of which is hereby incorporated by reference (<https://echa.europa.eu/documents/10162/f605d4b5-7c17-7414-8823-b49b9fd43aea> as accessed on May 2, 2023). In one embodiment, Group A Fluorinated Substances include, but are not limited to, trifluoroacetic acid (TFA).

[0070] In another embodiment, as used herein, "Group A Fluorinated Substances" includes any substance that has a Henry's Law constant $\leq 250 \text{ Pa}\cdot\text{m}^3/\text{mol}$ and contains at least one fully fluorinated methyl ($-\text{CF}_3$) or methylene ($-\text{CF}_2-$) carbon atom (without any H/Cl/Br/I attached to it). In one embodiment, Group A Fluorinated Substances include, but are not limited to, TFA.

[0071] Thus, according to some embodiments, compositions of the present invention which comprise, consist of, or consist essentially of stabilized chlorofluoroethylenes are free of or substantially free of Group A Fluorinated Substances, such as TFA. In one embodiment, the phrase "free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by gas chromatography with a flame ionization detector, gas chromatography with a mass detector by analysis of a gas sample or liquid sample, and/or ion chromatography by analysis of a water sample after bubbling the thermal fluid through water. Such methodologies are well known to those skilled in the art. In one embodiment, the phrase "substantially free of" as used herein with respect to the presence of Group A Fluorinated Substances in the present compositions means that the amount of such substances in the compositions is > 0 wt.% and ≤ 5 wt.%, or > 0 wt.% and ≤ 4 wt.%, or > 0 wt.% and ≤ 3 wt.%, or > 0 wt.% and ≤ 2 wt.%, or > 0 wt.% and ≤ 1 wt.%, and all values and ranges therebetween, when measured by gas chromatographic (GC) techniques, for example gas chromatography (GC) with a flame ionization or electron-capture detector, or GC coupled with a mass detector (gas chromatography/mass spectral (GC/MS) method), by ion chromatograph(IC) or ion chromatography mass spectrometry (IC-MS) techniques, or by high-performance liquid chromatography (HPLC) or high-performance liquid chromatography mass spectrometry (HPLC-MS) techniques. The TFA analytical standard may be used in either gas chromatography or ion chromatography and is available from, for example, Sigma Aldrich. In some embodiments, the stabilized 1,2-dichloro-1,2-difluoroethylene are free of Group A fluorinated Substances, meaning that these substances are non-detectable by the methods and techniques described herein.

[0072] Further, in some embodiments, degradation products of such compositions of the present invention which comprise, consist of, or consist essentially of stabilized chlorofluoroethylenes are free of or substantially free of Group A Fluorinated Substances, such as TFA. In one embodiment, the phrase "free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during

tropospheric degradation of the compositions is sufficiently low so as to not be detectable, including but not limited to 0%, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques. In one embodiment, the phrase "substantially free of" as used herein with respect to the formation of Group A Fluorinated Substances by the present compositions means that the theoretical molar yield of such substances in environmental compartments of air, soil/sediment and water produced during tropospheric degradation of the compositions is $> 0\%$ and $\leq 5\%$, or $> 0\%$ and $\leq 4\%$, or $> 0\%$ and $\leq 3\%$, or $> 0\%$ and $\leq 2\%$, or $> 0\%$ and $\leq 1\%$, and all values and ranges therebetween, when measured by GC techniques, for example GC with a flame ionization or electron-capture detector or GC/MS method, by IC or IC-MS techniques, or by HPLC or HPLC-MS techniques. In some embodiments, degradation products of such compositions of the present invention which comprise, consist of, or consist essentially of stabilized 1,2-dichloro-1,2-difluoroethylene are free of Group A Fluorinated Substances, such as TFA, meaning that these substances are non-detectable by the methods and techniques described herein.

[0073] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0074] As used herein, the term "consisting essentially of" is used to define a composition, method that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention, especially the mode of action to achieve the desired result of any of the processes of the present invention.

The term “consists essentially of” or “consisting essentially of” occupies a middle ground between “comprising” and “consisting of”.

[0075] Also, use of “a” or “an” are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0076] As used herein, the term “about” is meant to account for variations due to experimental error (e.g., plus or minus approximately 10% of the indicated value). All measurements reported herein are understood to be modified by the term “about”, whether or not the term is explicitly used, unless explicitly stated otherwise.

[0077] When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and/or lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

[0078] Refrigeration capacity (sometimes referred to as cooling capacity) is a term to define the change in enthalpy of a refrigerant or working fluid in an evaporator per unit mass of refrigerant or working fluid circulated. Volumetric cooling capacity refers to the amount of heat removed by the refrigerant or working fluid in the evaporator per unit volume of refrigerant vapor exiting the evaporator. The refrigeration capacity is a measure of the ability of a refrigerant, working fluid or heat transfer composition to produce cooling. Therefore, the higher the volumetric cooling capacity of the working fluid, the greater the cooling rate that can be produced at the evaporator with the maximum volumetric flow rate achievable with a given compressor. Cooling rate refers to the heat removed by the refrigerant in the evaporator per unit time.

[0079] Similarly, volumetric heating capacity is a term to define the amount of heat supplied by the refrigerant or working fluid in the condenser per unit volume of refrigerant or working fluid vapor entering the compressor. The higher the volumetric

heating capacity of the refrigerant or working fluid, the greater the heating rate that is produced at the condenser with the maximum volumetric flow rate achievable with a given compressor.

[0080] Coefficient of performance (COP) is the amount of heat removed in the evaporator divided by the energy required to operate the compressor. The higher the COP, the higher the energy efficiency. COP is directly related to the energy efficiency ratio (EER), that is, the efficiency rating for refrigeration or air conditioning equipment at a specific set of internal and external temperatures.

[0081] As used herein, a heat transfer medium comprises a composition used to carry heat from a heat source to a heat sink. For example, heat from a body to be cooled to a chiller evaporator or from a chiller condenser to a cooling tower or other configuration where heat can be rejected to the ambient.

[0082] As used herein, a working fluid or refrigerant comprises a compound or mixture of compounds (e.g., a composition provided herein) that function to transfer heat in a cycle wherein the working fluid undergoes a phase change from a liquid to a gas and back to a liquid in a repeating cycle.

[0083] Subcooling is the reduction of the temperature of a liquid below that liquid's saturation point for a given pressure. The saturation point is the temperature at which a vapor composition is completely condensed to a liquid (also referred to as the bubble point). But subcooling continues to cool the liquid to a lower temperature liquid at the given pressure. By cooling a liquid below the saturation temperature, the net refrigeration capacity can be increased. Subcooling thereby improves refrigeration capacity and energy efficiency of a system. Subcool amount is the amount of cooling below the saturation temperature (in degrees) or how far below its saturation temperature a liquid composition is cooled.

[0084] The term "superheat" defines how far above the saturation vapor temperature of a vapor composition a vapor composition is heated. Saturation vapor temperature is the temperature at which, if a vapor composition is cooled, the first drop of liquid is formed, also referred to as the "dew point".

[0085] The compositions provided herein can act as a working fluid used to carry heat from a heat source to a heat sink. Such heat transfer compositions may also be

useful as a refrigerant in a cycle wherein the fluid undergoes a phase change; that is, from a liquid to a gas and back, or vice versa. Examples of heat transfer systems include but are not limited to air conditioners, freezers, refrigerators, heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, high temperature heat pumps, mobile refrigerators, mobile air conditioning units, immersion cooling systems, data-center cooling systems, and combinations thereof. Accordingly, the present application provides a heat transfer system (e.g., a heat transfer apparatus) as described herein, comprising a composition provided herein. In some embodiments, the composition provided herein is useful as a working fluid (e.g., a working fluid for refrigeration or heating applications) in the heat transfer apparatus. In some embodiments, the compositions provided herein are useful in an apparatus or system comprising a high temperature heat pump. In some embodiments, the high temperature heat pump comprises a centrifugal compressor. In some embodiments, the compositions provided herein are useful in an apparatus or system comprising a chiller apparatus. In some embodiments, the compositions provided herein are useful in an apparatus or system comprising a centrifugal chiller apparatus. In some embodiments, the compositions provided herein are useful in an apparatus or system comprising a screw or scroll chiller apparatus. In some embodiments, the compositions provided herein are useful in a centrifugal high temperature heat pump.

[0086] Mechanical vapor-compression refrigeration, air conditioning and heat pump systems include an evaporator, a compressor, a condenser, and an expansion device. A refrigeration cycle re-uses refrigerant in multiple steps producing a cooling effect in one step and a heating effect in a different step. The cycle can be described as follows: Liquid refrigerant enters an evaporator through an expansion device, and the liquid refrigerant boils in the evaporator, by withdrawing heat from the environment, at a low temperature to form a gas and produce cooling. Often air or a heat transfer fluid flows over or around the evaporator to transfer the cooling effect caused by the evaporation of the refrigerant in the evaporator to a body to be cooled. The low-pressure gas enters a compressor where the gas is compressed to raise its pressure and temperature. The higher-pressure (compressed) gaseous refrigerant then enters the condenser in which the refrigerant condenses and discharges its heat to the environment. The refrigerant returns to the expansion

device through which the liquid expands from the higher-pressure level in the condenser to the low-pressure level in the evaporator, thus repeating the cycle.

[0087] A body to be cooled or heated may be defined as any space, location, object or body for which it is desirable to provide cooling or heating. Examples include spaces (open or enclosed) requiring air conditioning, cooling, or heating, such as a room, an apartment, or building, such as an apartment building, university dormitory, townhouse, or other attached house or single-family home, hospitals, office buildings, supermarkets, college or university classrooms or administration buildings and automobile or truck passenger compartments. Additionally, a body to be cooled may include electronic devices, such as computer equipment, central processing units (cpu), data-centers, server banks, and personal computers among others.

[0088] By “in the vicinity of” is meant that the evaporator of the system containing the refrigerant is located either within or adjacent to the body to be cooled, such that air moving over the evaporator would move into or around the body to be cooled. In the process for producing heating, “in the vicinity of” means that the condenser of the system containing the refrigerant is located either within or adjacent to the body to be heated, such that the air moving over the evaporator would move into or around the body to be heated. In some embodiments, for heat transfer, “in the vicinity of” may mean that the body to be cooled is immersed directly in the heat transfer composition or tubes containing heat transfer compositions run into around internally, and out of electronic equipment, for instance.

[0089] Exemplary refrigeration systems include, but are not limited to, equipment including commercial, industrial or residential refrigerators and freezers, ice machines, self-contained coolers and freezers, vending machines, flooded evaporator chillers, direct expansion chillers, water chiller, centrifugal chillers, screw chillers, scroll chillers, walk-in and reach-in coolers and freezers, and combination systems. In some embodiments, the compositions provided herein may be used in supermarket refrigeration systems. Additionally, stationary applications may utilize a secondary loop system that uses a primary refrigerant to produce cooling in one location that is transferred to a remote location via a secondary heat transfer fluid.

[0090] In some embodiments, the compositions provided herein are useful in mobile heat transfer systems, including refrigeration, air conditioning, chiller, or heat pump systems or apparatus. In some embodiments, the compositions are useful in stationary heat transfer systems, including refrigeration, air conditioning, chiller, or heat pump systems or apparatus.

[0091] As used herein, mobile refrigeration, air conditioning, chiller, or heat pump systems refers to any refrigeration, air conditioner, or heat pump apparatus incorporated into a transportation unit for the road, rail, sea or air. Mobile air conditioning or heat pumps systems may be used in automobiles, trucks, railcars or other transportation systems. Mobile refrigeration may include transport refrigeration in trucks, airplanes, or rail cars. In addition, apparatus which are meant to provide refrigeration for a system independent of any moving carrier, known as “intermodal” systems, are including in the present inventions. Such intermodal systems include “containers” (combined sea/land transport) as well as “swap bodies” (combined road and rail transport).

[0092] As used herein, stationary air conditioning or heat pump systems are systems that are fixed in place during operation. A stationary air conditioning or heat pump system may be associated within or attached to buildings of any variety. These stationary applications may be stationary air conditioning and heat pumps, including but not limited to chillers (including centrifugal, screw, or scroll chillers), heat pumps, including residential and high temperature heat pumps, residential, commercial or industrial air conditioning systems, and including window, ductless, ducted, packaged terminal, and those exterior but connected to the building such as rooftop systems.

[0093] Stationary heat transfer may refer to systems for cooling electronic devices, such as immersion cooling systems, submersion cooling systems, phase change cooling systems, data-center cooling systems or simply liquid cooling systems.

[0094] In some embodiments, a method is provided for using the present compositions as a heat transfer fluid. The method comprises transporting said composition from a heat source to a heat sink.

[0095] In some embodiments, a method is provided for producing cooling comprising evaporating any of the present compounds or compositions in the vicinity of a body to be cooled, and thereafter condensing said composition.

[0096] In some embodiments, a method is provided for producing heating comprising condensing any of the present compositions in the vicinity of a body to be heated, and thereafter evaporating said compositions.

[0097] In some embodiments, the composition is for use in heat transfer, wherein the working fluid is a heat transfer component.

[0098] In some embodiments, the compositions of the invention are for use in refrigeration or air conditioning.

[0099] In some embodiments, the compositions of the invention are for use in chillers or heat pumps.

[0100] In some embodiments, the compositions of the invention are for use in methods for replacing an incumbent refrigerant.

[0101] In some embodiments, compositions of the present invention may be useful for reducing or eliminating the flammability of flammable refrigerants provided herein. In some embodiments, the present application provided herein is a method for reducing the flammability of a flammable refrigerant comprising adding a composition comprising a composition as disclosed herein to a flammable refrigerant.

[0102] The compositions provided herein may be useful as a replacement for a currently used ("incumbent") refrigerant. As used herein, the term "incumbent refrigerant" shall be understood to mean the refrigerant for which the heat transfer system was designed to operate, or the refrigerant that is resident in the heat transfer system. . In some embodiments, the incumbent refrigerant is selected from R-123 (2,2-dichloro-1,1,1-trifluoroethane), R-245fa (1,1,1,3,3-pentafluoropropane), R-514A (a blend of 74.7 wt% HFO-1336mzzZ (Z-1,1,1,4,4,4-hexafluoro-2-butene) and 25.3 wt% trans-1,2-dichloroethylene), R-1233zdE (E-1-chloro-3,3,3-trifluoropropene), and R-1224ydZ (Z-1-chloro-2,3,3,3-tetrafluoropropene). In some embodiments, the incumbent refrigerant is R-123. In some embodiments, the incumbent refrigerant is R-245fa. In some embodiments, the incumbent refrigerant is

R-514A. In some embodiments, the incumbent refrigerant is R-1233zdE. In some embodiments, the incumbent refrigerant is R-1224ydZ.

[0103] Often replacement refrigerants are most useful if capable of being used in the original refrigeration equipment designed for a different refrigerant, *e.g.*, with minimal to no system modifications. In many applications, some embodiments of the disclosed compositions are useful as refrigerants and provide at least comparable cooling performance (meaning cooling capacity) as the refrigerant for which a replacement is being sought.

[0104] In some embodiments is provided a method for operating a heat transfer system or for transferring heat that is designed to operate with an incumbent refrigerant by charging an empty system with a composition of the present invention, or by substantially replacing said incumbent refrigerant with a composition of the present invention. In some embodiments, the incumbent refrigerant is selected from R-123, R-245fa, R-514A, R-1233zdE, and R-1224ydZ. In some embodiments, the incumbent refrigerant is R-123. In some embodiments, the incumbent refrigerant is R-245fa. In some embodiments, the incumbent refrigerant is R-514A. In some embodiments, the incumbent refrigerant is R-1233zdE. In some embodiments, the incumbent refrigerant is R-1224ydZ.

[0105] As used herein, the term “substantially replacing” shall be understood to mean allowing the incumbent refrigerant to drain from the system, or pumping the incumbent refrigerant from the system, and then charging the system with a composition of the present invention. The system may be flushed with one or more quantities of the replacement refrigerant before being charged. It shall be understood that in some embodiments, some small quantity of the incumbent refrigerant may be present in the system after the system has been charged with the composition of the present invention.

[0106] In another embodiment is provided a method for recharging a heat transfer system that contains an incumbent refrigerant and a lubricant, said method comprising substantially removing the incumbent refrigerant from the heat transfer system while retaining a substantial portion of the lubricant in said system and introducing one of the present compositions to the heat transfer system. In some embodiments, the lubricant in the system is partially replaced. In some

embodiments, the incumbent refrigerant is selected from R-123, R-245fa, R-514A, R-1233zdE, and R-1224ydZ. In some embodiments, the incumbent refrigerant is R-123. In some embodiments, the incumbent refrigerant is R-245fa. In some embodiments, the incumbent refrigerant is R-514A. In some embodiments, the incumbent refrigerant is R-1233zdE. In some embodiments, the incumbent refrigerant is R-1224ydZ.

[0107] In some embodiments, the compositions of the present invention may be used to top-off a refrigerant charge in a chiller. For example, if a chiller using one or more of the chlorofluoroethylenes provided herein has diminished performance due to decomposition (*e.g.*, oxidation) of the one or more chlorofluoroethylenes, leakage of refrigerant, and the like, the compositions as disclosed herein may be added to bring performance back up to specification.

[0108] In some embodiments, a heat exchange system containing any the presently disclosed compositions is provided, wherein said system is selected from the group consisting of air conditioners, freezers, refrigerators, heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, heat pumps, mobile refrigerators, mobile air conditioning units, and systems having combinations thereof. Additionally, the compositions provided herein may be useful in secondary loop systems wherein these compositions serve as the primary refrigerant thus providing cooling to a secondary heat transfer fluid that thereby cools a remote location.

[0109] Thus, the systems may operate more efficiently if the heat exchangers are operated in counter-current mode or cross-current mode with counter-current tendency. Counter-current tendency means that the closer the heat exchanger can get to counter-current mode the more efficient the heat transfer. Thus, air conditioning heat exchangers, in particular evaporators, are designed to provide some aspect of counter-current tendency.

[0110] Therefore, provided herein is an air conditioning or heat pump system wherein said system includes one or more heat exchangers (either evaporators, condensers or both) that operate in counter-current mode or cross-current mode with counter-current tendency.

[0111] In some embodiments, provided herein is a refrigeration system wherein said system includes one or more heat exchangers (either evaporators, condensers or both) that operate in counter-current mode or cross-current mode with counter-current tendency.

[0112] In some embodiments, the refrigeration, air conditioning or heat pump system is a stationary refrigeration, air conditioning or heat pump system. In some embodiments the refrigeration, air conditioning, or heat pump system is a mobile refrigeration, air conditioning or heat pump system.

[0113] Additionally, in some embodiments, the disclosed compositions may function as primary refrigerants in secondary loop systems that provide cooling to remote locations by use of a secondary heat transfer fluid, which may comprise water, an aqueous salt solution (e.g., calcium chloride), a glycol, carbon dioxide, or a fluorinated hydrocarbon fluid (meaning an HFC, HCFC, hydrofluoroolefin ("HFO"), hydrochlorofluoroolefin ("HCFO"), chlorofluoroolefin ("CFO"), or perfluorocarbon ("PFC"). In this case, the secondary heat transfer fluid is the body to be cooled as it is adjacent to the evaporator and is cooled before moving to a second remote body to be cooled. In some embodiments, the disclosed compositions may function as the secondary heat transfer fluid, thus transferring or providing cooling (or heating) to the remote location.

[0114] In some embodiments, the compositions provided herein further comprise a lubricant.

[0115] In one embodiment, the lubricant is selected from the group consisting of mineral oil, alkylbenzene, polyol esters, polyalkylene glycols, polyvinyl ethers, polycarbonates, perfluoropolyethers, silicones, silicate esters, phosphate esters, paraffins, naphthenes, polyalpha-olefins, and combinations thereof.

[0116] The lubricants as disclosed herein may be commercially available lubricants. For instance, the lubricant may be paraffinic mineral oil, sold by BVA Oils as BVM 100 N, naphthenic mineral oils sold by Crompton Co. under the trademarks Suniso® 1GS, Suniso® 3GS and Suniso® 5GS, naphthenic mineral oil sold by Pennzoil under the trademark Sontex® 372LT, naphthenic mineral oil sold by Calumet Lubricants under the trademark Calumet® RO-30,, linear alkylbenzenes sold by Shrieve Chemicals under the trademarks Zerol® 75, Zerol® 150 and Zerol® 500

and branched alkylbenzene sold by Nippon Oil as HAB 22, polyol esters (POEs) sold under the trademark Castrol® 100 by Castrol, United Kingdom, polyalkylene glycols (PAGs) such as RL-488A from Dow (Dow Chemical, Midland, Michigan), and mixtures thereof, meaning mixtures of any of the lubricants disclosed in this paragraph.

[0117] Notwithstanding the above weight ratios for compositions disclosed herein, it is understood that in some heat transfer systems, while the composition is being used, it may acquire additional lubricant from one or more equipment components of such heat transfer system. For example, in some refrigeration, air conditioning and heat pump systems, lubricants may be charged in the compressor and/or the compressor lubricant sump. Such lubricant would be in addition to any lubricant additive present in the refrigerant in such a system. In use, the refrigerant when in the compressor may pick up an amount of the equipment lubricant to change the refrigerant-lubricant composition from the starting ratio.

[0118] In some embodiments, the compositions provided herein further comprise at least one dye. The dye may be at least one ultra-violet (UV) dye. As used herein, “ultra-violet” dye is defined as a UV fluorescent or phosphorescent composition that absorbs light in the ultra-violet or “near” ultra-violet region of the electromagnetic spectrum. The fluorescence produced by the UV fluorescent dye under illumination by a UV light that emits at least some radiation with a wavelength in the range of from 10 nanometers to about 775 nanometers may be detected.

[0119] UV dye is a useful component for detecting leaks of the composition by permitting one to observe the fluorescence of the dye at or in the vicinity of a leak point in an apparatus (e.g., refrigeration unit, air-conditioner or heat pump). The UV emission, e.g., fluorescence from the dye may be observed under an ultra-violet light. Therefore, if a composition containing such a UV dye is leaking from a given point in an apparatus, the fluorescence can be detected at the leak point, or in the vicinity of the leak point.

[0120] In some embodiments, the UV dye may be a fluorescent dye. In some embodiments, the fluorescent dye is selected from the group consisting of naphthalimides, perylenes, coumarins, anthracenes, phenanthracenes, xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins, and derivatives of said dye, and

combinations thereof, meaning mixtures of any of the foregoing dyes or their derivatives disclosed in this paragraph.

[0121] In some embodiments, the compositions provided herein further comprise at least one solubilizing agent selected to improve the solubility of one or more dye in the disclosed compositions. In some embodiments, the weight ratio of dye to solubilizing agent ranges from about 99:1 to about 1:1. The solubilizing agents include at least one compound selected from the group consisting of hydrocarbons, hydrocarbon ethers, polyoxyalkylene glycol ethers (such as dipropylene glycol dimethyl ether), amides, nitriles, ketones, chlorocarbons (such as methylene chloride, trichloroethylene, chloroform, or mixtures thereof), esters, lactones, aromatic ethers, fluoroethers, and 1,1,1-trifluoroalkanes and mixtures thereof, meaning mixtures of any of the solubilizing agents disclosed in this paragraph.

[0122] In some embodiments, the compositions provided herein further comprise at least one compatibilizer to improve the compatibility of one or more lubricants with the disclosed compositions. The compatibilizer may be selected from the group consisting of hydrocarbons, hydrocarbon ethers, polyoxyalkylene glycol ethers (such as dipropylene glycol dimethyl ether), amides, nitriles, ketones, chlorocarbons (such as methylene chloride, trichloroethylene, chloroform, or mixtures thereof), esters, lactones, aromatic ethers, fluoroethers, 1,1,1-trifluoroalkanes, and mixtures thereof, meaning mixtures of any of the compatibilizers disclosed in this paragraph.

[0123] The solubilizing agent and/or compatibilizer provided herein may be selected from the group consisting of hydrocarbon ethers consisting of the ethers containing only carbon, hydrogen and oxygen, such as dimethyl ether (DME) and mixtures thereof, meaning mixtures of any of the hydrocarbon ethers disclosed in this paragraph.

[0124] The compatibilizer provided herein may be linear or cyclic aliphatic or aromatic hydrocarbon compatibilizer containing from 3 to 15 carbon atoms. The compatibilizer may be at least one hydrocarbon, which may be selected from the group consisting of at least propanes, including propylene and propane, butanes, including n-butane and isobutene, pentanes, including n-pentane, isopentane, neopentane and cyclopentane, hexanes, octanes, nonane, and decanes, among others. Commercially available hydrocarbon compatibilizers include but are not

limited to those from Exxon Chemical (USA) sold under the trademarks Isopar[®] H, a mixture of undecane (C₁₁) and dodecane (C₁₂) (a high purity C₁₁ to C₁₂ iso-paraffinic), Aromatic 150 (a C₉ to C₁₁ aromatic) (Aromatic 200 (a C₉ to C₁₅ aromatic) and Naptha 140 (a mixture of C₅ to C₁₁ paraffins, naphthenes and aromatic hydrocarbons) and mixtures thereof, meaning mixtures of any of the hydrocarbons disclosed in this paragraph.

[0125] The compatibilizer provided herein may alternatively be at least one polymeric compatibilizer. The polymeric compatibilizer may be a random copolymer of fluorinated and non-fluorinated acrylates, wherein the polymer comprises repeating units of at least one monomer represented by the formulae $\text{CH}_2=\text{C}(\text{R}^1)\text{CO}_2\text{R}^2$, $\text{CH}_2=\text{C}(\text{R}^3)\text{C}_6\text{H}_4\text{R}^4$, and $\text{CH}_2=\text{C}(\text{R}^5)\text{C}_6\text{H}_4\text{XR}^6$, wherein X is oxygen or sulfur; R¹, R³, and R⁵ are independently selected from the group consisting of H and C₁-C₄ alkyl radicals; and R², R⁴, and R⁶ are independently selected from the group consisting of carbon-chain-based radicals containing C, and F, and may further contain H, Cl, ether oxygen, or sulfur in the form of thioether, sulfoxide, or sulfone groups and mixtures thereof. Examples of such polymeric compatibilizers include those commercially available from E. I. du Pont de Nemours and Company, (Wilmington, DE, 19898, USA) under the trademark Zonyl[®] PHS. Zonyl[®] PHS is a random copolymer made by polymerizing 40 weight percent $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2(\text{CF}_2\text{CF}_2)_m\text{F}$ (also referred to as Zonyl[®] fluoromethacrylate or ZFM) wherein m is from 1 to 12, primarily 2 to 8, and 60 weight percent lauryl methacrylate ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_{11}\text{CH}_3$, also referred to as LMA).

[0126] In some embodiments, the compatibilizer component provided herein contains from about 0.01 to 30 weight percent (based on total amount of compatibilizer) of an additive which reduces the surface energy of metallic copper, aluminum, steel, or other metals and metal alloys thereof found in heat exchangers in a way that reduces the adhesion of lubricants to the metal. Examples of metal surface energy reducing additives include those commercially available from DuPont under the trademarks Zonyl[®] FSA, Zonyl[®] FSP, and Zonyl[®] FSJ.

[0127] In some embodiments, the compositions provided herein further comprise a metal surface deactivator. In some embodiments, the metal surface deactivator is selected from the group consisting of areoxalyl bis (benzylidene) hydrazide (CAS reg

no. 6629-10-3), N,N'-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine (CAS reg no. 32687-78-8), 2,2'-oxamidobis-ethyl-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate (CAS reg no. 70331-94-1), N,N'-(disalicyclidene)-1,2-diaminopropane (CAS reg no. 94-91-7) and ethylenediaminetetra-acetic acid (CAS reg no. 60-00-4) and its salts, and mixtures thereof, meaning mixtures of any of the metal surface deactivators disclosed in this paragraph.

[0128] In some embodiments, the compositions provided herein further comprise a tracer. The tracer may be two or more tracer compounds from the same class of compounds or from different classes of compounds. In some embodiments, the tracer is present in the compositions at a total concentration of about 50 parts per million by weight (ppm) to about 1000 ppm, based on the weight of the total composition. In some embodiments, the tracer is present at a total concentration of about 50 ppm to about 500 ppm. Alternatively, the tracer is present at a total concentration of about 100 ppm to about 300 ppm.

[0129] The tracer may be selected from the group consisting of hydrofluorocarbons (HFCs), deuterated hydrofluorocarbons, perfluorocarbons, fluoroethers, brominated compounds, iodinated compounds, alcohols, aldehydes and ketones, nitrous oxide and combinations thereof. Alternatively, the tracer may be selected from the group consisting of trifluoromethane (HFC-23), fluoroethane (HFC-161), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), 1,1,1,2,2,3-hexafluoropropane (HFC-236cb), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,2,2-pentafluoropropane (HFC-245cb), 1,1,2,2-tetrafluoropropane (HFC-254cb), 1,1,1,2-tetrafluoropropane (HFC-254eb), 1,1,1-trifluoropropane (HFC-263fb), 2,2-difluoropropane (HFC-272ca), 2-fluoropropane (HFC-281ea), 1-fluoropropane (HFC-281fa), 1,1,1,2,2,3,3,4-nonafluorobutane (HFC-329p), 1,1,1-trifluoro-2-methylpropane (HFC-329mmz), 1,1,1,2,2,4,4,4-octafluorobutane (HFC-338mf), 1,1,2,2,3,3,4,4-octafluorobutane (HFC-338pcc), 1,1,1,2,2,3,3-heptafluorobutane (HFC-347s), hexafluoroethane (perfluoroethane, PFC-116), perfluoro-cyclopropane (PFC-C216), perfluoropropane (PFC-218), perfluoro-cyclobutane (PFC-C318), perfluorobutane (PFC-31-10mc), perfluoro-2-methylpropane (CF₃CF(CF₃)₂), perfluoro-1,3-dimethylcyclobutane (PFC-C51-12mym), trans-perfluoro-2,3-dimethylcyclobutane (PFC-C51-12mym, trans), cis-perfluoro-2,3-dimethylcyclobutane (PFC-C51-12mym, cis), perfluoromethylcyclopentane,

perfluoromethylcyclohexane, perfluorodimethylcyclohexane (ortho, meta, or para), perfluoroethylcyclohexane, perfluoroindan, perfluorotrimethylcyclohexane and isomers thereof, perfluoroisopropylcyclohexane, cis-perfluorodecalin, trans-perfluorodecalin, cis- or trans-perfluoromethyldecalin and mixtures thereof. In some embodiments, the tracer is a blend containing two or more hydrofluorocarbons, or one hydrofluorocarbon in combination with one or more perfluorocarbons.

[0130] The tracer may be added to the compositions of the present invention in predetermined quantities to allow detection of any dilution, contamination or other alteration of the composition.

[0131] It will be recognized that certain of the additives referenced above as suitable for the non-refrigerant component have been identified as potential refrigerants. However, in accordance with this invention, when these additives are used, they are not present at an amount that would affect the novel and basic characteristics of the refrigerant mixtures of this invention.

[0132] In some embodiments, the refrigerant compositions disclosed herein may be prepared by any convenient method to combine the desired amounts of the individual components as is standard in the art. A preferred method is to weigh the desired component amounts and thereafter combine the components in an appropriate vessel. Agitation may be used, if desired.

EXAMPLES

[0133] The invention will be described in greater detail by way of specific examples. The following examples are offered for illustrative purposes, and are not intended to limit the invention in any manner. Those of skill in the art will readily recognize a variety of non-critical parameters which can be changed or modified to yield essentially the same results.

Example 1

[0134] A mixture of 1-chloro-2,2-difluoroethylene (HCFO-1122 (30 g)) with 1000 ppm air and 500 ppm moisture is heated to 50 °C in a 210 mL shaker tube for two weeks. The shaker tube is cooled to room temperature (rt) and 30 mL deionized water is added to the vessel. After phase separation, the water is tested for fluoride

and chloride using ion chromatography and pH using pH meter. The results of exemplary 1-chloro-2,2-difluoroethylene + stabilizer compositions are listed in Table 1. N/D = not detected.

TABLE 1.

Example	Stabilizer	Air (ppm)	Moisture (ppm)	T (°C)	Time	F ⁻	Cl ⁻	pH
Control 1	None	1000	500	50	2 weeks	300	286	1.1
1	meta-xylene (1000 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.8
2	ortho-xylene (1000 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.8
3	para-xylene (1000 ppm) + 1,2-epoxybutane (900 ppm)	1000	500	50	2 weeks	N/D	N/D	6.8
4	Thymol (500 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.8
5	Pinene (500 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.8
6	d-limonene (500 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.8

[0135] The following additional components are also identified in one or more more the compositions tested in Table 1: (E)-1-chloro-1,2-difluoroethene (E-1122a); (Z)-1-chloro-1,2-difluoroethene (Z-1122a); 1,2-dichloro-1,1-difluoroethane (R-132b); 2-chloro-1,1,1-trifluoroethane (R-133a); and 1-chloro-1,2,2,2-tetrafluoroethane (R-124).

Example 2.

[0136] A mixture of 1-chloro-1,2-difluoroethylene (HCFO-1122a, 1:1 E/Z mixture) (30 g) with 1000 ppm air and 500 ppm moisture is heated to 50 °C in a 210 mL shaker tube for two weeks. The shaker tube is cooled to room temperature and 30 mL deionized water is added to the vessel. After phase separation, the water is

tested for fluoride and chloride using ion chromatography and pH using pH meter. The results of exemplary 1-chloro-1,2-difluoroethylene + stabilizer compositions are listed in Table 2. N/D = not detected.

TABLE 2.

Example	Stabilizer	Air (ppm)	Moisture (ppm)	T (°C)	Time	F ⁻	Cl ⁻	pH
Control 1	None	1000	500	50	2 weeks	193	180	2
1	meta-xylene (1000 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.7
2	ortho-xylene (1000 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.7
3	para-xylene (1000 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.7
4	Thymol (500 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.7
5	Pinene (500 ppm) + 1,2-epoxybutane (900 ppm)	1000	500	50	2 weeks	N/D	N/D	6.7
6	d-limonene (500 ppm) + 1,2-epoxybutane (1000 ppm)	1000	500	50	2 weeks	N/D	N/D	6.7

[0137] The following additional components are also identified in one or more more the compositions tested in Table 2: 1-chloro-2,2-difluoroethylene (1122); (E)-1,2-dichloro-1,2-difluoroethylene (E-1112); (Z)-1,2-dichloro-1,2-difluoroethylene (Z-1112); 1-chloro-1,2,2-trifluoroethane (R-133); chlorotrifluoroethylene (R-1113); and 1-chloro-2,2,2-trifluoroethane (R-133a).

OTHER EMBODIMENTS

1. In some embodiments, the present application provides a composition comprising one or more chlorofluoroethylenes and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal

stabilizer, or any combination thereof; wherein each of the one or more chlorofluoroethylenes is independently selected from the group consisting of:

1,1,-dichloro-2,2-difluoroethylene;

chlorotrifluoroethylene;

1-chloro-2,2-difluoroethylene;

E-1-chloro-1,2-difluoroethylene;

Z-1-chloro-1,2-difluoroethylene;

E-1-chloro-2-fluoroethylene;

Z-1-chloro-2-fluoroethylene;

1-chloro-1-fluoroethylene;

1,2-dichloro-1-fluoroethylene; and

1,1-dichloro-2-fluoroethylene.

2. The composition of embodiment 1, wherein the chlorofluoroethylene is selected from the group consisting of 1-chloro-2,2-difluoroethylene and 1-chloro-1,2-difluoroethylene.
3. The composition of embodiment 1, wherein the chlorofluoroethylene is 1-chloro-2,2-difluoroethylene.
4. The composition of embodiment 3, wherein the 1-chloro-1,2-difluoroethylene is (E)-1-chloro-1,2-difluoroethylene.
5. The composition of embodiment 3, wherein the 1-chloro-1,2-difluoroethylene is (Z)-1-chloro-1,2-difluoroethylene.
6. The composition of any one of embodiments 1 to 5, wherein the composition comprises the one or more chlorofluoroethylenes and an antioxidant.
7. The composition of embodiment 6, wherein the antioxidant is selected from a terpene, butylated hydroxytoluene, butylated hydroxyanisole, *tert*-butylhydroquinone, propyl 3,4,5-trihydroxybenzoate, 2-phenyl-2-propanol, 1-(2,4,5-trihydroxyphenyl)-1-butanone, 4-methoxyphenol, bisphenol methane derivatives, 2,2'-methylene bis (4-methyl-6-*t*-butyl phenol, and 2-isopropyl-5-methylphenol.
8. The composition of any one of embodiments 1 to 5, wherein the composition comprises the one or more chlorofluoroethylenes and an acid scavenger.

9. The composition of embodiment 8, wherein the acid scavenger is selected from an epoxide and an amine.
10. The composition of embodiment 8 or 9, wherein the acid scavenger is epoxybutane.
11. The composition of any one of embodiments 1 to 5, wherein the composition comprises the one or more chlorofluoroethylenes and a metal stabilizer.
12. The composition of embodiment 11, wherein the metal stabilizer is selected from N,N'-bis(salicylidene)-1,2-propanediamine and benzotriazole.
13. The composition of any one of embodiments 1 to 5, wherein the composition comprises the one or more chlorofluoroethylenes, an antioxidant, and an acid scavenger.
14. The composition of any one of embodiments 1 to 5, wherein the composition comprises the one or more chlorofluoroethylenes, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene.
15. The composition of embodiment 1, wherein the composition comprises 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene.
16. The composition of embodiment 15, further comprising one or more additional compounds selected from:
 - (E)-1-chloro-1,2-difluoroethene (E-1122a);
 - (Z)-1-chloro-1,2-difluoroethene (Z-1122a);
 - 1,2-dichloro-1,1-difluoroethane (R-132b);
 - 2-chloro-1,1,1-trifluoroethane (R-133a); and
 - 1-chloro-1,2,2,2-tetrafluoroethane (R-124).
17. The composition of embodiment 1, wherein the composition comprises 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene.
18. The composition of embodiment 17, further comprising one or more additional compounds selected from:
 - 1-chloro-2,2-difluoroethylene (1122);
 - (E)-1,2-dichloro-1,2-difluoroethylene (E-1112);

(Z)-1,2-dichloro-1,2-difluoroethylene (Z-1112);

1-chloro-1,2,2-trifluoroethane (R-133);

chlorotrifluoroethylene (R-1113); and

1-chloro-2,2,2-trifluoroethane (R-133a).

19. The composition of any one of embodiments 1 to 5, consisting essentially of the one or more chlorofluoroethylenes and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.
20. The composition of any one of embodiments 1 to 5, consisting of the one or more chlorofluoroethylenes and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.
21. The composition of embodiment 16, consisting essentially of the 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene; and the one or more additional compounds.
22. The composition of embodiment 16, consisting of the 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene; and the one or more additional compounds.
23. The composition of embodiment 18, consisting essentially of the 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene; and the one or more additional compounds.
24. The composition of embodiment 18, consisting of the 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene; and the one or more additional compounds.
25. The composition of any one of embodiments 1 to 24, wherein said one or more stabilizer components is present in the composition at a concentration of about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about

1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, or about 1500 ppm.

26. The composition of any one of embodiments 1 to 25, wherein said one or more stabilizer components is present in the composition at a concentration of X to Y ppm, wherein:

a. X is selected from the group consisting of about 0.5 ppm, about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, and about 1400 ppm; and

b. Y is selected from the group consisting of about 30 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 200 ppm, about 300 ppm, about 400 ppm, about 500 ppm, about 600 ppm, about 700 ppm, about 800 ppm, about 900 ppm, about 1000 ppm, about 1100 ppm, about 1200 ppm, about 1300 ppm, about 1400 ppm, and about 1500 ppm.

27. In some embodiments, the present application provides a process for producing cooling, comprising condensing the composition of any one of embodiments 1 to 26 and thereafter evaporating said composition in the vicinity of a body to be cooled.

28. In some embodiments, the present application provides a process for producing heating, comprising evaporating the composition of any one of embodiments 1 to 26 and thereafter condensing said composition in the vicinity of a body to be heated.

29. In some embodiments, the present application provides an air conditioning system, heat pump system, chiller system, or refrigeration system comprising the composition of any one of embodiments 1 to 26.

30. The air conditioning system, heat pump system, chiller system, or refrigeration system of embodiment 29, wherein the system comprises an evaporator, compressor, condenser, and expansion device.

31. In some embodiments, the present application provides a method for replacing an incumbent refrigerant in an air conditioning system, heat pump

system, chiller system, or refrigeration system, said method comprising providing the composition of any one of embodiments 1 to 26.

32. The method of embodiment 31, wherein the incumbent refrigerant is selected from the group consisting of R-123, R-245fa, R-514A, R-1233zdE, and R-1224ydZ.

33. The composition of any of embodiments 1 to 26, wherein the composition is free of or substantially free of Group A Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.

[0138] It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims. It should be appreciated by those persons having ordinary skill in the art(s) to which the present invention relates that any of the features described herein in respect of any particular aspect and/or embodiment of the present invention can be combined with one or more of any of the other features of any other aspects and/or embodiments of the present invention described herein, with modifications as appropriate to ensure compatibility of the combinations. Such combinations are considered to be part of the present invention contemplated by this disclosure.

CLAIMS

What is claimed is:

1. A composition comprising one or more chlorofluoroethylenes and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof; wherein each of the one or more chlorofluoroethylenes is independently selected from the group consisting of:
trichlorofluoroethylene;
1,1,-dichloro-2,2-difluoroethylene;
chlorotrifluoroethylene;
1-chloro-2,2-difluoroethylene;
E-1-chloro-1,2-difluoroethylene;
Z-1-chloro-1,2-difluoroethylene;
E-1-chloro-2-fluoroethylene;
Z-1-chloro-2-fluoroethylene;
1-chloro-1-fluoroethylene;
1,2-dichloro-1-fluoroethylene; and
1,1-dichloro-2-fluoroethylene.
2. The composition of claim 1, wherein the chlorofluoroethylene is selected from the group consisting of 1-chloro-2,2-difluoroethylene and 1-chloro-1,2-difluoroethylene.
3. The composition of claim 1, wherein the chlorofluoroethylene is 1-chloro-2,2-difluoroethylene.
4. The composition of claim 1, wherein the chlorofluoroethylene is 1-chloro-1,2-difluoroethylene.
5. The composition of claim 1, wherein the 1-chloro-1,2-difluoroethylene is (E)-1-chloro-1,2-difluoroethylene.
6. The composition of claim 1, wherein the 1-chloro-1,2-difluoroethylene is (Z)-1-chloro-1,2-difluoroethylene.

7. The composition of claim 1, wherein the composition comprises the one or more chlorofluoroethylenes and an antioxidant.
8. The composition of claim 1, wherein the antioxidant is selected from a terpene, butylated hydroxytoluene, butylated hydroxyanisole, *tert*-butylhydroquinone, propyl 3,4,5-trihydroxybenzoate, 2-phenyl-2-propanol, 1-(2,4,5-trihydroxyphenyl)-1-butanone, 4-methoxyphenol, bisphenol methane derivatives, 2,2'-methylene bis (4-methyl-6-*t*-butyl phenol, and 2-isopropyl-5-methylphenol.
9. The composition of claim 1, wherein the composition comprises the one or more chlorofluoroethylenes and an acid scavenger.
10. The composition of claim 1, wherein the acid scavenger is selected from an epoxide and an amine.
11. The composition of claim 1, wherein the acid scavenger is epoxybutane.
12. The composition of claim 1, wherein the composition comprises the one or more chlorofluoroethylenes and a metal stabilizer.
13. The composition of claim 1, wherein the metal stabilizer is selected from N,N'-bis(salicylidene)-1,2-propanediamine and benzotriazole.
14. The composition of claim 1, wherein the composition comprises the one or more chlorofluoroethylenes, an antioxidant, and an acid scavenger.
15. The composition of claim 1, wherein the composition comprises the one or more chlorofluoroethylenes, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene.
16. The composition of claim 1, wherein the composition comprises 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene.
17. The composition of claim 16, further comprising one or more additional compounds selected from:
 - (E)-1-chloro-1,2-difluoroethene (E-1122a);
 - (Z)-1-chloro-1,2-difluoroethene (Z-1122a);
 - 1,2-dichloro-1,1-difluoroethane (R-132b);

2-chloro-1,1,1-trifluoroethane (R-133a); and

1-chloro-1,2,2,2-tetrafluoroethane (R-124).

18. The composition of claim 1, wherein the composition comprises 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, and one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, and pinene.
19. The composition of claim 18, further comprising one or more additional compounds selected from:
 - 1-chloro-2,2-difluoroethylene (1122);
 - (E)-1,2-dichloro-1,2-difluoroethylene (E-1112);
 - (Z)-1,2-dichloro-1,2-difluoroethylene (Z-1112);
 - 1-chloro-1,2,2-trifluoroethane (R-133);
 - chlorotrifluoroethylene (R-1113); and
 - 1-chloro-2,2,2-trifluoroethane (R-133a).
20. The composition of claim 1, consisting essentially of the one or more chlorofluoroethylenes and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.
21. The composition of claim 1, consisting of the one or more chlorofluoroethylenes and one or more stabilizer components selected from an antioxidant, an acid scavenger, and a metal stabilizer, or any combination thereof.
22. The composition of claim 17, consisting essentially of the 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene; and the one or more additional compounds.
23. The composition of claim 17, consisting of the 1-chloro-2,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene; and the one or more additional compounds.

24. The composition of claim 19, consisting essentially of the 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene; and the one or more additional compounds.
25. The composition of claim 19, consisting of the 1-chloro-1,2-difluoroethylene, 1,2-epoxybutane, the one or more antioxidants selected from meta-xylene, ortho-xylene, para-xylene, thymol, d-limonene, and pinene; and the one or more additional compounds.
26. A process for producing cooling, comprising condensing the composition of claim 1 and thereafter evaporating said composition in the vicinity of a body to be cooled.
27. A process for producing heating, comprising evaporating the composition of claim 1 and thereafter condensing said composition in the vicinity of a body to be heated.
28. An air conditioning system, heat pump system, chiller system, or refrigeration system comprising the composition of claim 1.
29. The air conditioning system, heat pump system, chiller system, or refrigeration system of claim 28, wherein the system comprises an evaporator, compressor, condenser, and expansion device.
30. A method for replacing an incumbent refrigerant in an air conditioning system, heat pump system, chiller system, or refrigeration system, said method comprising providing the composition of claim 1 in place of the incumbent refrigerant.
31. The method of claim 30, wherein the incumbent refrigerant is selected from the group consisting of R-123, R-245fa, R-514A, R-1233zdE, and R-1224ydZ.
32. The composition of claim 1, wherein the composition is free of or substantially free of Group A Fluorinated Substances, and wherein degradation products of the composition are free of or substantially free of Group A Fluorinated Substances.