

USE OF PERFLUOROALKYL SUBSTANCE-FREE HEAT TRANSFER FLUIDS IN SUBSTRATE PROCESSING TOOLS

BACKGROUND

[0001] Electronic device fabrication involves many steps of material deposition, patterning, and removal to form integrated circuits on substrates. Atomic layer deposition (ALD), chemical vapor deposition (CVD), and pulsed laser deposition (PLD) are examples of methods for depositing thin films of materials on substrates. Dry etching techniques such as reactive ion etching (RIE) and atomic layer etching (ALE) are examples of methods for removing materials from substrates.

[0002] Processing tools used to perform these and other processing techniques can include a number of systems to enable control of processing conditions. Among the variables that can be controlled in some substrate processing is temperature. Various components in a processing tool can utilize temperature control systems to maintain the components within a desired temperature range. Example components that can utilize temperature control systems include substrate pedestals, showerheads for dispensing processing chemicals into a processing chamber, and processing chamber walls.

[0003] Heat transfer fluids are often used as part of a temperature control system in a processing tool. Heat transfer fluids can be used to transfer heat to or from a component in a processing tool by circulating the heat transfer fluid through a loop including the component and a heat exchanger spatially separated from the component.

SUMMARY

[0004] This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter. Furthermore, the claimed subject matter is not limited to implementations that solve any or all disadvantages noted in any part of this disclosure.

[0005] Examples are disclosed that relate to PFAS-free-containing fluids that can be used for heat transfer in processing tools for use in electronics device fabrication. One example provides a processing tool for processing substrates. The processing tool comprises a heat transfer system comprising a heat transfer fluid circulation path and a

perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid disposed within the heat transfer fluid circulation path, wherein the PFAS-free heat transfer fluid comprises an ester lacking hydrogens on a beta carbon of an alcohol moiety of the ester.

[0006] In some such examples, the ester lacking hydrogens on the beta carbon comprises a neopentyl polyol ester.

[0007] Alternatively or additionally, in some such examples, an acyl group of the neopentyl polyol ester comprises 5 to 10 carbon atoms.

[0008] Alternatively or additionally, in some such examples, the acyl group of the neopentyl polyol ester comprises a fully saturated acyl group.

[0009] Alternatively or additionally, in some such examples, the acyl group of the neopentyl polyol ester comprises an unbranched alkane.

[0010] Alternatively or additionally, in some such examples, the neopentyl polyol ester comprises a plurality of identical acyl groups.

[0011] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more neopentyl polyol esters in a quantity of 90 to 99.6 mass percent.

[0012] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more of a triester of trimethylolethane, a triester of trimethylolpropane, or a tetraester of pentaerythritol.

[0013] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more aryl phosphate metal deactivators in a quantity of 0.1 to 5 mass percent.

[0014] Alternatively or additionally, in some such examples, the one or more aryl phosphate metal deactivators comprises tricresyl phosphate.

[0015] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more arylamine free radical scavengers in a quantity of 0.1 to 2 mass percent. Alternatively or additionally, in some such examples, the one or more arylamine free radical scavengers comprises one or more alkylated phenyl- α -naphthylamines.

[0016] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more sterically hindered phenolic free radical scavengers in a quantity of 0.02 to 0.5 mass percent.

[0017] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more hydroperoxide decomposers in a quantity of 0.05 to 1 mass percent.

[0018] Alternatively or additionally, in some such examples, the one or more hydroperoxide decomposers comprises didodecyl 3,3'-sulfanediyl dipropanoate.

[0019] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more aryl azole metal deactivators.

[0020] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises one or more polymeric tackifiers.

[0021] One example provides a processing tool for processing substrates. The processing tool comprises a heat transfer system comprising a heat transfer fluid circulation path and a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid disposed within the heat transfer fluid circulation path.

[0022] In some such examples, the PFAS-free heat transfer fluid comprises an aqueous fluid.

[0023] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises deionized water or a brine.

[0024] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a mixture of water and a polyhydric alcohol.

[0025] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a liquefied gas.

[0026] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a cryogenic liquid.

[0027] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a compressed gas.

[0028] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organic fluid.

[0029] Alternatively or additionally, in some such examples, the organic fluid comprises an organic ester.

[0030] Alternatively or additionally, in some such examples, the organic fluid comprises a polyalkylene glycol.

[0031] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organophosphorus material.

[0032] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organosilicon material.

[0033] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a surfactant.

[0034] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an ionic liquid.

[0035] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a metallic liquid.

[0036] Another example provides a method of operating a processing tool for processing substrates. The method comprises circulating a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid within a heat transfer fluid circulation path of the processing tool while processing a substrate using the processing tool.

[0037] In some such examples, the PFAS-free heat transfer fluid comprises an aqueous fluid.

[0038] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises deionized water or a brine.

[0039] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a mixture of water and a polyhydric alcohol.

[0040] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a liquefied gas.

[0041] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a cryogenic liquid.

[0042] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a compressed gas.

[0043] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organic fluid.

[0044] Alternatively or additionally, in some such examples, the organic fluid comprises an organic ester.

[0045] Alternatively or additionally, in some such examples, the organic fluid comprises a polyalkylene glycol.

[0046] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organophosphorus material.

[0047] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organosilicon material.

[0048] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a surfactant.

[0049] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an ionic liquid.

[0050] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a metallic liquid.

[0051] Another example provides a method of servicing a processing tool for processing substrates. The method comprises adding a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid to a heat transfer fluid circulation path of the processing tool.

[0052] In some such examples, the PFAS-free heat transfer fluid comprises an aqueous fluid.

[0053] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises deionized water or a brine.

[0054] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a mixture of water and a polyhydric alcohol.

[0055] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a liquefied gas.

[0056] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a cryogenic liquid.

[0057] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a compressed gas.

[0058] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organic fluid.

[0059] Alternatively or additionally, in some such examples, the organic fluid comprises an organic ester.

[0060] Alternatively or additionally, in some such examples, the organic fluid comprises a polyalkylene glycol.

[0061] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organophosphorus material.

[0062] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an organosilicon material.

[0063] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a surfactant.

[0064] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises an ionic liquid.

[0065] Alternatively or additionally, in some such examples, the PFAS-free heat transfer fluid comprises a metallic liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

[0066] FIG. 1 shows an example substrate processing tool comprising example thermal control systems.

[0067] FIG. 2 shows an example esterification reaction of neopentyl glycol with a carboxylic acid.

[0068] FIG. 3 shows an example neopentyl glycol diester.

[0069] FIG. 4 shows an example trimethylolpropane triester.

[0070] FIG. 5 shows an example pentaerythritol tetraester.

DETAILED DESCRIPTION

[0071] The term “aldehyde” as used herein generally represents a molecule in which a carbon atom is double bonded to an oxygen atom, bonded to a hydrogen atom, and bonded to another functional group.

[0072] The term “aliphatic” as used herein generally represents an organic compound that lacks delocalized pi bonding of aromatic molecules.

[0073] The term “amide” as used herein generally represents an organic compound that comprises a general formula of $R-C(=O)-NR'R''$, where R, R', and R'' represent any group or groups.

[0074] The term “amine” as used herein generally represents an organic compound that comprises a nitrogen atom with a lone pair of electrons and that is bonded to at least one organic moiety other than hydrogen.

[0075] The term “aromatic” as used herein generally represents an organic molecule comprising a cyclic structure with delocalized pi bonding.

[0076] The term “aqueous” as used herein generally represents a solution in which the solvent is water.

[0077] The term “autoignition temperature” as used herein generally represents a minimum temperature at which a substance in air must be heated to initiate self-sustaining combustion independent of the heat source.

[0078] The term “boiling point” as used herein generally represents the temperature at which a substance undergoes a phase change from a liquid to a gas phase.

[0079] The term “brine” as used herein generally represents a solution of a salt dissolved in water.

[0080] The term “burst point” as used herein generally represents a temperature at which a heat transfer fluid will freeze solid and expand. The burst point can be lower than the freezing point for heat transfer solutions such as glycol/water mixtures. The freezing point in such a heat transfer fluid is the temperature at which ice crystals first form. The burst point can be substantially lower than the freezing point.

[0081] The term “circulation path” as used herein generally represents a closed loop through which a flow of a heat transfer fluid is conducted.

[0082] The term “combustion products” as used herein generally represents chemical substances that are produced by burning another substance.

[0083] The term “decomposition products” as used herein generally represents chemical substances that are produced when another substance decomposes by a mechanism other than burning.

[0084] The term “deep eutectic solvent” as used herein generally represents a type of ionic fluid comprising two or more constituent substances capable of self-association to form a eutectic mixture with a melting point lower than the melting points of the individual constituent substances.

[0085] The term “deionized water” as used herein generally represents purified water produced by removing ions through an ion exchange process.

[0086] The term “ester” as used herein generally represents a compound having a general formula of $R-C(=O)-O-R'$, where R' is an organyl group.

[0087] The term “ester lacking hydrogens on the beta carbon” as used herein generally represents a compound having a general formula $C(CH_3)_x(CH_2O-C(=O)-R)_{4-x}$, where $2 \leq x \leq 4$ and R comprises an alkyl group, which may be identical or different on each acyl group. Examples include neopentylpolyol esters, such as neopentyl glycol diesters having a general formula $C(CH_3)_2(CH_2OCOR_1)(CH_2OCOR_2)$, trimethylolethane triesters having a general

formula $C(CH_3)(CH_2OCOR_1)(CH_2OCOR_2)(CH_2OCOR_3)$, trimethylolpropane triesters having a general formula $C(C_2H_5)(CH_2OCOR_1)(CH_2OCOR_2)(CH_2OCOR_3)$, and pentaerythritol tetraesters having a general formula $C(CH_2OCOR_1)(CH_2OCOR_2)(CH_2OCOR_3)(CH_2OCOR_4)$, where each of R_1 , R_2 , R_3 , and R_4 each independently represent an alkyl group.

[0088] The term “ether” as used herein generally represents a compound having a general formula of $R-O-R'$, where R and R' are aryl or hydrocarbyl groups. The term “hydrocarbyl group” generally represents a functional group derived by removal of a hydrogen from an alkane, alkene, or alkyne. The term “aryl group” generally represents a functional group derived from an aromatic ring.

[0089] The term “fatty acid” as used herein generally represents a carboxylic acid with an aliphatic chain, which can be saturated or unsaturated.

[0090] The term “fire point” as used herein generally represents the lowest temperature at which a vapor of a substance will continue to burn for at least five seconds after ignition by an open flame of standard dimension. The term “flash point” as used herein generally represents a lowest liquid temperature at which, under certain standardized conditions (e.g. as specified by ISO 2719:2016 – “Determination of Flash Point, Pensky-Martens Closed Cup Method”) a liquid gives off vapors in a quantity such as to be capable of forming an ignitable vapor/air mixture.

[0091] The term “heat transfer system” as used herein generally represents a system in which a heat transfer fluid flows between a heat exchanger and a component that is cooled or heated by the heat transfer fluid.

[0092] The term “heat transfer fluid” as used herein generally represents a fluid that receives heat from one location (e.g. a component in a processing tool) and transports the heat to a different location (e.g. a heat exchanger) in a heat transfer system.

[0093] The term “ionic liquid” as used herein generally represents a salt in the liquid state.

[0094] The term “ketone” as used herein generally represents a compound with the general formula of $R-C(=O)-R'$, where R and R' are organyl groups.

[0095] The term “liquefied gas” as used herein generally represents a liquid material that is a gas at standard temperature and pressure. Liquefied gases can be condensed by cooling or by pressure. The term “cryogenic liquid” generally represents

a liquified gas that is condensed by cooling. The term “compressed gas” generally represents a liquefied gas that is condensed by pressure.

[0096] The term “melting point” as used herein generally represents a temperature at which a solid/liquid phase change occurs for a substance.

[0097] The term “organophosphorus” as used herein generally represents organic compounds that contain phosphorus. The term “phosphate ester” generally represents an organophosphorus compound having the general structure of $P(=O)(OR)(OR')(OR'')$, where R, R' and R'' can be the same or different, and at least one of R, R' and R'' is an organyl group.

[0098] The term “organosilicon” as used herein generally represents compounds having carbon-silicon bonds.

[0099] The term “pour point” as used herein generally represents a lowest temperature at which a fluid, such as a wax or oil, will pour or flow when it is cooled, without stirring, under standard cooling conditions (e.g. as specified by ASTM D97-17b (2022), “Standard Test Method for Pour Point of Petroleum Products”).

[0100] The term “PFAS” as used herein generally represents all chemistries and materials that contain molecules with $-CF_2-$ and $-CF_3$.

[0101] The term “polyhydric alcohol” as used herein generally represents an alcohol comprising two or more hydroxyl groups. Example polyhydric alcohols include ethylene glycol, glycerol, propylene glycol, and 1,3-propanediol.

[0102] The term “polyalkylene glycol” as used herein generally represents homopolymers of ethylene oxide, propylene oxide, or butylene oxide, or copolymers of two or more of these materials.

[0103] The term “processing tool” as used herein generally represents a machine configured to perform processes on substrates in integrated circuit fabrication.

[0104] The term “salt” as used herein generally represents an ionic compound that can be in crystalline form when dried. Salts can be produced by a neutralization reaction between an acid and a base.

[0105] The term “substrate” as used herein generally represents a structure on which thin films can be formed and patterned in an integrated circuit fabrication process.

[0106] The term “surfactant” as used herein generally represents a compound decrease surface tension or interfacial tension between two materials, such as two liquids, a liquid and a solid, or a liquid and a gas.

[00107] As mentioned above, processing tools used in the fabrication of integrated circuits can use heat transfer fluids to control the temperatures of various systems of the tool. As examples, heat transfer fluids can be used to heat or cool substrate supports and showerheads in various processing tools, as well as to heat or cool processing chamber walls.

[00108] Processing tool temperature control systems often use heat transfer fluids comprising perfluorinated or polyfluorinated alkyl substances (PFAS). Many different PFAS heat transfer fluids are known. PFAS heat transfer fluids can have various advantageous properties. For example, PFAS heat transfer fluids are nonflammable, and thermally and chemically stable. PFAS heat transfer fluids also can have low acute toxicities, high dielectric strength & stable resistivities, and low pour points. Further, boiling points of PFAS heat transfer fluids can be tailored over a wide range. The chemical and thermal stability of PFAS heat transfer fluids provide for a long service life and low maintenance requirements.

[00109] However, the chemical and thermal stability of PFAS heat transfer fluids also pose problems. For example, PFAS heat transfer fluids are highly stable when they contaminate outside environments. PFAS heat transfer fluids can disperse in outside environments quickly, and degrade very slowly. As such, PFAS heat transfer fluids can accumulate in water and soils. Further, the PFAS heat transfer fluids can enter human food and water sources. Additionally, some volatile PFAS heat transfer fluids can be potent greenhouse gases. As such, the manufacture of PFAS-based heat transfer fluids is being phased out in many jurisdictions.

[00110] Accordingly, examples are disclosed that relate to PFAS-free heat transfer fluids that can be used for heat transfer in processing tools for use in electronics device fabrication. Prior to discussing these examples, an example processing tool 100 is described with reference to FIG. 1. Processing tool 100 can represent a deposition tool or an etching tool in various examples. Processing tool 100 comprises a processing chamber 102 and a pedestal 104 within the processing chamber 102. The pedestal 104 is configured to support a substrate 106 disposed within the processing chamber 102. The pedestal 104 comprises fluid channels 108 as a part of a heat transfer fluid circulation path through which a PFAS-free heat transfer fluid flows. The PFAS-free heat transfer fluid is circulated through fluid channels 108 by a pedestal temperature control system 110, as indicated by arrows 111a and 111b. The pedestal temperature control system 110 comprises a pump 112 to circulate the PFAS-free heat transfer fluid,

a heat exchanger 114, and the PFAS-free heat transfer fluid 115. The heat exchanger is configured to dissipate heat removed from the pedestal 104 by the heat transfer fluid. In other examples, the pedestal temperature control system 110 can include a heater to heat a heat transfer fluid for circulation to a pedestal to thereby transfer heat to the pedestal. In other examples, a heater can be omitted, or can be located elsewhere within processing chamber 102. In some examples, the substrate heater is configured to heat to a temperature of 50 °C to 650 °C. Further, in some examples, a pedestal temperature control system can include a heat pump operable to cool a heat transfer fluid below an ambient temperature.

[00111] The processing tool 100 further comprises a showerhead 116. A temperature of the showerhead 116 can be controlled using a showerhead temperature control system 118. The showerhead temperature control system 118 is configured to circulate a heat transfer fluid through channels (not shown) within the showerhead 116. As described above with regard to the pedestal temperature control system 110, the showerhead temperature control system 112 comprises a pump (not shown) to circulate a heat transfer fluid, and a heat exchanger (not shown) to remove heat from the heat transfer fluid. Further, in some examples, a showerhead temperature control system can include a heat pump operable to cool a heat transfer fluid below an ambient temperature.

[00112] The showerhead is fluidly connected to flow control hardware 120 further comprises flow control hardware 120. The flow control hardware 120 connects processing gas source(s) 122 to the processing chamber 102. The flow control hardware 120 can include any suitable components. Examples include mass flow controllers, valves, and conduits.

[00113] The processing tool 100 further comprises an exhaust system 124. The exhaust system 124 is configured to exhaust gases from the processing chamber 102. The exhaust system 124 can comprise any suitable hardware, including one or more low vacuum pumps and one or more high vacuum pumps. Together, flow control hardware 120 and exhaust system 124 can be operated to achieve a selected pressure and a selected mixture of processing gases in the processing chamber 102 during substrate processing.

[00114] The processing tool 100 further comprises a radiofrequency power source 126 that is electrically connected to showerhead 116. Radiofrequency power source 126 is configured to form a capacitively coupled plasma within processing

chamber 102, with the pedestal 104 as a counter electrode. In other examples, a radiofrequency power source can be used to form an inductive plasma. In yet further examples, a microwave power source can be used to form a plasma for processing substrates.

[00115] The processing tool 100 further includes include a matching network 128 for impedance matching of the radiofrequency power source 126. The radiofrequency power source 126 can be configured to provide radiofrequency energy of any suitable frequency and power. Examples frequencies include 400 kHz, 13.56 MHz, 27 MHz, 60 MHz, and 90 MHz. In some examples, the radiofrequency power source 126 is configured to operate at a plurality of different frequencies and/or powers.

[00116] In addition to the pedestal 104 and the showerhead 116, other components of the processing tool 100 can be thermally managed. As examples, FIG. 1 shows a chamber wall temperature control system 130 for cooling the walls of the processing chamber 102. FIG. 1 also shows an electronics temperature control system 132 for controlling the temperature of electronics 134 of the processing tool 100. In some examples, one or both of the chamber wall temperature control system 130 and the electronics temperature control system 132 can comprise a heat pump operable to cool a heat transfer fluid below an ambient temperature.

[00117] The processing tool 100 further comprises a controller 136 configured to control operation of the processing tool. The controller 136 is operatively coupled to other components of the processing tool to control the processing of substrates. For example, the controller 136 is operatively coupled to the pedestal temperature control system 110, the showerhead temperature control system 118, the chamber wall temperature control system 130, and the electronics temperature control system 132 to control the circulation of a heat transfer fluid though each of these temperature control systems. While processing tool 100 comprises temperature control systems for the pedestal 104, showerhead 118, walls of processing chamber 102, and electronics 134, in other examples a processing tool can comprise temperature control systems for a subset of these components and/or for additional components.

[00118] Depending upon a particular use context, a suitable PFAS-free heat transfer fluid can be selected based upon various combinations of desired properties, including safety, environmental impact, material compatibility with other processing tool materials, and thermophysical properties (e.g. phase change behavior).

[00119] Heat transfer fluid safety can depend upon any one or more of a number of material properties. Example material properties relevant to heat transfer fluid safety include combustibility, instability, and health hazards posed by exposure to the heat transfer fluid. Factors that relate to dangers posed by combustibility include autoignition temperature, fire point, flash point, combustion products, and energy release/thermal radiation due to combustion. Similarly, factors that relate to dangers posed by instability also include energy release and reaction/decomposition products. Factors that relate to health hazards posed by exposure include inhalation hazards, oral toxicity/carcinogenicity/etc., and dermal toxicity and sensitization. It can be desirable for a PFAS-free heat transfer fluid to have relatively low risks for such health hazards.

[00120] Factors that relate to environmental impact can include factors that relate to manufacture of the heat transfer fluids as well as factors that relate to use of the heat transfer fluids. Environmental impact factors that relate to the manufacture of the heat transfer fluids include the manufacture of precursors, waste generation, and embodied energy resulting from the manufacture. Environmental impact factors that relate to the use of the heat transfer fluids include ozone depletion, global warming, persistence, bioaccumulation, and aquatic toxicity. It can be desirable for a PFAS-free heat transfer fluid to have relatively low environmental impacts compared to other heat transfer fluid options.

[00121] Factors that relate to material compatibility can include the existence of suitable extinguishing agents, corrosive effects of the PFAS-free heat transfer fluid on metals in a heat transfer system, any alloying or dealloying caused by the PFAS-free heat transfer fluids, and degradation of polymers (e.g. o-rings, tubing, etc.) in a heat transfer system caused by a PFAS-free heat transfer fluids. Other factors that relate to material compatibility can include factors that relate to the stability of a PFAS-free heat transfer fluid. Such stability factors include thermal stability (i.e. stability when exposed to heat), oxidative stability (i.e. stability when exposed to oxidizing agents), and hydrolytic stability (i.e. stability when exposed to water). It can be desirable for a PFAS-free heat transfer fluid to be compatible with other materials that can be used in a heat transfer system and that are exposed to the PFAS-free heat transfer fluid, and to be stable when exposed to temperatures and other materials in a heat transfer system so that the PFAS-free heat transfer fluid does not decompose to an unsuitable degree under use conditions.

[00122] Thermophysical properties that can be factors in the selection of a PFAS-free heat transfer fluid include phase change behavior and thermal performance. Phase change behavior can include such factors as a burst point, a melting or pour point, a boiling point, a vapor pressure, and an enthalpy of vaporization. Thermal performance factors can include factors such as mass density (mass per unit volume), thermal conductivity, specific heat capacity, and dynamic viscosity.

[00123] Other properties than those listed above also can be taken into account when in the selection of a PFAS-free heat transfer fluid. Examples include electromagnetic properties, tribocharging properties (electric charge transfer due to contact between the PFAS-free heat transfer fluid and other materials), surface tension, reactive wetting (a tendency for a liquid to react with/adsorb to a surface when spreading on the surface), expansion upon freezing, susceptibility to biogrowth, difficulty of spill cleanup, and odor. Yet further factors can include acquisition costs, monitoring and maintenance costs and efforts, responsible disposal costs and efforts, and collateral impacts such as the effect on wetted materials, safety/contamination/cleanup, and effect on energy consumption.

[00124] One possible way to quantify combustibility-related factors of a heat transfer fluid is by using Factory Mutual Standard (FM) 6930, *Flammability Classification of Industrial Fluids*, promulgated by FM Approvals of West Gloucester, RI, USA. FM 6930 is used by some insurance underwriters as a criterion for acceptable fire risk. FM 6930 classifies an industrial fluid based upon whether the fluid has a fire point, and the Spray Flammability Parameter (SFP) of the fluid. The SFP is defined as follows.

$$SFP_{(normalized)} = 11.02 \times 10^6 \times Q_{ch} / (\rho_r q_{cr} m_f) \quad (1)$$

where:

Q_{ch} is the chemical heat release rate determined per section 4.2 of FM 6930 and is expressed in units of kW (kilowatts);

ρ_r is the density of the PFAS-free heat transfer fluid, in units of kg/m³, determined per Section 4.3 of FM 6930;

q_{cr} is the critical heat flux for ignition determined per section 4.4 of FM 6930 in units of kW/m²; and

m_f is the fluid mass flow rate during the chemical heat release rate measurement, in units of g/s.

Fluids can be eligible for approval by FM Approvals if the SFP is less than 5.5×10^4 . Some examples of currently approved fluids include various phosphate esters, organic esters, polyalkylene glycols (PAG), polyhydric alcohols (e.g. glycol), and water + polyhydric alcohol solutions (e.g. water-glycol solutions).

[00125] A potentially large number of fluids can be suitable for use as a PFAS-free heat transfer fluid, depending upon a particular use case. Possible candidates for PFAS-free heat transfer fluids include aqueous fluids, ionic fluids, metallic fluids, organic fluids, liquefied gases, organohalogens that fall outside of PFAS as defined herein, organophosphorus compounds, organosilicon compounds and halides/interhalogens.

[00126] Aqueous PFAS-free heat transfer fluids can provide various advantages over PFAS-containing heat transfer fluids. For example, aqueous heat transfer fluids are not combustible, have relatively low viscosity and relatively high surface tension compared to other example fluids (e.g. organic fluids), and have good heat transfer characteristics. One disadvantage of aqueous heat transfer fluids is that they expand upon freezing. However, processing tool design and operating temperature range can be designed to address this factor. Further, some aqueous heat transfer solutions can be electrically conductive, and potentially corrosive. Also, some aqueous heat transfer solutions can support biogrowth. As such, equipment and/or other fluid additives can be designed to address these factors. As a more specific example, corrosion-resistant materials can be selected for use with aqueous heat transfer solutions. Further, anti-biogrowth additives, such as fungicides and biocides, can be added to prevent biogrowth. Example biocides can include halogen-based biocides (e.g. bromine, chlorine, and/or iodine) and isothiazolinones (e.g. 2-methyl-4-isothiazolin-3-one). Example fungicides can include compounds such as bupirimate, metalaxyl, carbendazium, pencycuron, axoxystrobin, binapacryl, boscalid, carbonix, cyanofamid, pydiflumetofen, propamocarb, pyrazophos, tecnazene, tricyclazole, fenpropimorph, hexaconazole, imazalil, myclobutanil, propinconazole, dimethomorph, polyoxins, acibenzolar, Foxetyl-AI, phosphoric acid, phosphorus acid salts (e.g. sodium phosphonate, potassium phosphonate), chlorothanlonil, copper, mancozeb, sulfur, and Zineb. Also, anti-corrosion additives can be added to an aqueous PFAS-free heat transfer fluid. For example, one or more silicate salts can be added to an aqueous PFAS-free heat transfer fluid. Sodium silicate and potassium silicate are examples of silicate

salts. Silicate salts can form passivating layers on metals in a heat transfer system. The use of such salts thus can reduce a corrosive effect of an aqueous PFAS-free heat transfer fluid, such as deionized water, on metal parts. In some examples, one or more pH buffers can be added to an aqueous PFAS-free heat transfer fluid. Further, in some examples, amines and/or amides can be added to a PFAS-free heat transfer fluid to manage interaction with polymer parts, such as o-rings. This may allow use of elastomers such as EPDM (ethylene propylene diene terpolymer), which swell in hydrocarbons but can have more manageable response in formulations that contain other functionalities. This may allow for more options of polymers to use in a processing tool thermal management system. Other additives, such as thermal stabilizers and viscosity modifiers, also can be added.

[00127] Some more specific examples of aqueous PFAS-free heat transfer fluids include water (deionized, plant cooling water, etc.), water + alcohols (including water/polyol mixtures), water + ionic substances (brines), and water + ammonia mixtures. Example water/alcohol mixtures include mixtures of water with pure cuts and blends of linear alcohols (e.g. C₃ – C₂₈ alcohols, where the number following the letter C indicates a number of carbons in an alcohol molecule). Other examples include mixtures of water with branched alcohols, such as Guerbet alcohols. The term “Guerbet alcohol” generally represents a branched alcohol prepared by the condensation of two primary alcohols, and derivatives thereof. Guerbet alcohols and Guerbet alcohol derivatives can have various advantageous properties. For example, Guerbet alcohols and Guerbet alcohol derivatives can have anti-corrosive properties, and can be colorless and odorless, and can have relatively high thermal and oxidative stability. Examples of branched alcohols include 2-alkyl-1-alkanols (C₁₂ – C₃₂) such as 2-butyloctanol, 2-butyldecanol, 2-butylohexyldecanol, 2-hexyldecanol, 2-octyldecanol, 2-hexyldodecanol, 2-octyldodecanol, 2-decyltetradecanol, 2-dodecylhexadecanol, and 2-tetradecyloctadecanol. The mixture of water with such branched alcohols can be a mixture of water with a single branched alcohol, with mixtures of branched alcohols, and/or with mixtures of linear and branched alcohols. Other examples include water mixed with pure cuts and blends of Ziegler alcohols (e.g. C₆ to C₂₂ Ziegler alcohols). The term “Ziegler alcohol” generally represents linear primary alcohols with even numbers of carbon atoms that are prepared by the Ziegler synthesis. Example water/polyol mixtures include mixtures of water with ethylene glycol and propylene glycol.

[00128] Water/alcohol mixtures, including water/polyol mixtures such as water/glycol mixtures, may be well suited as PFAS-free heat transfer fluids for use in applications in which the PFAS-free heat transfer fluid is exposed to relatively moderate temperatures, such as a working temperature range of between -127 °C and +100 °C. Possible additives to water/alcohol mixtures, including water/polyol mixtures, include pH buffers and corrosion inhibitors.

[00129] In the specific example of mixtures of water and polyols, the resulting PFAS-free heat transfer fluids are noncombustible, and have a low burst point. The water/polyol PFAS-free heat transfer fluids also are biodegradable, and have good heat transfer characteristics. Some possible disadvantages of water/polyol PFAS-free heat transfer fluids include possibly combustible dehydrated residues, the toxicity of some glycols (including the least-viscous glycols), expansion upon freezing, relatively high viscosity at lower temperatures, possible biogrowth, and possible electrical conductivity. Also, glycols can oxidize to form potentially corrosive acids. As mentioned above, such factors can be taken into account during system design. Example compositions can include water, a monoalkylene glycol, one or more pH buffers, one or more biocides, one or more fungicides, and one or more corrosion inhibitors.

[00130] Brines (water with dissolved ionic compounds) also can potentially be well-suited for use as PFAS-free heat transfer fluids. The use of a brine may provide for a lower and higher operating temperature than a water/polyol mixture due to freezing point depression and boiling point elevation. For example, some brines can be used within a temperature range of -60 °C to + 20 °C for a cooled process. Example use cases for brines include uses in chilled applications that require no fire risk and no siloxane contamination risk that could be posed, for example, by the use of a siloxane or other organosilicon material as a PFAS-free heat transfer solution. For example, siloxanes like PDMS (polydimethylsiloxane) can be incompatible with wetted coolant recirculatory hardware. Some advantages offered by brines as PFAS-free heat transfer solutions are that the brines are non-combustible, can have a lower freezing point than water/alcohol-based PFAS-free heat transfer solutions, and can offer good heat transfer performance compared to non-aqueous fluids. Some possible disadvantages are high electrical conductivity, potential corrosivity to metals, and the toxicity of some brines. Further, brines expand upon freezing due to being aqueous. Example compositions can

include water, one or more ionic freezing point depressants, one or more pH buffers, one or more biocides, one or more fungicides, and one or more corrosion inhibitors.

[00131] Organic PFAS-free heat transfer fluids comprise a variety of different fluids for potential uses in various processing tool applications. Organic PFAS-free heat transfer fluids offer different, and a variety of, sets of advantages and disadvantages. Some potential general advantages include wide operating temperature ranges and low pour points compared to aqueous PFAS-free heat transfer fluids, low corrosiveness, and relatively high lubriciousness compared to other fluids. Some potential general disadvantages include non-zero combustibility risk, susceptibility to degradation by moisture, incompatibility with some polymer materials used in a heat transfer system, and less advantageous heat transfer characteristics than aqueous PFAS-free heat transfer fluids. Other potential advantages and disadvantages are discussed below with reference to more specific examples of organic PFAS-free heat transfer fluids.

[00132] Some classes of possible PFAS-free organic heat transfer fluids include aliphatic hydrocarbons, saturated fatty acids and mixtures thereof, alcohols [including higher alcohols (waxes of alcohols) and polyols], ketones, aldehydes, esters, amines, amides, sulfur-containing, carbene/carbene derivatives, surfactants, aromatic hydrocarbons, and halogenated hydrocarbons.

[00133] More specific examples of aliphatic hydrocarbons include low melting waxes, various oils such as biomass pyrolysis oils and mineral oil, synthetic C₁₀ – C₁₃ isoalkanes, and polyalphaolefins, such as LVLVPAOs (low-volatility low-viscosity polyalphaolefins). In some examples, pour point depressants can be used to prevent wax crystallization, and/or to lower wax solidification temperatures. Additionally, in some examples, mixtures of different aliphatic hydrocarbons can be used. Polydisperse selections of hydrocarbons based upon melting points (e.g. by choosing aliphatic hydrocarbon molecules of different sizes) can spread out a melting point of a fluid, and thereby avoid having a sharp melting point. Fischer Tropsch (FT) waxes are another type of material that can potentially be used as a PFAS-free heat transfer fluid. FT waxes comprise linear, saturated high-carbon alkanes generated, for example, as a biproduct of the production of liquid fuels and other products from coal and natural gas.

[00134] Example fatty acids that can potentially be used as or in PFAS-free heat transfer fluids include caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, hardened tallow fatty acid, hydrogenated castor oil (wax) (12-hydroxystearic acid), medium chain fatty acid triglyceride(s) (e.g. Panacet

810 (caprylic/capric acid triglyceride) and Panacet 800b (2-ethylhexyl triglyceride), available from NOF Corporation of Tokyo, Japan).

[00135] Example alcohols that can potentially be used as or in PFAS-free heat transfer fluids include lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, cetyl stearyl alcohol, and mixtures thereof. Such alcohols also can be referred to as waxes of alcohol. Example polyols that can potentially be used as or in PFAS-free heat transfer fluids include glycerin, polyethylene glycol, and polypropylene glycol. As described above, in some examples, pour point depressants can be used to prevent wax crystallization, and/or to lower wax solidification temperatures. Additionally, in some examples, mixtures of different alcohols can be used to spread out a melting point of a PFAS-free heat transfer fluid. Some examples include ternary, quaternary, etc. mixtures of water and multiple alcohols, or of alcohols and brines. As one example, a eutectic mixture of lauryl alcohol and stearyl alcohol can be used as heat transfer fluid in some applications. For example, a 90:10 (e.g. mole fraction or volume fraction) composition of lauryl alcohol and stearyl alcohol may have a melting point of around 23 °C.

[00136] Polyalkylene glycol-based heat transfer fluids can potentially be well-suited for some applications as PFAS-free heat transfer fluids. Example applications include those where the fluid is exposed to relatively higher working temperatures (for example, working temperatures of -20 °C to +260 °C), and where high lubricity and FM6930 approval are desired. Polyalkylene glycol-based heat transfer fluids include homo- and/or copolymers of alkylene oxides, as well as additives such as antioxidants, among other possible additives. Polyalkylene glycol-based PFAS-free heat transfer fluids can offer various advantageous properties. For example, polyalkylene glycol-based PFAS-free heat transfer fluids can be difficult to ignite (FM approved), have a moderate heat of combustion, relatively low toxicity compared to other possible fluids, can be biodegradable, can be compatible with metals, not degraded by water, lubricious, and non-sludging. However, polyalkylene glycol-based PFAS-free heat transfer fluids also can have some degree of combustibility, and not be self-extinguishing. Also, polyalkylene glycols can be irritating to the respiratory system, have moderate thermochemical stability, can be degraded by oxygen, can be hygroscopic, incompatible with some polymers, and have moderate heat transfer performance compared to other possible PFAS-free heat transfer fluid materials. Such properties can be modified and/or mitigated by addition of other fluids to a polyalkylene glycol-

based heat transfer fluid. Examples of other fluids that can be mixed with a polyalkylene glycol material in a PFAS-free heat transfer fluid to modify the properties of the polyalkylene glycol material include aliphatic hydrocarbons and organic esters.

[00137] Example ketones that can potentially be used as or in PFAS-free heat transfer fluids include acetylacetone, acetone, 2-butanone, pentanones (2-pentanone, 3-pentanone), hexanones (2-hexanone, 3-hexanone), heptanones (2-heptanone, 3-heptanone, 4-heptanone), octanones (2-octanone, 3-octanone, 4-octanone), nonanones (2-nonanone, 3-nonanone, 4-nonanone, 5-nonanone), and decanones (2-decanone, 3-decanone, 4-decanone, 5-decanone). Other example ketones that can potentially be used as or in PFAS-free heat transfer fluids include acetophenone, 3-hydroxyacetophenone, cyclohexanone, benzophenone, butyrophenone, acetylpyrazine, 2-acetyl pyridine, acrylophenone, capillin, dibenzoylmethane, indanone, 1-indanone, 2-indanone, aroxypropione, piceol, picolinic acid, propiophenone, 2,4,6-trihydroxyacetophenone, 2,4,5-trihydroxyacetophenone, and valerophenone.

[00138] Example aldehydes that can potentially be used as or in a PFAS-free heat transfer fluid include phenylglyoxal, pyridoxal, glyoxal, and furfural.

[00139] Example esters that can potentially be used as or in PFAS-free heat transfer fluids include ester waxes and hydrocarbon/ester blends. Ester waxes are fatty acids that are esterified with alcohols. Example ester waxes include methyl laurate, methyl stearate, butyl laurate, butyl stearate, ethyl oleate, isopropyl myristate, isopropyl palmitate, octyl palmitate, octyl stearate, and octyl oleate. Further examples of esters that can be used as or in PFAS-free heat transfer fluids include esters lacking hydrogens on a beta carbon of the polyol moiety. Such esters can comprise relatively high thermal stability and resistance to ignition due to resistance/immunity to beta-elimination reactions. Additionally, esters lacking beta hydrogens can comprise relatively low vapor pressure (due to polarity of ester linkages), relatively high ignition resistance, and relatively low heat of combustion. Esters lacking beta hydrogens also may be characterized by relatively high lubricity, relatively low corrosivity, relatively high resistance to dielectric breakdown, very low toxicity and eco toxicity, and good biodegradability. Further, esters lacking beta hydrogens can contribute zero or near-zero ozone depletion potential and global warming potential. Esters lacking beta hydrogens also may be manufactured with low to moderate cost using manufacturing methods having relatively low environmental impact.

[00140] Examples of esters lacking hydrogens on a beta carbon of the polyol moiety include neopentyl polyol esters, such as those described below with regard to FIGS. 2-5. A neopentyl polyol ester can be obtained from esterification of a neopentyl polyol with two or more carboxylic acids. Examples of neopentyl polyols include neopentyl glycol, trimethylolethane, trimethylolpropane, and pentaerythritol. Examples of carboxylic acids include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, and/or decanoic acid. As the esterification reaction can be controlled by the choice of neopentyl polyol and carboxylic acid, the composition of the ester product can be tailored for an application. For example, the chemical and physical properties of the neopentyl polyol ester can be controlled based on an intended use in a heat transfer fluid. Such controllable parameters include number of carbon atoms on acyl groups, degree of saturation, degree of branching, and aromaticity. In some examples, a heat transfer fluid can be further tailored by including a selected statistical distribution of mixed esters.

[00141] FIG. 2 shows an example esterification reaction of neopentyl glycol 202 ($(C(CH_3)_2(CH_2OH)_2)$) with a carboxylic acid 204 ($R-COOH$, where R represents an organyl group). The esterification reaction forms a neopentyl glycol diester 206 and water 208. As illustrated in FIG. 2, the diester product comprises a beta carbon 210 that lacks hydrogen atoms. Beta carbon 210 is bonded to two methyl groups 212 and two alpha carbons 214. Due to the lack of hydrogens on the beta carbon, the neopentyl glycol diester 206 is immune to beta hydrogen elimination reactions. This gives neopentyl glycol diesters a relatively high thermal-oxidative stability. As such, when neopentyl glycol diesters are used in a heat transfer fluid, the heat transfer fluid may exhibit high thermal stability and resistance to ignition.

[00142] In various examples, one or more different carboxylic acids can be used in the esterification reaction. This can result in formation of a neopentyl polyol ester comprising different acyl groups ($R-C=O$). FIG. 3 shows an example neopentyl glycol diester 300 comprising a first acyl group 302 ($R_1-C=O$) and a second acyl group 304 ($R_2-C=O$).

[00143] FIG. 4 shows trimethylolpropane triester 400. Trimethylolpropane triester 400 can be formed by reacting trimethylolpropane with one or more carboxylic acids. As shown in FIG. 4, trimethylolpropane triester 400 comprises three acyl groups, where each of $R_1-C=O$, $R_2-C=O$, and $R_3-C=O$ independently comprise any suitable acyl group.

[00144] FIG. 5 shows pentaerythritol tetraester 500. Pentaerythritol tetraester 500 can be formed by reacting pentaerythritol with one or more carboxylic acids. As shown in FIG. 5, pentaerythritol tetraester 500 comprises four acyl groups, where each of $R_1-C=O$, $R_2-C=O$, $R_3-C=O$, and $R_4-C=O$ independently comprise any suitable acyl group.

[00145] As mentioned above, various factors that relate to dangers posed by combustibility can be considered when tuning the properties of a PFAS-free heat transfer fluid. As an example, ester fluids can use mixed and/or branched acyl groups to achieve a low pour point. While a low pour point can result in higher viscosity and lower fire point, this can be acceptable for applications that prioritize low pour points. On the other hand, low pour points are less important in high-temperature heat transfer fluid applications. Rather, high-temperature heat transfer fluid applications may desire a low viscosity, and prioritize a high fire point due to safety concerns. As such, acyl diversity and branching can be eliminated in neopentyl polyol esters for use in a high-temperature heat transfer fluid. Thus, in some examples, a heat transfer fluid can comprise a single neopentyl polyol ester as this can result in relatively higher fire points and lower viscosity than examples that use a mixture of neopentyl polyol esters.

[00146] In some examples, thermo-oxidative stability can be increased by increasing the number of acyl groups per neopentyl polyol moiety. That is, a pentaerythritol tetraester may comprise a higher thermo-oxidative stability than neopentyl glycol diester. Further, in some examples, use of fully saturated acyl groups can provide greater thermo-oxidative stability than unsaturated acyl groups in a neopentyl polyol ester. In some examples, use of linear acyl groups can provide greater thermo-oxidative stability, lower volatility, and lower viscosity than branched acyl groups in a neopentyl polyol ester.

[00147] In some examples, an acyl group of the neopentyl polyol ester comprises 5 to 10 carbon atoms. In other examples, an acyl group can have a number of carbon atoms outside of this range.

[00148] In some examples, one or more acyl groups of the neopentyl polyol ester comprises a fully saturated acyl group. In some such examples, each acyl group comprises a fully saturated acyl group. In other examples, one or more acyl groups can comprise an unsaturated acyl group.

[00149] In some examples, one or more acyl groups of the neopentyl polyol ester comprises an unbranched alkane. In some such examples, each acyl group comprises an unbranched alkane.

[00150] In some examples, the neopentyl polyol ester comprises a plurality of identical acyl groups. For example, a neopentyl polyol ester can comprise a neopentyl glycol diester as shown in FIG. 3 where R_1 and R_2 are identical. In some examples, the neopentyl polyol ester can comprise a trimethylolpropane triester as shown in FIG. 4 where two or three of R_1 , R_2 , and R_3 are identical. In some examples, the neopentyl polyol ester can comprise a pentaerythritol tetraester as shown in FIG. 5 where two, three, or four of R_1 , R_2 , R_3 , and R_4 are identical. In other examples, a neopentyl polyol ester can comprise different acyl groups.

[00151] The PFAS-free heat transfer fluid can comprise any suitable proportion of neopentyl polyol esters. In some examples, the amount of neopentyl polyol ester is in a quantity of 90 to 99.6 mass percent. In other examples, a mass percentage outside this range can be used.

[00152] In some examples, the PFAS-free heat transfer fluid can comprise a mixture of two or more esters. In some examples, esters of the two or more esters independently is a triester of trimethylolethane, a triester of trimethylolpropane, or a tetraester of pentaerythritol.

[00153] A PFAS-free heat transfer fluid comprising an ester lacking hydrogens on the beta carbon can further comprise additional fluid components. For example, active metal surfaces can catalyze thermal decomposition of neopentyl polyol esters via free-radical mechanisms. As such, a heat transfer fluid can include additives for deactivating iron and/or copper. Examples of metal deactivators include aryl phosphates (e.g., tricresyl phosphate) for deactivating iron and aryl azoles (e.g., benzotriazole) for deactivating copper. Example additives further include arylamine free radical scavengers (e.g., alkylated phenyl- α -naphthylamines) and sterically hindered phenolic free radical scavengers. Free radical scavengers can help avoid thermo-oxidative degradation by removing free radical species from the PFAS-free heat transfer fluid. Example additives further include hydroperoxide decomposers (e.g., didodecyl 3,3'-sulfanedioldipropionate) that can reduce organyl hydroperoxides to nonradical, less reactive alcohols. In some examples, a combination of additives can help inhibit formation of insoluble deposits that can impede heat transfer between the heat transfer fluid and other tool components.

[00154] Further examples of additives include polymeric tackifiers that can be used to help control a viscosity and help with fire safety of a PFAS-free heat transfer fluid. Tackifiers can inhibit formation of small droplets by increasing extensional viscoelasticity of the heat transfer fluid. As a heat transfer fluid can be pressurized, inadvertent leakage can generate a mist or aerosol, which can be a concern for ignition. As such, use of tackifiers to inhibit small droplet formation can help improve fire safety of the heat transfer fluid.

[00155] In some particular examples, the PFAS-free heat transfer fluid comprises one or more aryl phosphate metal deactivators in a quantity of 0.1 to 5 mass percent. In other examples, a mass percent outside this range can be used. In some examples, the PFAS-free heat transfer fluid comprises one or more arylamine free radical scavengers in a quantity of 0.1 to 2 mass percent. In other examples, a mass percent outside this range can be used. In some examples, the PFAS-free heat transfer fluid comprises one or more sterically hindered phenolic free radical scavengers in a quantity of 0.02 to 0.5 mass percent. In other examples, a mass percent outside this range can be used. In some examples, the PFAS-free heat transfer fluid comprises one or more hydroperoxide decomposers in a quantity of 0.05 to 1 mass percent. In other examples, a mass percent outside this range can be used.

[00156] Further examples include esters obtained from esterification of neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, and/or dipentaerythritol with pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, and/or decanoic acid, such as sold under the trade names Midel 7131 and Mivolt DFK, sold by M&I Materials of Manchester, UK. Further examples of esters that can potentially be used as or in PFAS-free heat transfer fluids include cetyl myristate, stearyl stearate, behenyl behenate, pentaerythritol tetrastearate, and pentaerythritol distearate. As described above, in some examples, pour point depressants can be used to prevent wax crystallization, and/or to lower wax solidification temperatures. However, pour point depressants can be omitted from heat transfer fluids comprising synthetic esters that do not contain paraffins. Additionally, in some examples, mixtures of different esters can be used to spread out a melting point of a PFAS-free heat transfer fluid.

[00157] Esters obtained from esterification of pentaerythritol and/or dipentaerythritol with pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, and/or decanoic acid can potentially be well-suited for use in a PFAS-

free heat transfer fluid. For example, such PFAS-free heat transfer fluids can potentially be used in relatively higher temperature applications (for example, within a working temperature range of -20 °C to +300 °C) that require FM 6930 approval and low toxicity. The lower limit of a working temperature range of a heat transfer fluid is potentially limited only by the pour point of a heat transfer fluid. However, due to viscosity properties, a practical limit may be higher for some heat transfer fluids. Organic ester PFAS-free heat transfer fluids have various advantages for some use cases. For example, organic ester PFAS-free heat transfer fluids are difficult to ignite, have a moderate heat of combustion, have low toxicities, are nonirritating, odorless, biodegradable, have good thermo-oxidative stability, are compatible with most metals, and are somewhat lubricious. Further, they have a low pour point, and a relatively wide operating temperature range. Further still, esters that lack beta hydrogens may exhibit higher thermo-oxidative stability compared to esters that contain beta hydrogens. In addition to thermal-oxidative stability, esters lacking hydrogens on the beta carbon can help provide a heat transfer fluid comprising a lower heat of combustion than other hydrocarbon heat transfer fluids. Further, neopentyl polyol esters (such as those shown in FIGS. 2-5) can have a higher resistance to ignition than other polyol ester-based heat transfer fluids having similar viscosity. Additionally, a heat transfer fluid comprising a neopentyl polyol ester can comprise a lower vapor pressure than hydrocarbon-based and/or siloxane-based fluids having similar viscosity. Esters lacking hydrogens on the beta carbon also can help provide a heat transfer fluid that is PFAS-free. Such heat transfer fluids also may have zero ozone depletion potential and/or zero global warming potential. However, some organic esters also can be combustible, not fully self-extinguishing, degraded by moisture, incompatible with some polymers, and can have moderate heat transfer performance compared to other PFAS-free heat transfer fluid options.

[00158] Examples of ethers that can potentially be used as or in a PFAS-free heat transfer fluid include cyclic ethers such as furan, 2-methyl furan, tetrahydrofuran, furfurylamine, and furoic acid.

[00159] Examples of amines that potentially can be used as or in a PFAS-free heat transfer fluid include ammonia (anhydrous or aqueous), and unsaturated or saturated heterocyclic ring compounds such as pyridine, pyrazine, 2-methylpyridine, phenyl 2-pyridyl carbinol, imidazole, pyrrole, *n*-iminopyridinium ylides, triazole, *N*-methylimidazole, 2,6-lutidine, and 4, *N*, *N*-dimethylaminopyridine.

[00160] Examples of amides that potentially can be used as or in a PFAS-free heat transfer fluid include amide waxes, such as ethylene bis stearamide, stearamide, oleylamide, and erucamide.

[00161] Examples of sulfur-containing compounds that can potentially be used as or in PFAS-free heat transfer fluids include thiophene, methylthiophene, 2-methylthiophene, 3-methylthiophene, 2-acetyl,4-methylthiophene, 2,4-dimethylthiophene, benzothiophene, 2-methylbenzothiophene, thiazolium, and thiazole.

[00162] Examples of carbenes and carbene derivatives that can potentially be used as or in PFAS-free heat transfer fluids include (Sn, N, B, S, Si, O, P-heterocyclic carbenes (pyridine-, pyrazine-, imidazole-, pyrrole-, N-iminopyridinium ylide-, triazole-, N-methylimidazole-, 2,6-lutidine-, 4-N,N-dimethylaminopyridine-, silylene-, boranylidene-, stannylene-, nitrene-, phosphinidene-, thiazol-2-ylidene-, dihydroimidazol-2-ylidene-, and cyclopropenyliidene-based moieties..

[00163] Some branched and linear oligomers also can be used as PFAS-free heat transfer fluids.

[00164] In some examples, one or more surfactants can be used as or in a PFAS-free heat transfer fluid. Such surfactants include anionic surfactants, cationic surfactants, nonionic surfactants, and amphoteric surfactants. Example anionic surfactants that can potentially be used in a PFAS-free heat transfer fluid include alkyl sulfates, lauryl sulfate ester – sodium salt, polyoxyethylenelauryl ether sulfate – sodium salt, polyoxyethylenealkyl ether sulfate – sodium salt, lauryl sulfate ester – triethanolamine salt, polyoxyethylenelauryl ether sulfate – triethanolamine salt, 2-ethylhexyl sulfate ester - sodium salt, sodium dialkyl sulfosuccinate, alkylbenzene sulfonate, potassium laurate, potassium cocoate, potassium myristate, potassium palmitate, potassium stearate, potassium oleate, sodium cocoate, sodium myristate, sodium salt of fatty acids, sodium stearate, sodium oleate, calcium stearate, zinc laurate, zinc stearate, magnesium stearate, barium stearate, N-(fatty acid acyl)-N-methyltaurine - sodium salt, N-(coconut oil acyl)-N-methyltaurine - sodium salt, N-decanoyl-N-methyltaurine - sodium salt, TEA-lauroyl-methylaminopropionate, alpha-sulfonated fatty acid-methyl ester - sodium salt, polyoxyethylene fatty acid- monoethanolamide sulfate, N-oleoyl-N-methylglycine (oleoyl sarcosine), and N-Lauroyl-N-methylglycine-sodium salt (sodium lauroyl sarcosine).

[00165] Example cationic surfactants that can potentially be used as or in a PFAS-free heat transfer fluid include tetradecylamine acetate, dodecyl trimethylammonium chloride, coco alkyl trimethylammonium chloride (CAS (Chemical Abstracts Service) Registry No. 61789-18-2, hexadecyl trimethylammonium chloride, tallow-alkyl trimethylammonium chloride (CAS Registry No. 8030-78-2), octadecyl trimethylammonium chloride, behenyl trimethylammonium chloride, behenyl trimethylammonium chloride, dodecyl dimethylammonium chloride, bis(hydrogenated tallow-alkyl)dimethylammonium chloride (CAS No. 61789-81-9), diolel dimethylammonium chloride, coco-alkyl dimethyl benzylammonium chloride, tetradecyl dimethyl benzylammonium chloride, N,N-diacycloxyethyl-N-hydroxyethyl-N-methylammonium methylsulfate, and 1-methyl-1-hydroxyethyl-2-alkyl tallow imidazolium chloride (sold, for example, under the name Nissan Cation AR-4 by NOF Corporation of Tokyo, Japan).

[00166] Example nonionic surfactants that can potentially be used as or in a PFAS-free heat transfer fluid include polyoxyethylene laurel ether, polyoxyethylene alkyl ether, polyoxyethylene alkyl ether, polyoxyethylene cetyl ether, polyoxyethylene oleyl ether, polyoxyethylene stearyl ether, polyoxyethylene isodecyl ether, polyoxyethylene-2-ethylhexyl ether, polyoxyethylene alkyl (branched) ether, polyoxyethylene polyoxypropylene alkyl ether, polyoxypropylene stearyl ether, polyoxyethylene monolaurate, polyoxyethylene monostearate, polyoxyethylene monooleate, sorbitan monocaprylate, sorbitan monolaurate, sorbitan monomyristate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monooleate, sorbitan sesquioleate, sorbitan trioleate, polyoxyethylenesorbitan monolaurate, polyoxyethylenesorbitan monostearate, polyoxyethylenesorbitan monooleate, polyoxyethylenesorbitan monolaurate, polyoxyethylenesorbitan monostearate, polyoxyethylenesorbitan monooleate, ethylene glycol distearate, polyethylene glycol distearate, polyethylene glycol dioleate, polypropylene glycol distearate, polypropylene glycol dissuccinate, glycerol monostearate, glycerol monomyristate, polyoxyethyleneglyceryl monococoate, polyoxyethylene hydrogenated castor oil, triisostearic acid polyoxyethylene glyceryl, polyoxyethylene sorbitol tetraoleate, polyglycerin oleate ester, polyglycerin laurate ester, polyglycerin stearate ester, ethanol 2,2'-(dodecylimino)bis, polyoxyethylene polyoxypropylene lauryl amine, polyoxyethylene coco alkyl amine, polyoxyethylene stearyl amine, polyoxyethylene oleyl amine, polyoxyethylene tallow alkyl amine, polyoxyethylene alkyl propylene

diamine, coconut fatty acid-diethanolamide (a mixture of diethanolamides of the fatty acids that constitute coconut oil), tallow fatty acid diethanolamide (a mixture of diethanolamides of the fatty acids that constitute tallow), lauric acid diethanolamide, oleic acid diethanolamide, coconut fatty acid monoisopropanolamide (a mixture of monoisopropanolamides of the fatty acids that constitute coconut oil), polyoxyethylene fatty acid monoethanolamide, lauryl dimethylamine oxide, stearyl dimethylamine oxide, dihydroxyethyl laurylamine oxide, polyethylene glycol-polypropylene glycol-polyethylene glycol block copolymer, previously-mentioned polyethylene glycol, polyethylene glycol monomethyl ether, polyethylene glycol dimethyl ether, polyethylene glycol glycerol ether, polypropylene glycol (diol type), polypropylene glycol glycerol ether (triol type), polypropylene glycol diglyceryl ether, polypropylene glycol sorbitol ether, polybutylene glycol, polyoxytetramethylen-polyoxyethylene glycol, polyoxytetramethylen-polyoxypropylene glycol, trimethylolpropane tris polyoxytetramethylen-polyoxypropylene glycol ether, polyoxyethylene-bisphenol A ether, polyoxypropylene bisphenol A ether, polyoxyethylene-polyoxypropylene-bisphenol A ether, polyalkylene glycol derivatives (water soluble and non-water soluble types), polyethylene glycol allyl ether, methoxypolyethylene glycol allyl ether, polyethylene glycol polypropyleneglycol allyl ether, polypropylene glycol allyl ether, butoxy polyethylene glycol polypropylene glycol allyl ether, polyethylene glycol diallyl ether, alkyl polyglucosides, and Nymeen L-201 (alkylethoxylated coco amines, available from the previously-mentioned NOF Corporation).

[00167] Examples of amphoteric surfactants that can potentially be used as or in a PFAS-free heat transfer fluid include 1-dodecanaminium-N-(carboxymethyl)-N,N-dimethyl-,inner salt (decyl betaine); 1-propanaminium, 3-amino-n-(carboxymethyl)-N,N-dimethyl-N0=coco alyl derivs-hydroxides, inner salt; 1-propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[(1-oxododecyl)-amino]-, inner salt; glycine,-N0[2[[2(dodecylamino)-ethyl]amino]ethyl]-ethano;I; 10(carboxymethyl)-4,5-dihydro-1-(hydroxyethyl)-2-norcoco alkyl, hydroxides, inner salts (CAS Registry Number 68334-21-4); and sodium laurylamino diacetate.

[00168] Examples of polymer surfactants that can potentially be used as or in a PFAS-free heat transfer fluid include sodium salts of high molecular weight polycarbonates, ammonium salts of high molecular weight polycarbonates, and amine functional polymers.

[00169] Examples of aromatic hydrocarbons that can potentially be used as or in a PFAS-free heat transfer fluid include diphenyl oxide + diphenyl; diphenyl oxide + 1,2,3,4-tetrahydro-6-(1-phenylethyl)naphthalene + 1,2,3,4-tetrahydro-5-(1-phenylethyl)naphthalene; diethylbenzene; 1,1-biphenyl, bis(1-methylethyl)-alkylbiphenyls; diphenyltheane + alkylated aromatic hydrocarbons; 1,2,3,4-tetrahydro-5-(1-phenylethyl)naphthalene + 1,2,3,4-tetrahydro-5-(1-phenylethyl)naphthalene; C14-30 alkyl-benzenes; benzyltoluene + dibenzyl ar-methyl derivative; dibenzyl ar-methyl derivative; isopropylbenzene; C10-13 alkyl-benzene; ethyl diphenylethane + diphenylethane + ethyl(phenylethyl)benzene; diisopropylbiphenyl + triisopropylbiphenyl; hydrogenated terphenyl; hydrogenated terphenyl + polyphenyls + terphenyl; diphenyl oxide + diphenyl + phenanthrene + terphenyl; terphenyl + phenanthrene; diethylbenzene; methylcyclohexane + trimethylpentane; diphenyl oxide + diphenyl; and phenylcyclohexane + bicyclohexyl.

[00170] Some organic materials that can potentially be used as or in PFAS-free heat transfer fluids are bio-based, in that the materials are derived from biological sources. Examples of bio-based materials that can possibly be used as or in PFAS-free heat transfer fluids include alcohols, terpenes, furfurals, glycerols, furan, ethyl lactate, ethyl acetate, glycerol, and mixtures of glycerol and 2-hydroxypropyl-beta-cyclodestrin.

[00171] Organophosphorus materials are another example of a type of material that can potentially be used as or in a PFAS-free heat transfer fluid. Example organophosphorus materials include phosphate esters. A phosphate ester PFAS-free heat transfer fluid composition can include trialkylphosphates, aryl phosphates, phosphate esters, organic esters, lubricants and an identification dye or dyes. Such phosphate ester fluids can be suitable for use in higher temperature settings. An example temperature range is $+20 < T < 420$ °C. Phosphate ester-based PFAS-free heat transfer fluids can have various advantages. For example, they can be difficult to ignite, self-extinguishing, have relatively low viscosities compared to other types of PFAS-free heat transfer fluids, and low pour points compared to other types of PFAS-free heat transfer fluids. However, phosphate ester-based PFAS-free heat transfer fluids can also have various disadvantages. For example, phosphate ester-based PFAS-free heat transfer fluids can be toxic, possibly carcinogenic, and, when ignited, can produce toxic combustion products. Further, the materials can be incompatible with commonly-used materials in processing tools, such as aluminum and various polymers. Further,

phosphate ester PFAS-free heat transfer fluids can have relatively poor hydrolytic stability, relatively poor lubricity, and moderate heat transfer capabilities compared to other possible PFAS-free heat transfer fluids.

[00172] Organosilicon materials are another example of a type of material that can potentially be used as or in a PFAS-free heat transfer fluid. Example organosilicon materials include siloxanes such as alkyl-siloxanes, aryl-siloxanes, and chloro-aryl-siloxanes. More specific examples include longer chain polysiloxanes with narrow molecular weight cuts to minimize short chain species migration. Fluorosiloxanes also can potentially be used as or in a PFAS-free heat transfer fluid.

[00173] Liquified gases are another example of a type of material that can potentially be used as a PFAS-free heat transfer material. Liquified gases can be liquified by cooling (cryogases) and/or by compression. Example liquified gases include nitrogen (N₂) as a cryogas, and carbon dioxide (CO₂) and sulfur hexafluoride (SF₆) as example compressed gases. The compressed gases can be in a liquid or supercritical phase. Each of these materials is incombustible. However, liquified gases also can pose an asphyxiation hazard, and carbon dioxide can be toxic in higher concentrations. In some examples, various materials can be mixed with a condensed gas. For example, n-methyl pyrrolidone and/or other ketones can be used in a solution with condensed-phase carbon dioxide (supercritical or liquid).

[00174] Molten salts are another example of a type of material that can potentially be used as a PFAS-free heat transfer material. Example salts that potentially can be used as a PFAS-free heat transfer fluid in a molten phase include nitrates and carbonates. Example alkali nitrates include sodium nitrate and potassium nitrate. Such materials can potentially be used within a temperature range of 220-600 °C in some examples. Carbonates can have higher melting points, but also potentially broader material compatibility, than nitrates. Example carbonates include alkali carbonates. Example alkali carbonates include lithium carbonate, sodium carbonate, and potassium carbonate, as well as eutectic mixtures of two or three of these.

[00175] Ionic liquids are another example of a type of material that can potentially be used as a PFAS-free heat transfer material. Ionic liquids can possess various advantageous properties for use as PFAS-free heat transfer fluids. For example ionic liquids can have relatively low vapor pressures compared to other liquids for use as PFAS-free heat transfer materials, and also can be incombustible. Example ionic liquids include deep eutectic liquids. Four example types of deep eutectic liquids are

as follows – type I (quaternary ammonium salt + metal chloride), type II (quaternary ammonium salt + metal chloride hydrate), type III (quaternary ammonium salt + hydrogen bond donor), and type IV (metal chloride hydrate + hydrogen bond donor). Some common cations found in ionic liquids include imidazoliums (e.g. 1-alkyl-3-methylimidazolium), pyridiniums (e.g. 1-alkylpyridinium), pyrrolidiniums (e.g. 1-alkyl-1-methylpyrrolidinium), ammoniums (e.g. tetraalkylammonium), phosphoniums (e.g. tetraalkylphosphonium), thiazolium, triazolium, and trialkylsulfonium. Some common anions found in ionic liquids include alkylsulfates (e.g. methylsulfate, ethylsulfate), dicyanamide, hexafluorophosphate, tetrafluoroborate, tetraborate, tetraacetate, acetate, halides (non-F), and docusate. Some general examples of ionic liquids include imidazolium borates and alkyl ammonium borates. Some more specific examples of ionic liquids include bis(imidazolium)/bis(ammonium)-di[bis(salicylato)borate]; 1-butyl-3-methylimidazolium iodide; 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide; 1-ethyl-3-methylimidazolium dicyanamide; 1-ethyl-3-methylimidazolium diethyl phosphate; 1-ethyl-3-methylimidazolium iodide; 1-ethyl-3-methylimidazolium methyl-phosphonate;; 1,3-dimethylimidazolium methyl-phosphonate; 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate; 1-butyl-1-methylpyrrolidinium bis(oxalate)borate; 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide; 1-butyl-1-methylpyrrolidinium dicyanamide;; 1-butyl-2,3-dimethylimidazolium tetrafluoroborate; 1-butyl-2,3-dimethylimidazolium azide; (N,N-diethyl-N-methyl-N(2-methoxyethyl)ammonium bis(fluorosulfonyl) imide; ; 1,3-dimethylimidazolium iodide; 1-methyl-1-(2-methoxyethyl)pyrrolidinium bis(fluorosulfonyl)imide; 1-methyl-1-(3-methoxypropyl)pyrrolidinium bis(fluorosulfonyl)imide; N,N-diethyl-N-methyl-N-propylammonium bis(fluorosulfonyl)imide; N,N-dimethyl-N-ethyl-N-(3-methoxypropyl)ammonium bis(trifluoromethanesulfonyl)imide; N-ethyl-N,N-dimethyl-N-(2-methoxyethyl)ammonium bis(fluorosulfonyl)imide; N-propyl-N-methylpiperidinium bis(fluorosulfonyl)imide; N-propyl-N-methylpiperidinium bis(fluorosulfonyl)imide; N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide; N-tributyl-N-methylammonium dicyanamide; N-tributyl-N-methylammonium bis(trifluoromethanesulfonyl)imide; N-tributyl-N-methylammonium iodide; N-trimethyl-N-butylammonium bis(fluorosulfonyl)imide; N-trimethyl-N-butylammonium bromide; N-trimethyl-N-propylammonium bis(fluorosulfonyl)imide; N-trimethyl-N-propylammonium bis(fluorosulfonyl)imide; and

trihexyl(tetradecyl)phosphonium chloride. Further examples include alumina-based deep eutectic solvents comprising benzophenone and biphenyl, boron nitride-based nanofluids comprising eutectic mixtures of diphenyl ether and menthol, mixtures of choline chloride and urea, and mixtures of choline chloride and carboxylic acids.

[00176] Various additives can be added to ionic liquids in a PFAS-free heat transfer fluid composition. In addition to the above-mentioned examples (biocides, fungicides, anticorrosives, etc.), stabilizing agents can be added. Further, nanoparticles in a colloidal solution can be used in an ionic liquid-based PFAS-free heat transfer fluid to help improve heat transfer properties. An ionic liquid-based liquid comprising a suspension of nanoparticles also can be referred to as an ionic liquid-based nanofluid. In some examples, an ionic liquid-based nanofluid can utilize a deep eutectic solvent as the ionic liquid. Ionic liquid (IL) deep eutectic solvents (i-DES) i-DES-based nanofluids can have a wide range of tunable qualities, including viscosity and heat capacity. Further, i-DES-based nanofluids can be more stable than other types of nanofluids (e.g. water-based or ethylene glycol-based nanofluids) in terms of longevity, cost, viscosity, and toxicity. As described above, an i-DES can comprise two components blended together in a ratio selected to form a eutectic mixture. The two components can be a hydrogen bond acceptor (e.g. a Lewis base) and a hydrogen bond donor. In applications where clogging due to nanoparticles poses a risk, an i-DES that omits nanoparticles can potentially be used as a PFAS-free heat transfer fluid. Ionic fluids can offer advantages over the use of other types of fluids as a PFAS-free heat transfer fluid. For example, some ionic fluids can have more effective heat transfer (e.g. 44% increase) and higher thermal stability than a fluorinated or hydrocarbon fluid. Also, some ionic fluids can have working temperature ranges that exceed 400 °C. Some ionic fluids have been found to have GWP (global warming potential) indices ranging from 1 – 26. In contrast, fluorinated fluids and hydrocarbon fluids have very low specific heat capacity (e.g. 0.9-2J/g C at 25 °C) and GWP indices ranging from 1700 to 9100. They have a limited operating temperature range (<270 C), high toxicity and are highly flammable. Ionic fluids can be non-flammable, non-corrosive, easier to handle than hydrocarbon and fluorinated hydrocarbon fluids, customizable for temperature ranges, and widely available. Also, the increased heat transfer rate offered by some ionic fluids can better control the temperature of components that may have relatively lower heat transfer coefficients. As a more specific example, ceramic pedestal surfaces can have thermal gradients due to the thermal conductivity of the ceramic material. Further, the large

thermal masses (high heat capacities) of such materials can prolong temperature transients in response to heat inputs.

[00177] A benefit of higher thermal conductivity can be seen as follows. In the case of internal laminar flow that is fully developed, the Nusselt numbers approach a stable value for extended pipes. For internal flow, $Nu = hd/k$, where: d = Hydraulic diameter, k = thermal conductivity of the fluid and h = convective heat transfer coefficient. In the case of convection involving circular tubes with uniform temperature, the Nusselt number remains constant. This can be expressed as $h = (Nu)(k)/d$. This expression suggests that to enhance the convective heat transfer coefficient, one must consider two variables, namely hydraulic diameter and thermal conductivity, particularly when dealing with fluids. While the hydraulic diameter (channel dimension) is constant, so thermal conductivity is the variable which need to be enhanced. and nanofluids are known to have higher thermal conductivities, as mentioned above.

[00178] Further, nanofluids can exhibit enhanced cooling efficiency at elevated temperatures, which is sometimes referred to as the 'smart effect'. This results in heightened coolant activity upon exposure to elevated temperatures. Therefore, a greater level of consistency in temperature can be attained. As such, the use of an i-DES-based nanofluid can potentially provide enhanced heat transfer performance at elevated temperatures than at relatively lower temperatures.

[00179] Nanofluid stability can be characterized by zeta potential, which analyses nanofluid electrophoretic motion to determine stability. The Stern layer and diffuse layer form around nanoparticles dispersed in a base fluid. The Stern layer has strongly bound charged ions, whereas the diffuse layer has weakly bound and diffusive ions. Surface charge, Stern layer, and diffuse layer cause electrical double layer (EDL). Positive and negative ions coexist in the EDL, which is electrically neutral. The zeta potential, ζ , is the electrical potential differential between the bulk fluid and the particle-attached stern layer. Millivolts (mV) are used to measure this. When the zeta potential is around 30 mV, nanofluids should be stable. Nanofluids are stable if the zeta potential is at least ± 45 mV. Stabilizing agents are often needed for unstable water-based nanofluids. Stabilizers reduce nanofluid performance. Organic nanofluids are more stable than water-based ones. Organic nanofluids are also more stable. As an example, the above-reference Al_2O_3 spherical nanoparticle – DES organic nanofluid has a zeta potential of 35.40 mV.

[00180] Metallic fluids are another example of a type of fluid that can potentially be used as a PFAS-free heat transfer fluid in a processing tool. Example metallic liquids include gallium, gallium/tin/indium/copper alloys (including alloys of subsets of these materials), tin/silver/copper/zinc/magnesium alloys (including alloys of subsets of these materials), bismuth/lead/tin/cadmium/indium/thallium alloys (including alloys of subsets of these materials), mercury, and sodium-potassium alloys.

[00181] Halides, including interhalogens, are another example of a type of fluid that can potentially be used as a PFAS-free heat transfer fluid in a processing tool. Example halides include bromine, iodine bromide (IBr), iodine chloride (ICl), and iodine tribromide (IBr₃). Organohalogens are another example of a type of fluid that can potentially be used as or in PFAS-free heat transfer fluids in a processing tool. Example organohalogens include halohydrocarbons with one or more of chlorine, bromine, or iodine.

[00182] Supramolecular solvents are another example of a type of fluid that can potentially be used as or in a PFAS-free heat transfer fluid in a processing tool. Example supramolecular solvents include supramolecular deep eutectic solvents comprising cyclodextrins and cyclodextrin derivatives. Cyclodextrins can be formed from the enzymatic degradation of starch, and commonly have six, seven or eight D-glucopyranose units which are linked by α - (1–4) bonds. Example cyclodextrins and cyclodextrin derivatives (collectively “cyclodextrins”) include α -cyclodextrin, β -cyclodextrin, 2-hydroxypropyl- β -cyclodextrin, sulfobutylether β -cyclodextrin sodium salt, randomly methylated β -cyclodextrin, 6-O-maltosyl- β -cyclodextrin, γ -cyclodextrin, and 2-hydroxypropyl- γ -cyclodextrin. The term “supramolecular” refers to at least two chemical compounds that interact with each other through intermolecular forces, for example, such as hydrogen bonds, coordination interactions, and hydrophobic interactions. Cyclodextrins can act as a hydrogen bond acceptor in a supramolecular solvent. One example of a hydrogen bond donor is levulinic acid. Another is lactic acid. Lactic acid combined with beta-cyclodextrin provides for a liquid supramolecular deep eutectic solvent at room temperature. Urea and urea derivatives, such as dimethyl, urea also can be used as hydrogen bond donors. Further examples of hydrogen bond donors include other organic acids, such as citric acid, malic acid, and tartaric acid. Supramolecular deep eutectic solvents also can be produced by mixing conventional deep eutectic solvents with cyclodextrins. In addition to cyclodextrins,

other examples of hydrogen bond acceptors can include L-alanine, nicotinamide, choline chloride, and glycine.

[00183] Selection of fluid or fluids for use in a PFAS-free heat transfer fluid can depend upon an intended use of the fluid. Different thermally controlled components in a processing tool can be operated within different working temperature ranges. As an example, pedestal cooling can be utilized in a dry etching system to maintain a temperature of -100 to 20 °C. As another example, electronics in a processing tool can be cooled to maintain a temperature in a range of 20 to 70 °C. As a further example, a processing chamber can be cooled to maintain a temperature of 20 to 200 °C. As another example, a showerhead in a deposition or etching chamber can be cooled to maintain a temperature of 20 to 400 °C.

[00184] In such applications, it can be desirable to utilize a single phase heat transfer fluid that does not utilize a phase change for heat transfer. Desired thermophysical properties for single-phase heat transfer fluids include a low melting or pour point and a high boiling point and/or decomposition temperature to provide a wide working temperature range. Other desired thermophysical properties can include a high enthalpy of vaporization, a high mass density, a high thermal conductivity, a high specific heat capacity, and a low dynamic viscosity.

[00185] Of the example materials above, some more well-suited PFAS-free heat transfer fluids include water, brines, mixtures of water and polyhydric alcohols, organic esters, and polyalkylene glycols. Such materials can present particularly low hazards to people equipment, facilities, and the environment compared to other example materials listed above. For example, most of these are either incombustible, or approved under FM 6930. Likewise, other possible PFAS-free heat transfer fluids include ionic fluids, some organophosphorus compounds such as phosphate esters, and some organosilicon compounds such as siloxanes. However, depending upon a particular use context, any of a wide range of the example materials above, and derivatives thereof, can possibly be used.

[00186] Examples also are disclosed that relate to operating a processing tool for processing substrates. Processing tool 100 is an example of a processing tool that can be operated as described below. One example method includes circulating a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid within a heat transfer fluid circulation path of the processing tool while processing a substrate using the processing tool. Examples are also disclosed that relate to methods

of servicing a processing tool for processing substrates. One example method comprises adding a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid to a heat transfer fluid circulation path of the processing tool. Example fluids that can be used as the PFAS-free heat transfer fluid include those described above.

[00187] The subject matter of the present disclosure includes all novel and non-obvious combinations and sub-combinations of the various processes, systems and configurations, and other features, functions, acts, and/or properties disclosed herein, as well as any and all equivalents thereof.

CLAIMS:

1. A processing tool for processing substrates, the processing tool comprising:
a heat transfer system comprising a heat transfer fluid circulation path and a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid disposed within the heat transfer fluid circulation path, wherein the PFAS-free heat transfer fluid comprises an ester lacking hydrogens on a beta carbon of an alcohol moiety of the ester.
2. The processing tool of claim 1, wherein the ester lacking hydrogens on the beta carbon comprises a neopentyl polyol ester.
3. The processing tool of claim 2, wherein an acyl group of the neopentyl polyol ester comprises 5 to 10 carbon atoms.
4. The processing tool of claim 3, wherein the acyl group of the neopentyl polyol ester comprises a fully saturated acyl group.
5. The processing tool of claim 3, wherein the acyl group of the neopentyl polyol ester comprises an unbranched alkane.
6. The processing tool of claim 3, wherein the neopentyl polyol ester comprises a plurality of identical acyl groups.
7. The processing tool of claim 2, wherein the PFAS-free heat transfer fluid comprises one or more neopentyl polyol esters in a quantity of 90 to 99.6 mass percent.
8. The processing tool of claim 1, wherein the PFAS-free heat transfer fluid comprises one or more of a triester of trimethylolethane, a triester of trimethylolpropane, or a tetraester of pentaerythritol.
9. The processing tool of claim 1, wherein the PFAS-free heat transfer fluid comprises one or more aryl phosphate metal deactivators in a quantity of 0.1 to 5 mass percent.

10. The processing tool of claim 9, wherein the one or more aryl phosphate metal deactivators comprises tricresyl phosphate.
11. The processing tool of claim 1, wherein the PFAS-free heat transfer fluid comprises one or more arylamine free radical scavengers in a quantity of 0.1 to 2 mass percent.
12. The processing tool of claim 11, wherein the one or more arylamine free radical scavengers comprises one or more alkylated phenyl- α -naphthylamines.
13. The processing tool of claim 1, wherein the PFAS-free heat transfer fluid comprises one or more sterically hindered phenolic free radical scavengers in a quantity of 0.02 to 0.5 mass percent.
14. The processing tool of claim 1, wherein the PFAS-free heat transfer fluid comprises one or more hydroperoxide decomposers in a quantity of 0.05 to 1 mass percent.
15. The processing tool of claim 14, wherein the one or more hydroperoxide decomposers comprises didodecyl 3,3'-sulfanedioldipropionate.
16. The processing tool of claim 1, wherein the PFAS-free heat transfer fluid comprises one or more aryl azole metal deactivators.
17. The processing tool of claim 1, wherein the PFAS-free heat transfer fluid comprises one or more polymeric tackifiers.
18. A processing tool for processing substrates, the processing tool comprising:
a heat transfer system comprising a heat transfer fluid circulation path and a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid disposed within the heat transfer fluid circulation path.

19. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises an aqueous fluid.
20. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises deionized water or a brine.
21. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises a mixture of water and a polyhydric alcohol.
22. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises a liquefied gas.
23. The processing tool of claim 22, wherein the PFAS-free heat transfer fluid comprises a cryogenic liquid.
24. The processing tool of claim 22, wherein the PFAS-free heat transfer fluid comprises a compressed gas.
25. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises an organic fluid.
26. The processing tool of claim 18, wherein the organic fluid comprises an organic ester.
27. The processing tool of claim 18, wherein the organic fluid comprises a polyalkylene glycol.
28. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises an organophosphorus material.
29. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises an organosilicon material.

30. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises a surfactant.
31. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises an ionic liquid.
32. The processing tool of claim 18, wherein the PFAS-free heat transfer fluid comprises a metallic liquid.
33. A method of operating a processing tool for processing substrates, the method comprising:
circulating a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid within a heat transfer fluid circulation path of the processing tool while processing a substrate using the processing tool.
34. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises an aqueous fluid.
35. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises deionized water or a brine.
36. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises a mixture of water and a polyhydric alcohol.
37. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises a liquefied gas.
38. The method of claim 37, wherein the PFAS-free heat transfer fluid comprises a cryogenic liquid.
39. The method of claim 37, wherein the PFAS-free heat transfer fluid comprises a compressed gas.

40. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises an organic fluid.
41. The method of claim 33, wherein the organic fluid comprises an organic ester.
42. The method of claim 33, wherein the organic fluid comprises a polyalkylene glycol.
43. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises an organophosphorus material.
44. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises an organosilicon material.
45. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises a surfactant.
46. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises an ionic liquid.
47. The method of claim 33, wherein the PFAS-free heat transfer fluid comprises a metallic liquid.
48. A method of servicing a processing tool for processing substrates, the method comprising:
adding a perfluorinated and polyfluorinated alkyl substance-free (PFAS-free) heat transfer fluid to a heat transfer fluid circulation path of the processing tool.
49. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises an aqueous fluid.
50. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises deionized water or a brine.

51. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises a mixture of water and a polyhydric alcohol.
52. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises a liquefied gas.
53. The method of claim 52, wherein the PFAS-free heat transfer fluid comprises a cryogenic liquid.
54. The method of claim 52, wherein the PFAS-free heat transfer fluid comprises a compressed gas.
55. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises an organic fluid.
56. The method of claim 55, wherein the organic fluid comprises an organic ester.
57. The method of claim 55, wherein the organic fluid comprises a polyalkylene glycol.
58. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises an organophosphorus material.
59. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises an organosilicon material.
60. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises a surfactant.
61. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises an ionic liquid.
62. The method of claim 48, wherein the PFAS-free heat transfer fluid comprises a metallic liquid.