

CLAIMS

1. A composition comprising:
- (a) from about 2 to about 15 weight % of 1,1-difluoroethene (R-1132a);
 - 5 (b) from about 20 to about 60 weight % of difluoromethane (R-32);
 - (c) from about 25 to about 70 weight % of 2,3,3,3-tetrafluoropropene (R-1234yf); and
 - (d) from about 2 to about 12 weight % of carbon dioxide (CO₂, R-744);
- based on the total weight of the composition.
- 10
2. A composition according to claim 1, wherein the composition comprises:
- (a) from about 4 to about 10 weight % of R-1132a;
 - (b) from about 30 to about 48 weight % of R-32;
 - 15 (c) from about 34 to about 64 weight % of R-1234yf; and
 - (d) from about 2 to about 8 weight % of CO₂;
- based on the total weight of the composition.
- 20
3. A composition according to claim 1 or claim 2, wherein the composition comprises from about 4 or 5 or 6 to about 10 weight % of R-1132a, preferably from about 4 or 5 or 6 to about 9 weight %, such as from about 4 or 5 or 6 to about 8 weight % based on the total weight of the composition.
- 25
4. A composition according to claims 1 to 3, wherein the composition comprises from about 32 to about 44 weight % of R-32, preferably from about 36 to about 44 weight %, such as from about 36 to about 40 weight % based on the total weight of the composition.
- 30
5. A composition according to claims 1 to 4, wherein the composition comprises from about 34 to about 60 weight % of R-1234yf, preferably from about 39 to about 56 weight %, such as from about 43 to about 54 weight %, for example from about 43 to about 51 weight % based on the total weight of the composition.

- 6 A composition according to claims 1 to 5, wherein the composition comprises from about 2 or 3 to about 7 weight % of CO₂, such as from about 3 or 4 to about 6 weight %, for example from about 3 to about 5 weight % based on the total weight of the composition.
- 5 7. A composition according to claims 1 to 6, wherein the composition comprises:
- about 6 weight % R-1132a, about 40 weight % R-32, about 51 weight % R-1234yf and about 3 weight % CO₂;
- about 7 weight % R-1132a, about 36 weight % R-32, about 54 weight % R-1234yf and about 3 weight % CO₂;
- 10 about 9 weight % R-1132a, about 44 weight % R-32, about 43 weight % R-1234yf and about 4 weight % CO₂; or
- about 7 weight % R-1132a, about 30 weight % R-32, about 60 weight % R-1234yf and about 3 weight % CO₂;
- 15 based on the total weight of the composition.
8. A composition according to claims 1 to 7, wherein the manufacturing tolerances are +1 / -0.5 weight % CO₂; +0.5 / -1 weight % R-1132a; ±1 weight % R-32; ±2 weight % R-1234yf.
- 20 9. A composition according to claims 1 to 8, wherein the Worst-Case Formulation for Flammability (WCFF) of the composition in accordance with ASHRAE Standard 34 Appendix B has a molar volume concentration of R-1132a which is less than about 35% v/v and preferably less than about 30% v/v based on the total volume of the composition.
- 25 10. A composition comprising 1,1-difluoroethylene (R-1132a), difluoromethane (R-32), 2,3,3,3-tetrafluoropropene (R-1234yf) and at least one compound selected from the group consisting of: pentafluoroethane (R-125), 1,1-difluoroethane (R-152a), 1,1,1,2-tetrafluoroethane (R-134a), trans-1,3,3,3-tetrafluoropropene (R-1234ze(E)) and 1,1,1,2,3,3,3-heptafluoropropane (R-227ea), optionally wherein the composition comprises at least one further compound selected from the group consisting of trifluoroethylene (R-1123), propane (R-290), propylene (R-1270), isobutane (R-600a) and carbon dioxide (CO₂, R-744).
- 30 11. A composition according to claim 10, wherein the composition comprises R-1132a, R-32 and R-1234yf in a combined amount of from about 1 to about 99 weight %, optionally from about 1 to about 90 weight %, preferably from about 1 to about 80 weight %, such as from
- 35

about 1 to about 75 weight %, for example from about 1 to about 70 weight %, based on the total weight of the composition.

12. A composition according to claim 10 or 11, wherein the composition comprises CO₂ in an amount of from about 1 to about 30 weight %, for example from about 2 to about 20 weight %.

13. A composition according to any of claims 10 to 12, wherein the composition comprises R-1123 in an amount of from about 1 to about 30 weight %, for example from about 2 or 5 to about 20 weight %.

14. A composition according to any of claims 10 to 13, wherein the composition comprises R-134a in an amount of from about 1 to about 40 weight %, for example from about 2 to about 30 weight %.

15. A composition according to any of claims 10 to 14, wherein the composition comprises R-125 in an amount of from about 1 to about 20 weight %, for example from about 2 to about 15 weight %.

16. A composition according to any of claims 10 to 15, wherein the composition comprises R-1234ze(E) in an amount of from about 1 to about 40 weight %, for example from about 2 to about 30 weight %.

17. A composition according to any of claims 10 to 16, wherein the composition comprises R-152a in an amount of from about 1 to about 30 weight %, for example from about 2 to about 20 weight %.

18. A composition according to any of claims 10 to 17, wherein the composition comprises R-600a in an amount of from about 1 to about 20 weight %, such as from about 1 to about 10 weight %, preferably from about 1 to about 5 weight %.

19. A composition according to any of claims 10 to 18, wherein the composition comprises R-290 in an amount of from about 1 to about 20 weight %, such as from about 1 to about 10 weight %, preferably from about 1 to about 5 weight %.

20. A composition according to any of claims 10 to 19, wherein the composition comprises R-1270 in an amount of from about 1 to about 20 weight %, such as from about 1 to about 10 weight %, preferably from about 1 to about 5 weight %.
- 5 21. A composition according to any claims 10 to 20, wherein the composition comprises:
 R-1132a, R-32, R-1234yf and R-152a;
 R-1132a, R-32, R-1234yf and R-134a;
 R-1132a, R-32, R-1234yf and R-1234ze(E);
 R-1132a, R-32, R-1234yf and R-125; or
 10 R-1132a, R-32, R-1234yf and R-227ea.
22. A composition according to claims 10 to 20, wherein the composition comprises:
 R-1132a, R-32, R-1234yf, CO₂ and R-1234ze(E);
 R-1132a, R-32, R-1234yf, CO₂ and R-125;
 15 R-1132a, R-32, R-1234yf, CO₂ and R-152a;
 R-1132a, R-32, R-1234yf, CO₂ and R-134a;
 R-1132a, R-32, R-1234yf, CO₂ and R-227ea;
 R-1132a, R-32, R-1234yf, R-1123 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-1123 and R-125;
 20 R-1132a, R-32, R-1234yf, R-1123 and R-152a;
 R-1132a, R-32, R-1234yf, R-1123 and R-134a;
 R-1132a, R-32, R-1234yf, R-1123 and R-227ea;
 R-1132a, R-32, R-1234yf, R-290 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-290 and R-125;
 25 R-1132a, R-32, R-1234yf, R-290 and R-152a;
 R-1132a, R-32, R-1234yf, R-290 and R-134a;
 R-1132a, R-32, R-1234yf, R-290 and R-227ea;
 R-1132a, R-32, R-1234yf, R-1270 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-1270 and R-125;
 30 R-1132a, R-32, R-1234yf, R-1270 and R-152a;
 R-1132a, R-32, R-1234yf, R-1270 and R-134a;
 R-1132a, R-32, R-1234yf, R-1270 and R-227ea;
 R-1132a, R-32, R-1234yf, R-600A and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-600A and R-125;
 35 R-1132a, R-32, R-1234yf, R-600A and R-152a;
 R-1132a, R-32, R-1234yf, R-600A and R-134a;
 R-1132a, R-32, R-1234yf, R-600A and R-227ea;

- R-1132a, R-32, R-1234yf, R-1234ze(E) and R-125;
 R-1132a, R-32, R-1234yf, R-1234ze(E) and R-152a;
 R-1132a, R-32, R-1234yf, R-1234ze(E) and R-134a;
 R-1132a, R-32, R-1234yf, R-1234ze(E) and R-227ea;
 5 R-1132a, R-32, R-1234yf, R-125 and R-152a;
 R-1132a, R-32, R-1234yf, R-125 and R-134a;
 R-1132a, R-32, R-1234yf, R-125 and R-227ea;
 R-1132a, R-32, R-1234yf, R-152a and R-134a;
 R-1132a, R-32, R-1234yf, R-152a and R-227ea; or
 10 R-1132a, R-32, R-1234yf, R-134a; and R-227ea.
23. A composition according to any of claims 10 to 20, wherein the composition comprises:
 R-1132a, R-32, R-1234yf, CO₂, R-1123 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, CO₂, R-1123 and R-125;
 15 R-1132a, R-32, R-1234yf, CO₂, R-1123 and R-152a;
 R-1132a, R-32, R-1234yf, CO₂, R-1123 and R-134a;
 R-1132a, R-32, R-1234yf, CO₂, R-1123 and R-227ea;
 R-1132a, R-32, R-1234yf, CO₂, R-290 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, CO₂, R-290 and R-125;
 20 R-1132a, R-32, R-1234yf, CO₂, R-290 and R-152a;
 R-1132a, R-32, R-1234yf, CO₂, R-290 and R-134a;
 R-1132a, R-32, R-1234yf, CO₂, R-290 and R-227ea;
 R-1132a, R-32, R-1234yf, CO₂, R-1270 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, CO₂, R-1270 and R-125;
 25 R-1132a, R-32, R-1234yf, CO₂, R-1270 and R-152a;
 R-1132a, R-32, R-1234yf, CO₂, R-1270 and R-134a;
 R-1132a, R-32, R-1234yf, CO₂, R-1270 and R-227ea;
 R-1132a, R-32, R-1234yf, CO₂, R-600a and R-1234ze(E);
 R-1132a, R-32, R-1234yf, CO₂, R-600a and R-125;
 30 R-1132a, R-32, R-1234yf, CO₂, R-600a and R-152a;
 R-1132a, R-32, R-1234yf, CO₂, R-600a and R-134a;
 R-1132a, R-32, R-1234yf, CO₂, R-600a and R-227ea;
 R-1132a, R-32, R-1234yf, R-1234ze(E), R-125 and R-152a;
 R-1132a, R-32, R-1234yf, R-1234ze(E), R-125 and R-134a;
 35 R-1132a, R-32, R-1234yf, R-1234ze(E), R-125 and R-227ea;
 R-1132a, R-32, R-1234yf, R-1234ze(E), R-152a and R-134a;
 R-1132a, R-32, R-1234yf, R-1234ze(E), R-152a and R-227ea;

- R-1132a, R-32, R-1234yf, R-1234ze(E), R-134a and R-227ea;
 R-1132a, R-32, R-1234yf, R-125, R-134a and R-227ea;
 R-1132a, R-32, R-1234yf, R-125, R-134a and R-152a;
 R-1132a, R-32, R-1234yf, R-125, R-152a and R-227ea;
 5 R-1132a, R-32, R-1234yf, R-227ea, R-152a and R-134a;
 R-1132a, R-32, R-1234yf, R-1123, R-290 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-1123, R-290 and R-125;
 R-1132a, R-32, R-1234yf, R-1123, R-290 and R-152a;
 R-1132a, R-32, R-1234yf, R-1123, R-290 and R-134a;
 10 R-1132a, R-32, R-1234yf, R-1123, R-290 and R-227ea;
 R-1132a, R-32, R-1234yf, R-1123, R-1270 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-1123, R-1270 and R-125;
 R-1132a, R-32, R-1234yf, R-1123, R-1270 and R-152a;
 R-1132a, R-32, R-1234yf, R-1123, R-1270 and R-134a;
 15 R-1132a, R-32, R-1234yf, R-1123, R-1270 and R-227ea;
 R-1132a, R-32, R-1234yf, R-1123, R-600a and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-1123, R-600a and R-125;
 R-1132a, R-32, R-1234yf, R-1123, R-600a and R-152a;
 R-1132a, R-32, R-1234yf, R-1123, R-600a and R-134a;
 20 R-1132a, R-32, R-1234yf, R-1123, R-600a and R-227ea;
 R-1132a, R-32, R-1234yf, R-290, R-1270 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-290, R-1270 and R-125;
 R-1132a, R-32, R-1234yf, R-290, R-1270 and R-152a;
 R-1132a, R-32, R-1234yf, R-290, R-1270 and R-134a;
 25 R-1132a, R-32, R-1234yf, R-290, R-1270 and R-227ea;
 R-1132a, R-32, R-1234yf, R-290, R-600a and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-290, R-600a and R-125;
 R-1132a, R-32, R-1234yf, R-290, R-600a and R-152a;
 R-1132a, R-32, R-1234yf, R-290, R-600a and R-134a;
 30 R-1132a, R-32, R-1234yf, R-290, R-600a and R-227ea;
 R-1132a, R-32, R-1234yf, R-600a, R-1270 and R-1234ze(E);
 R-1132a, R-32, R-1234yf, R-600a, R-1270 and R-125;
 R-1132a, R-32, R-1234yf, R-600a, R-1270 and R-152a;
 R-1132a, R-32, R-1234yf, R-600a, R-1270 and R-134a; or
 35 R-1132a, R-32, R-1234yf, R-600a, R-1270 and R-227ea.

24. A composition according to any of claims 10 to 23 essentially of the stated components.

25. A composition according to any of claims 10 to 24, wherein the composition is less flammable than R-1132a alone, preferably wherein the composition has:
- a. a higher flammable limit
 - 5 b. a higher ignition energy; and/or
 - c. a lower flame velocity
- compared to R-1132a alone.
26. A composition according to any of claims 10 to 25 wherein the composition is non-
10 flammable, for example wherein the composition is non-flammable at ambient temperature, preferably wherein the composition is non-flammable at 60 °C.
27. A composition according to any of the preceding claims, wherein the composition has a temperature glide in an evaporator or condenser of less than about 15K, preferably less than
15 about 10K, for example less than about 6K such as less than about 5K, even more preferably less than about 4K.
28. A composition according to any of the preceding claims wherein the composition has a volumetric refrigeration capacity which is within about 15% of that of R-410A, preferably within
20 about 10% of R-410A.
29. A composition according to any of the preceding claims, wherein the operating condenser pressure in a condenser containing the composition is within about 10% of that of the condenser containing R-410A, preferably within about 5%.
25
30. A composition according to any of the preceding claims, wherein the operating condenser pressure in a condenser containing the composition is lower than that of the condenser containing R-410A.
31. A composition according to any of the preceding claims, wherein the composition has
30 a Global Warming Potential (GWP) of less than about 300, such as less than about 280.
32. A composition according to any of the preceding claims wherein the composition has a burning velocity of less than about 10 cm/s as measured by ASHRAE Standard 34.
33. A composition comprising a lubricant and a composition according to any of the preceding claims, optionally wherein the lubricant is selected from mineral oil, silicone oil, polyalkyl benzenes (PABs), polyol esters (POEs), polyalkylene glycols (PAGs), polyalkylene

glycol esters (PAG esters), polyvinyl ethers (PVEs), poly alpha-olefins and combinations thereof, preferably wherein the lubricant is selected from PAGs or POEs.

34. A composition comprising a stabiliser and a composition according to any of the preceding claims, optionally wherein the stabiliser is selected from diene-based compounds, phosphates, phenol compounds and epoxides, and mixtures thereof.

35. A composition comprising a flame retardant and a composition according to any of the preceding claims, optionally wherein the flame retardant is selected from the group consisting of tri-(2-chloroethyl)-phosphate, (chloropropyl) phosphate, tri-(2,3-dibromopropyl)-phosphate, tri-(1,3-dichloropropyl)-phosphate, diammonium phosphate, various halogenated aromatic compounds, antimony oxide, aluminium trihydrate, polyvinyl chloride, a fluorinated iodocarbon, a fluorinated bromocarbon, trifluoro iodomethane, perfluoroalkyl amines, bromo-fluoroalkyl amines and mixtures thereof.

36. A heat transfer device containing a composition as defined in any one of claims 1 to 35, preferably wherein the heat transfer device is a refrigeration device, preferably wherein the heat transfer device comprises a residential or commercial air conditioning system, a heat pump or a commercial or industrial refrigeration system.

37. A sprayable composition comprising material to be sprayed and a propellant comprising a composition as defined in any of claims 1 to 35.

38. A method for cooling an article which comprises condensing a composition defined in any of claims 1 to 35 and thereafter evaporating the composition in the vicinity of the article to be cooled.

39. A method for heating an article which comprises condensing a composition as defined in any one of claims 1 to 35 in the vicinity of the article to be heated and thereafter evaporating the composition.

40. A method for extracting a substance from biomass comprising contacting biomass with a solvent comprising a composition as defined in any of claims 1 to 35 and separating the substance from the solvent.

41. A method of cleaning an article comprising contacting the article with a solvent comprising a composition as defined in any of claims 1 to 35.

42. A method of extracting a material from an aqueous solution or from a particulate solid matrix comprising contacting the aqueous solution or the particulate solid matrix with a solvent comprising a composition as defined in any of claims 1 to 35 and separating the material from the solvent.

43. A mechanical power generation device containing a composition as defined in any of claims 1 to 35, preferably wherein the mechanical power generating is adapted to use a Rankine Cycle or modification thereof to generate work from heat.

44. A method of retrofitting a heat transfer device comprising the step of removing an existing heat transfer composition, and introducing a composition as defined in any one of claims 1 to 35, preferably wherein the heat transfer device is a commercial or industrial refrigeration device, a heat pump, or a residential or commercial air conditioning system.

45. A method for reducing the environmental impact arising from the operation of a product comprising an existing compound or composition, the method comprising replacing at least partially the existing compound or composition with a composition as defined in any one of claims 1 to 35, optionally wherein the use of the composition of the invention results in a lower Total Equivalent Warming Impact, and/or a lower Life-Cycle Carbon Production than is attained by use of the existing compound or composition, preferably wherein the method is carried out on a product from the fields of air-conditioning, refrigeration, heat transfer, aerosols or sprayable propellants, gaseous dielectrics, flame suppression, solvents, cleaners, topical anaesthetics, and expansion applications, such as wherein the product is selected from a heat transfer device, a sprayable composition, a solvent or a mechanical power generation device, preferably a heat transfer device, for example wherein the product is a heat transfer device, preferably a residential or commercial air conditioning system, a heat pump or a commercial or industrial refrigeration system.

46. A method according to claims 44 or 45 wherein the existing compound or composition is a heat transfer composition, preferably wherein the heat transfer composition is a refrigerant selected from R-410A, R-454B, R-452B and R-32.

47. A composition comprising:

- (a) from about 6 to about 18 weight % of 1,1-difluoroethene (R-1132a);
- (b) from about 20 to about 65 weight % of difluoromethane (R-32);

(c) from about 15 to about 60 weight % of 2,3,3,3-tetrafluoropropene (R-1234yf) based on the total weight of the composition.

48. A composition according to claim 47 comprising from about 6 to about 15 weight % of R-1132a, preferably from about 6 to about 12 weight %, such as from about 7 to about 10 weight % based on the total weight of the composition.

49. A composition according to claim 47 or 48 comprising from about 25 to about 65 weight % of R-32, preferably from about 35 to about 60 weight %, such as from about 40 to about 60 weight % based on the total weight of the composition.

50. A composition according to claims 47 to 49 comprising from about 20 to about 60 weight % of R-1234yf, preferably from about 25 to about 55 weight %, such as from about 30 to about 55 weight % based on the total weight of the composition.

51. A composition according to any of claims 47 to 50, wherein the composition comprises:

about 7 weight % R-1132a, about 50 weight % R-32 and about 43 weight % R-1234yf;
about 7 weight % R-1132a, about 55 weight % R-32 and about 38 weight % R-1234yf;
about 8 weight % R-1132a, about 40 weight % R-32 and about 52 weight % R-1234yf;
about 8 weight % R-1132a, about 60 weight % R-32 and about 32 weight % R-1234yf; or
about 10 weight % R-1132a, about 55 weight % R-32 and about 35 weight % R-1234yf;
based on the total weight of the composition.

52. A composition according to any of claims 47 to 51, wherein the composition comprises from about 6 to about 7 weight % R-1132a.

53. A composition according to any of claims 47 to 52, wherein the composition has a volumetric cooling capacity that is within about 15% of that of R-410A, preferably within about 10% of that of R-410A.

54. A composition according to any of claims 47 to 53, wherein the composition has a temperature glide in an evaporator or condenser of less than about 10K, preferably less than about 7K, such as less than about 5K.

55. A composition according to any of claims 47 to 54, wherein the operating condenser pressure in a condenser containing the composition is within about 10% of that of the condenser containing R-410A, preferably within about 5%.
- 5 56. A composition according to any of claims 47 to 55, wherein the operating condenser pressure in a condenser containing the composition is lower than of that of the condenser containing R-410A.
57. A composition according to any of claims 47 to 56, wherein the composition has a
10 Global Warming Potential (GWP) of less than about 300, such as less than about 280.
58. A composition according to any of claims 47 to 57, wherein the Worst-Case Formulation for Flammability (WCFF) of the composition in accordance with ASHRAE Standard 34 Appendix B has a molar volume concentration of R-1132a which is less than about 35% v/v
15 and preferably less than about 30% v/v based on the total volume of the composition.
59. A composition according to any of claims 47 to 58, wherein the composition has a compressor discharge temperature which is within about 10K of that of R-410A, such as within about 5K of that of R-410A.
20
60. A composition according to any of claims 47 to 59 wherein the manufacturing tolerances of the composition are +0.5 / -1 weight % R-1132a; ± 1 weight % R-32; ± 1.5 weight % R-1234yf.]
- 25 61. Use of a composition comprising a POE lubricant and a composition according to claims 47 to 60 as a replacement for an existing heat transfer composition in a commercial air conditioning system.
62. Use of a composition comprising a POE lubricant and a composition according to
30 claims 47 to 60 as a replacement for an existing heat transfer composition in a commercial refrigeration system.
63. The use according to claim 61 or 62 wherein the existing heat transfer composition is R-410A.
35
64. A vessel comprising a composition according to any of claims 47 to 60 in an amount of up to about 90% v/v based on the total volume of the vessel, wherein the vessel has a

temperature of about -40°C and wherein the composition comprises R-1132a in a molar volume concentration of less than about 35% v/v, preferably less than about 30% v/v, based on the total volume of the composition, preferably wherein the vessel is a cylinder.