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(54) FINE PARTICLE DISPERSION COMPOSITIONS AND USES THEREOF

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(57) ABSTRACT

The present invention relates to dispersion compositions comprising synthetic oils or other heat transfer fluids and fine particles. The compositions also comprise at least one dispersant. The dispersion compositions have improved thermal conductivity properties, which may translate to improved energy efficiency performance in a variety of heat transfer applications. Such applications include vapor compression air conditioning and refrigeration systems of all types, secondary heat transfer fluids, and other heating or cooling fluid applications.

FINE PARTICLE DISPERSION COMPOSITIONS AND USES THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority benefit of U.S. provisional application 60/599,330, filed on Aug. 5, 2004.

FIELD OF THE INVENTION

[0002] The present invention relates to dispersion compositions comprising synthetic oils and fine particles. The compositions also contain at least one dispersant to provide for more uniform suspensions. Some of these dispersion compositions have improved thermal conductivity properties, which may translate to improved energy efficiency performance in a variety of heat transfer dependant applications. Such applications include vapor compression air conditioning and refrigeration systems of all types, secondary heat transfer fluids, and other heating or cooling fluid applications.

BACKGROUND

[0003] Environmental concerns regarding excessive energy consumption have prompted many industries to modify their commercial products and/or equipment designs to conserve energy. In addition, the U.S. Government has mandated minimum energy efficiency requirements for home air conditioners and for domestic refrigerators. Consistent with the objective of energy conservation, the refrigeration and air-conditioning industries constantly seek to improve energy efficiency of vapor compression refrigeration and air-conditioning systems. Many proposals to address this problem include chemical additives and changes in the design of refrigeration and air-conditioning systems. Most of the proposals introduce additional complications or disadvantages into the refrigeration and air-conditioning systems.

[0004] Accordingly, there is a need for new means to improve the energy efficiency of vapor-compression air-conditioning and refrigeration systems and other heat transfer systems.

BRIEF SUMMARY OF THE INVENTION

[0005] The present invention relates to a dispersion composition, said composition comprising fine particles of metal or metal oxide dispersed in a synthetic oil medium and at least one dispersant.

[0006] The present invention additionally relates to a synthetic oil composition comprising fine particles of metal or metal oxide and at least one dispersant, said oil having enhanced thermal conductivity based on the presence of the dispersed fine particles.

[0007] The present invention additionally relates to a method for preparing a dispersion composition comprised of fine particles of metal or metal oxide, synthetic oil and at least one dispersant, said method comprising combining at least one dispersant with synthetic oil, combining fine particles of metal or metal oxide with the dispersant and synthetic oil combination to form a slurry, and providing the resultant slurry to a milling device to produce said composition.

[0008] The present invention additionally relates to a method of using a fine particle dispersion composition, said method comprising providing said synthetic oil to a mechanical system to transfer heat from a heat source to a heat sink.

[0009] The present invention further relates to a method of using a heat transfer fluid dispersion composition comprising fine particles of metal or metal oxide dispersed in a heat transfer fluid selected from water, aliphatic alcohols, aliphatic glycols, silicones, hydrocarbons, or fluorine-containing refrigerants, or non-fluorine containing refrigerants and at least one dispersant, said method comprising providing said heat transfer fluid dispersion composition to a mechanical system to transfer heat from a heat source to a heat sink, wherein said composition acts as a secondary heat transfer medium.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The compositions of the present invention are dispersions of fine particles in synthetic oils. By dispersion is meant a slurry of solid particles in a liquid that is non-sedimenting (not visually settling out) over the period of its use.

[0011] The fine particles of the present invention are metal or metal oxide particles. Representative metals are copper and silver. Representative metal oxides are magnesium oxide (MgO), silicon dioxide (SiO_2 or silica), titanium dioxide (TiO_2), iron oxide (Fe_2O_3 or FeO), copper oxide (Cu_2O), zinc oxide (ZnO), zirconium oxide (ZrO_2), stannic oxide (SnO_2), and cerium oxide (CeO_2).

[0012] The fine particles of the present invention may be particles having a median particle size of about 10 micrometers or less, on a volume basis, as measured by dynamic light scattering. Preferably, the fine particles have median particle size of about 500 nanometers or less. More preferably the fine particles are nanoparticles with median particle size of about 100 nanometers or less. Most preferably, the fine particles are nanoparticles with median particle size of about 50 nanometers or less. Of particular usefulness in the present invention are nanoparticles with median particles size of about 30 nanometers or less.

[0013] Fine particles of metals and metal oxides are available commercially from such suppliers as Nanophase Technologies (Romeoville, Ill.), Altair Nanomaterials (Reno, Nev.), Degussa A G, (Düsseldorf, Germany), and Nanotechnologies (Austin, Tex.), and Mach I, Inc. (King of Prussia, Pa.). Silica powders are available from Grace Davison (Columbia, Md.). Additionally, fine particles including nano-size metal oxide and metal powders may be produced in house by one of several methods known in the art, including gas condensation (IGC), vacuum evaporation onto a running oil substrate (VEROS), mechanical attrition, chemical precipitation, gas phase or liquid phase reactions, or as described herein.

[0014] The synthetic oil of the present invention may be any high purity synthetic oil. Preferably, the synthetic oils may be synthetic refrigeration oils. Synthetic refrigeration oils of the present invention include those, which have been designed for use with fluorine-containing refrigerants and are miscible with fluorine-containing refrigerants under compression refrigeration and air-conditioning systems' operating conditions. Such oils and their properties are discussed in "Synthetic Lubricants and High-Performance Fluids", R. L. Shubkin, editor, Marcel Dekker, 1993. Refrigeration oils include, but are not limited to, polyol esters (POEs), polyalkylene glycols (PAGs), and polyvinyl ethers (PVEs). POEs can be obtained through sources such as NuCalgon Wholesalers (St. Louis, Mo.) and distributors such as Greenburg Supply (Wilmington, Del.). PAGs are available from Dow Chemical (Midland, Mich.).

[0015] Synthetic oils of the present invention may further comprise alkylaryls (i.e. linear and branched alkyl alkylbenzenes), synthetic paraffins and naphthenes, and poly(alpha-olefins). Examples of such synthetic oils of the present invention are the commercially available Zerol® 75 and Zerol® 150 (linear alkylbenzenes sold by Shrieve Chemicals, The Woodlands, Tex.) and HAB 22 (branched alkylbenzene sold by Nippon Oil, Tokyo, Japan). These synthetic alkylaryls, paraffins, naphthenes and poly(alpha-olefins) are particularly useful in the present invention for compositions that include non-fluorine-containing refrigerants such as CO_2, hydrocarbons, or dimethyl ether.

[0016] Certain other refrigeration oils are useful for non-fluorine-containing refrigerants of the present invention. Those oils commonly known as "mineral oils" in the field of compression refrigeration include paraffins (i.e. straight chain and branched-carbon-chain, saturated hydrocarbons), naphthenes (i.e. cyclic paraffins) and aromatics (i.e. unsaturated, cyclic hydrocarbons containing one or more rings characterized by alternating double bonds). Examples of such mineral oils of the present invention are the commercially available BVM 100 N (paraffinic mineral oil sold by BVA Oils, Wixon, Mich.), Suniso® 3GS (naphthenic mineral oil sold by Crompton Co., Middlebury, Conn.), Sontex® 372LT (naphthenic mineral oil sold by Penreco, Karns City, Pa.)), and Calumet® RO-30 (naphthenic mineral oil sold by Calumet Lubricants, Indianapolis, Ind.).

[0017] The term refrigeration oil is meant to encompass synthetic oils and mineral oils as described above.

[0018] Heat transfer fluids of the present invention are useful in heat transfer systems and include any fluid capable of absorbing heat from a heat source and transporting that heat to a heat sink. Such heat transfer fluids include, but are not limited to, water, aliphatic alcohols, aliphatic glycols, silicones, hydrocarbons and fluorine-containing refrigerants. These fluids are also useful as secondary heat transfer media.

[0019] The aliphatic alcohols of the present invention may be any aliphatic alcohol used as a heat transfer fluid. Such aliphatic alcohols include, but are not limited to, methanol (CH_3OH), ethanol (CH_3CH_2OH), propanol ($CH_3CH_2CH_2OH$), and isopropanol ($CH_3CH(OH)CH_3$).

[0020] The aliphatic glycols of the present invention may be any aliphatic glycol used as a heat transfer fluid. Such aliphatic glycols include but are not limited to ethylene glycols and propylene glycols. Such aliphatic glycols are available commercially as the Dowtherm™, Dowcal™ or Dowfrost™ (Dow Chemical, Midland, Mich.) for different temperature range applications.

[0021] The silicone heat transfer fluids of the present invention may be any silicon based heat transfer fluid. These include polysiloxane fluids, such as dimethyl polysiloxane (sold by Dow Chemical, Midland, Mich. as Syltherm™ heat transfer fluids).

[0022] The hydrocarbon heat transfer fluid of the present invention may be any hydrocarbon compound used in a heat transfer application. Particularly useful are the hydrocarbon oils as described in the above sections.

[0023] The dispersants of the present invention may be any anionic or non-ionic dispersant, or combinations thereof, found to produce a non-sedimenting dispersion composition when combined with synthetic oils and fine particles of the present invention. Dispersants that display some of the character of ionic or anionic dispersants, such as amphoteric dispersants, may also be used. Either polymeric or non-polymeric dispersants may be used. Combinations of polymeric and non-polymeric dispersants are preferred.

[0024] Non-polymeric dispersants are generally molecules with two functionalities, one of which acts to anchor the dispersant to a particle and one which maintains compatibility with the liquid. They generally have molecular weights of less than 1000. Some non-polymeric dispersants have multiple identical segments or groups but these molecules do not regularly repeat segments (such as in polymers) and are generally smaller molecules (less than 1000 MW).

[0025] In non-ionic dispersants and anionic dispersants, there is generally a hydrophobic functionality and a hydrophilic functionality. Typical examples of hydrophobic segments include alkyl, aryl, alkaryl, siloxane, polysiloxane, fluoroether, and flouroalkyl groups. In anionic dispersants, the hydrophilic group has anionic character. Examples of these segments include but are not limited to: carboxylates, sulfonates, sulfates, phosphates, phosphonates, quaternary salts, and amine oxides. Other hydrophilic groups included in non-ionic dispersants include, but are not limited to: ethoxylates or alkoxylates and hydroxylates including saccharides.

[0026] Examples of non-ionic dispersants that may be used include the C10-C18 N-alkyl polyhydroxy fatty acids and fatty acid amides; C12-C18 alkyl ethoxylates ("AE"-type surfactants), the C10-C18 glycerol ethers, C10-C18 alkyl alkoxy carboxylates, C10-C18 alkyl polyglycosides, and C6-C12 alkyl phenol alkoxylates. These materials are available commercially from various sources. For example, the Triton "X" series, such as X-45, X-100, X-114, and X-102 from Rohm and Haas, are examples of alkyl phenol alkoxylates of various structures.

[0027] Examples of anionic dispersants that may be used include C8-C22 primary or secondary alkane sulfonates, sulfonated polycarboxylic acids, alkyl glyceryl sulfonates, alkyl phenol ethylene sulfates, alkyl phosphates, and sulfosuccinates. Anionic dispersants of the present invention are available commercially. Representative sulfosuccinate dispersants are Aerosol OT, (Cytec, West Paterson, N.J.,), Anionyx 12s (Stepan, Northfield, Ill.), Mackanate DOS-100 (Mcintyre, University Park, Ill.), and Monawet MB-100 (Uniqema, New Castle, Del.).

[0028] Polymeric dispersants have repeating segments, at least some of which contain functionality for anchoring the dispersant to the surface, and generally have molecular weights exceeding about 1000. They may be homopolymers, where the segments are all the same, or co-polymers, where there are multiple types of segments.

[0029] In non-ionic polymeric dispersants, there are generally some segments, which are largely hydrophobic, and others that are largely hydrophilic. In largely non-polar solvents, the hydrophilic portion of the dispersant anchors the dispersant to the particle. In largely polar solvents, the hydrophobic portion of the dispersant anchors the dispersant to the particle. Typical hydrophilic segments include, but are not limited to, ethoxylates or alkoxylates, highly polar ethers, and hydroxylates including saccharides. Typical hydrophobic segments include, but are not limited to, alkyl groups, alkylene groups, aryl groups, aromatic groups, fluorocarbons, silicones, hydrophobic ethers (such as styrene oxide, propylene oxide, butylene oxide, and dodecyl glycidyl ether) and hydrophobic polyesters such as methycrylate esters, methacrylate esters, and caprolactone. In some non-ionic polymer dispersants, other anchoring strategies, such as hydrogen bonding, are used and segments are included in the polymers to create this functionality in the dispersant.

[0030] In anionic polymeric dispersants, anionic groups including, but not limited to carboxylates, sulfonates, sulfates, phosphates, phosphonates, quaternary salts, and amine oxides are incorporated in the polymer, in addition to other hydrophobic or hydrophilic segments, as described above for non-ionic polymeric dispersants.

[0031] Non-ionic dispersants of the present invention may be alkoxylated polyaromatics, 12-hydroxystearic acid and polyhydroxystearic acid. A representative alkoxylated polyaromatic is Solsperse 27000 (Avecia, Manchester, England).

[0032] The fine particles of metal or metal oxide of the present invention are present in the dispersion composition in a concentration of not greater than about 50 weight percent based upon the total weight of the dispersion composition, preferably not greater than about 25 weight percent based upon the total weight of the dispersion composition, and most preferably not greater than about 6 weight percent based upon the total weight of the dispersion composition.

[0033] The dispersants of the present invention are present in the dispersion composition in a concentration of about 1 weight percent to about 6 weight percent based upon the total weight of the dispersion composition, preferably about 1 weight percent to about 4 weight percent.

[0034] The dispersant compositions of the present invention are prepared by a method comprising combining at least one dispersant with synthetic oil, combining fine particles of metal or metal oxide with the dispersant and synthetic oil combination to form a slurry, and providing the resultant slurry to a milling device to produce said dispersion composition.

[0035] The present invention further relates to a method for preparing a dispersion composition comprised of fine particles of metal or metal oxide, synthetic oil and at least one dispersant, said method comprising combining said at least one dispersant with said synthetic oil, combining said fine particles of metal or metal oxide with the dispersant and synthetic oil combination to form a slurry, and providing the resultant slurry to a milling device to produce said dispersion composition.

[0036] The fine particles used to prepare the dispersion composition of the present invention comprise powders that may include agglomerates or clumps of multiple fine particles. In order to create the present dispersion composition of fine particles in the synthetic oil, use of a milling device is necessary. The milling device breaks up the clumps and agglomerates to allow direct contact and wetting of the surfaces of the individual particles.

[0037] Milling devices of the present invention include any device or method that achieves reduction in the size of particles through a grinding process, optionally utilizing grinding media. The milling device can be any that uses an attritor, a tumbling ball mill, a vibratory ball mill, a planetary ball mill, a bead mill, a horizontal media mill, a vertical media mill, an annular media mill, a rotor-stator or a high pressure jet mill, such as a Microfluidizer® (Microfluidics™, Newton, Mass.). Preferred mills for the present invention are ball mills, bead mills or media mills.

[0038] The milling step of the present invention may use grinding media, which is added to the mill prior to milling. Grinding media is generally known to those of ordinary skill in this field and is generally comprised of any material of greater hardness and rigidity than the particle to be ground. The grinding media can be comprised of almost any hard, tough material including, for example, ceramics such as zirconia, nylon and polymeric resins, metals, and a range of naturally occurring substances, such as sand, silica, or chitin obtained from crab shells. Additionally, the grinding media may be comprised of mixtures of any materials that are suitable for grinding. The typical grinding media should be. Any size of grinding media suitable to achieve the desired particle size can be utilized. However, in many applications the preferred size range of the grinding media will be from about 15 millimeters to about 200 micrometers range for continuous media milling with media retention in the mill. Largely spherical (i.e. close to perfect spheres) media may be used, although use of largely cubic (i.e. close to perfect cubes) media is possible. Media aspect ratios (ratio of height to width) are commonly near about 1 and seldom exceed about 10.

[0039] The dispersion compositions of the present invention demonstrate enhanced thermal conductivity as compared to the pure synthetic oils. This enhanced thermal conductivity may be attributed to the presence of the fine particles in the compositions. By enhanced thermal conductivity is meant that the fluid conducts heat more readily, or the ability to transmit heat is improved as compared to the pure synthetic oil. The thermal conductivity as measured by thermal diffusivity or other heat conduction based techniques is greater by at least about 2 percent as compared to the pure synthetic oils not containing the fine particles.

[0040] Thermal conductivity is a property defined by the quantity of heat that passes in unit time through a unit area of a substance whose thickness is unity, when its opposite faces differ in temperature by one degree. The SI derived unit of thermal conductivity is watt per meter-Kelvin ($W\ m^{-1}\ K^{-1}$). For convenience herein, milliwatts per meter-Kelvin, or $mWm^{-1}K^{-1}$ are used.

[0041] Thermal conductivity may be determined by making a series of measurements on a sample, including density (d), heat capacity (Cp), and thermal diffusivity (k). The thermal conductivity (K) may be expressed as a function of those three values:

$$K=f\{(k),(d),(C_p)\}$$

[0042] Density (d) may be determined by any conventional method such as by determining the mass of a carefully measured volume of liquid in precision laboratory glassware on a certified electronic balance.

[0043] Heat capacity (C_p) may be determined using standard calorimetric techniques, such as described herein. A known amount of electrical energy from a regulated power supply is used to heat a precision resistor, which is fully immersed in a measured mass of test liquid inside of a borosilicate glass laboratory Dewar flask. The resulting temperature rise of the liquid is measured with a thermocouple probe. A calorimeter correction constant is determined by making measurements of well-characterized liquids including water, methanol, and toluene. The calorimeter correction factor allows correction for the amount of heat absorbed by the Dewar flask itself, and that absorbed by the heating resistor and the thermocouple probe. The heat capacity of any fluid, slurry or dispersion may then be determined by this same technique, by applying the calorimeter correction factor to the measurement.

[0044] Thermal diffusivity (k) measurement may be done in a specially constructed cell comprised of insulated walls, a thin copper foil on the bottom, and a thermocouple probe situated inside the cell, a few millimeters above the copper foil. The inside radius of the cell is several times the distance between the thermocouple tip and the bottom of the cell.

[0045] To make the thermal diffusivity measurement, a liquid sample is placed inside the cell and the cell and thermocouple assembly is mounted in a vibration resistant support apparatus. The cell and liquid are allowed to rest in a quiescent state to allow any convection or other movement of the liquid within the cell to come to rest. Then, while the temperature of the liquid is being monitored, an ice water bath is raised to a position such that the copper foil of the cell bottom is submerged to a depth of about one millimeter below the surface of the ice water. A timer is started at the moment of contact of the ice water with the copper foil. The rate of cooling of the liquid within the cell, as measured at the tip of the thermocouple, is then monitored and recorded, and a cooling curve is thus generated. Thermal diffusivity is extracted from the cooling curve data using appropriate mathematical algorithms.

[0046] By measuring the cooling rate curves of a series of known pure liquids with well known thermal conductivity values in the published literature, such as water, methanol, and toluene, it is possible to calibrate and verify the accuracy of the system for determination of thermal diffusivity and hence thermal conductivity values.

[0047] The median particle size of the metal oxide particles in the dispersion compositions of the present invention is determined by dynamic light scattering. This technique is well established for measuring particle size over the size range from a few nanometers to a few micrometers (or microns). The technique uses the concept that small particles in a dispersion move in a random pattern known as "Brownian motion". When a coherent source of light (such as a laser) having a known frequency is directed at the moving particles, the light is scattered, but at a different frequency. The change in frequency of the scattered light in comparison to the light source is termed a Doppler shift. This shift in light frequency is related to the size of the particles causing the shift.

[0048] The present invention further relates to a method of using a fine particle dispersion composition, said method comprising providing said composition to a mechanical system to transfer heat from a heat source to a heat sink.

[0049] The present invention further relates to a method of using a heat transfer fluid dispersion composition comprising fine particles of metal or metal oxide dispersed in a heat transfer fluid selected from water, aliphatic alcohols, aliphatic glycols, silicones, hydrocarbons, or fluorine-containing refrigerants and at least one dispersant, said method comprising providing said heat transfer fluid dispersion composition to a mechanical system to transfer heat from a heat source to a heat sink, wherein said composition acts as a secondary heat transfer medium.

[0050] A heat source is meant to include any space, location, object or body from which it is desirable to remove heat. Examples of heat sources may be spaces (open or enclosed) requiring refrigeration or cooling, such as refrigerator or freezer cases in a supermarket, building spaces requiring air conditioning, or the passenger compartment of an automobile requiring air conditioning. A heat sink may be defined as any space, location, object or body capable of absorbing heat. A vapor compression refrigeration system is one example of such a heat sink.

[0051] A mechanical system of the present invention may be any system utilized to transfer heat from one location to another. Such mechanical systems may include heat pumps, refrigerators, air conditioners, or secondary loop systems. The secondary loop systems are utilized in applications where it is undesirable to have bulky and potentially noisy equipment at the heated or cooled location. The secondary loop serves to transport a heat transfer fluid from a remote cooling or heating device to the location to be heated or cooled. Supermarket refrigerated cases are one example of a secondary loop cooling system, wherein the vapor compression refrigeration system is located outside of the building enclosure.

[0052] In the present inventive method of using a refrigeration oil having fine particle dispersion to transfer heat from a heat source to a heat sink, the refrigeration oil may be combined with a refrigerant composition. The refrigerant composition of the present invention may be one or more fluorine-containing refrigerants, such as hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), or hydrofluorocarbon ethers (HFEs), or pure hydrocarbons, dimethyl ether, ammonia, carbon dioxide, nitrous oxide, sulfur dioxide or any combination thereof.

[0053] Fluorine-containing refrigerants of the present invention contain at least one carbon atom and one fluorine atom. Of particular utility are fluorine-containing refrigerants having 1-6 carbon atoms containing at least one fluorine atom, optionally containing chlorine and oxygen atoms, and having a normal boiling point of from −90° C. to 80° C. These fluorocarbons may be represented by the general formula $C_wF_{2w+2-x-y}H_xCl_yO_x$, wherein w is 1-6, x is 0-9, y is 0-3, and z is 0-2. Preferred of the fluorine-containing refrigerants are those in which w is 1-6, x is 1-5, y is 0-1, and z is 0-1. Fluorine-containing refrigerants are commercial products available from a number of sources such as E. I. du Pont de Nemours & Co., Fluoroproducts, Wilmington, Del., 19898, USA, or are available from custom chemical synthesis companies such as PCR Inc., P.O. Box 1466, Gainesville, Fla., 32602, USA, and additionally by synthetic processes disclosed in art such as The Journal of Fluorine Chemistry, or Chemistry of Organic Fluorine Compounds, edited by Milos Hudlicky, published by The MacMillan Company, New York, N.Y., 1962. Representative fluorine-containing refrigerants include but are not limited to: $CHClF_2$ (HCFC-22), CHF_3 (HFC-23), CH_2F_2 (HFC-32), CH_3F (HFC-41), CF_3CF_3 (FC-116), $CHClFCF_3$ (HCFC-124), CHF_2CF_3 (HFC-125), CH_2ClCF_3 (HCFC-133a), CHF_2CHF_2 (HFC-134), CH_2FCF_3 (HFC-134a), $CClF_2CH_3$ (HCFC-142b), CHF_2CH_2F (HFC-143), CF_3CH_3 (HFC-143a), CHF_2CH_3 (HFC-152a), $CHF_2CF_2CF_3$ (HFC-227ca), CF_3CFHCF_3 (HFC-227ea), (HFC-236ca), $CH_2FCF_2CF_3$ (HFC-236cb), CHF_2CHFCF_3 (HFC-236ea), $CF_3CH_2CF_3$ (HFC-236fa), $CH_2FCF_2CHF_2$ (HFC-245ca), $CH_3CF_2CF_3$ (HFC-245cb), $CHF_2CHFCHF_2$ (HFC-245ea), $CH_2FCHFCF_3$ (HFC-245eb), $CHF_2CH_2CF_3$ (HFC-245fa), $CH_2FCF_2CH_2F$ (HFC-254ca), $CH_2CF_2CHF_2$ (HFC-254cb), $CH_2FCHFCHF_2$ (HFC-254ea), CH_3CHFCF_3 (HFC-254eb), $CHF_2CH_2CHF_2$ (HFC-254fa), $CH_2FCH_2CF_3$ (HFC-254fb), $CH_3CF_2CH_3$ (HFC-272ca), CH_3CHFCH_2F (HFC-272ea), $CH_2FCH_2CH_2F$ (HFC-272fa), $CH_3CH_2CF_2H$ (HFC-272fb), CH_3CHFCH_3 (HFC-281ea), $CH_3CH_2CH_2F$ (HFC-281fa), $CHF_2CF_2CF_2CF_2H$ (HFC-338pcc), $CF_3CHFCHFCF_2CF_3$ (HFC43-10mee), and fluorinated ethers such as Freon® E2 or E1 (E. I. du Pont de Nemours & Co., Fluoroproducts, Wilmington, Del.), $C_4F_9OCH_3$, and $C_4F_9OC_2H_5$.

[0054] The present invention is particularly useful with the hydrofluorocarbon and hydrochlorofluorocarbon-based refrigerants, such as, $CHClF_2$ (HCFC-22), CHF_3 (HFC-23), CH_2F_2 (HFC-32), $CHClFCF_3$ (HCFC-124), CHF_2CF_3 (HFC-125), CHF_2CHF_2 (HFC-134), CH_2FCF_3 (HFC-134a), CF_3CH_3 (HFC-143a), CHF_2CH_3 (HFC-152a), $CHF_2CF_2CF_3$ (HFC-227ca), CF_3CFHCF_3 (HFC-227ea), $CF_3CH_2CF_3$ (HFC-236fa), $CHF_2CH_2CF_3$ (HFC-245fa), $CHF_2CF_2CF_2CF_2H$ (HFC-338pcc), $CF_3CHFCHFCF_2CF_3$ (HFC43-10mee); fluorinated ethers such as Freon® E2, $C_4F_9OCH_3$, and $C_4F_9OC_2H_5$; and the azeotropic and azeotrope-like fluorine-containing refrigerant compositions, such as, HCFC-22/HFC-152a/HCFC-124 (known by the ASHRAE designations, R401A, R401B, and R401C), HFC-125/HFC-143a/HFC-134a (known by the ASHRAE designation, R404A), HFC-32/HFC-125/HFC-134a (known by ASHRAE designations, R407A, R407B, and R407C), HCFC-22/HFC-143a/HFC-125 (known by the ASHRAE designation, R408A), HCFC-22/HCFC-124/HCFC-142b (known by the ASHRAE designation: R409A), HFC-32/HFC-125 (R410A), HFC-125/HFC-143a (known by the ASHRAE designation: R-507) and others.

[0055] Additionally, the fluorine-containing refrigerants of the present invention may optionally further comprise up to 10 weight percent of dimethyl ether, or at least one C_3 to C_5 hydrocarbon, e.g., propane, propylene, cyclopropane, n-butane, isobutane, n-pentane, cyclopentane and neopentane (2,2-dimethylpropane). Examples of refrigerant compositions containing such C_3 to C_5 hydrocarbons are azeotrope-like compositions of HCFC-22/HFC-125/propane (known by the ASHRAE designation, R402A and R402B), HCFC-22/octafluoropropane/propane (known by the ASHRAE designation, R-403A and R403B), octafluoropropane/HFC-134a/isobutane (known by the ASHRAE designation, R-413A), HCFC-22/HCFC-124/HCFC-142b/isobutane (known by the ASHRAE designation, R414A and R414B), HFC-134a/HCFC-124/n-butane (known by the ASHRAE designation, -R416A), HFC-125/HFC-134a/n-butane (known by the ASHRAE designation, R417A), HFC-125/HFC-134a/dimethyl ether (known by the ASHRAE designation, R-419A).

[0056] Newer fluorine-containing refrigerant blends containing some percentage hydrocarbon are also intended for use in the present invention. One example is a refrigerant blend comprising HFC-134a, HFC-125 and isobutane, which has recently been assigned ASHRAE designation R422A.

[0057] In addition to the fluorine-containing refrigerants, the refrigerant compositions of the present invention may comprise non-fluorine-containing refrigerants including pure hydrocarbons. The preferred pure hydrocarbon refrigerants of the present invention comprise at least one C_3 to C_5 hydrocarbon, e.g., propane, propylene, cyclopropane, n-butane, isobutane, n-pentane, cyclopentane and neopentane (2,2-dimethylpropane).

[0058] Further, the refrigerant compositions of the present invention may comprise other non-fluorine-containing refrigerants selected from dimethyl ether, ammonia, carbon dioxide, nitrous oxide, sulfur dioxide or any combination thereof or mixture thereof with at least one fluorine-containing refrigerant composition.

EXAMPLES

[0059] The following examples are provided to illustrate certain aspects of the present invention, and are not intended to limit the scope of the invention.

Example 1

Preparation of Silver Nanoparticles

[0060] Silver nanoparticles were prepared by heating silver stearate to a temperature of 200° C. in an alumina boat in a tube furnace for one hour. A white solid sublimed to the cool portion of the tube. The black product in the boat was washed with acetone, which was decanted and the solid was air dried. A portion of the dried solid material was combined with 2,2,4-trimethylpentane producing a yellow colored mixture. The yellow mixture was shaken by hand until the the mixture developed a brown color indicating that the particles were well dispersed. A transmission electron micrograph of an evaporate of this dispersion showed well separated particles of 10-20 nanometer size.

Example 2

Preparation of Copper Nanoparticles

[0061] Copper nanoparticles were prepared by heating copper formate to a temperature of 150° C. in an alumina boat for one hour. The resulting solid from the boat was combined with octane to produce a colorless suspension. Tyndall scattering was produced by shining a light beam through the suspension indicating a particles size of less than 50 nanometers.

Example 3

Preparation of a Silver Dispersion in Lubricating Oil

[0062] A dispersion of silver particles was prepared by combining silver stearate and Zerol® 150 (linear alkylbenzenes sold by Shrieve Chemicals, The Woodlands, Tex.) in a 1 liter round bottom flask. The flask was then heated with stirring for one hour at 200° C. The product was a black dispersion of silver particles in oil. The particles were collected and analyzed by transmission electron microscopy and shown to be in the 10 to 20 nanometers in size range.

Example 4

Preparation of Iron Oxide/POE Oil Dispersion

[0063] A dispersion composition was prepared by combining POE 32-3MA oil (Hatco Corporation, Fords, N.J.) with Aerosol OT-100 (AOT, Cytec) and Solsperse 21000 (Avecia, Manchester, England). Iron oxide particles (Nanocat® Superfine iron oxide, Mach I, King of Prussia, Pa., size reported by manufacturer to be 5-7 nanometers) were added to the oil/dispersant mixture and the resultant combination was milled in a Netzsch Labstar (Netzsch USA, Exton, Pa.) recirculating bead mill. The grinding media used was 0.2 millimeter diameter YTZ (Yttria-stabilized Zirconia from TOSOH, Tokyo, Japan), a specialty ceramic bead. The mill was operated at a mill rate of 14 meters/second and the recirculation rate was about 50 mL/min. The slurry composition had the following make-up: 6 weight percent iron oxide particles, 1.25 weight percent AOT-1 00, 1.25 weight percent Solsperse 21000 and 91.25 weight percent POE oil. 1.5 liters of slurry was recirculated through the mill for 2 hours. The iron oxide particle size was measured with a Microtrac® UPA (Microtrac®, Montgomeryville, Pa.) dynamic light scattering instrument after being diluted approximately 100/1 using the base oil as a diluent prior to measurement. The resultant slurry distribution was found to have a D50 (median, or 50 percent particles smaller than) of 175 nanometers and a D90 (90 percent of particles smaller than) of 230 nanometers and was visually non-sedimenting over a period of several months.

Example 5

Preparation of Iron Oxide/POE Oil Dispersion

[0064] A dispersion composition was prepared by combining POE 32-3MA oil (Hatco Corporation, Fords, N.J.) with Aerosol OT-100 (AOT, Cytec) and Solsperse 21000 (Avecia, Manchester, England). Iron oxide particles (Nanocat® Superfine iron oxide, Mach I, King of Prussia, Pa., size reported by manufacturer to be 5-7 nanometers) were added to the oil/dispersant mixture and the resultant combination was milled in a baffled 500 mL metal beaker for 8 hours. The agitator used was a standard ¾" HSD (high speed dispersion) blade made of polyurethane from Firestone Associates (Philadelphia, Pa.). The rotation rate was 10 meters/second. The beaker was filled with milling media at a ratio of 669 grams of milling media per 150 grams of liquid in the beaker. The grinding media used was 0.2 millimeter diameter YTZ (Yttria-stabilized Zirconia from TOSOH, Tokyo, Japan), a specialty ceramic bead. The slurry composition had the following make-up: 6 weight percent iron oxide particles, 1.25 weight percent AOT-100, 1.25 weight percent Solsperse 21000 and 91.25 weight percent POE oil. The iron oxide particle size was measured with a Microtrac® UPA (Microtrac®, Montgomeryville, Pa.) dynamic light scattering instrument after being diluted approximately 100/1 using the base oil as a diluent prior to measurement. The resultant slurry had a particle size with a D50 of 24 nanometers and a D90 of 190 nanometers and the dispersion composition was visually non-sedimenting over a period of several months.

Example 6

Preparation of Iron Oxide/PAG Oil Dispersion

[0065] A dispersion composition was prepared by combining PAG RL-488 oil (Dow Chemical, Midland, Mich.) with Solsperse 27000 (Avecia, Manchester, England). Iron oxide particles (Nanocat® Superfine iron oxide, Mach I, King of Prussia, Pa., size reported by manufacturer to be 5-7 nanometers) were added to the oil/dispersant mixture and the resultant combination was milled in a Netzsch Labstar (Netzsch USA, Exton, Pa.) recirculating bead mill. The grinding media used was 0.2 millimeter diameter YTZ (Yttria-stabilized Zirconia from TOSOH, Tokyo, Japan), a specialty ceramic bead. The mill was operated at a mill rate of 14 meters/second and the recirculation rate was about 50 mL/min. The slurry composition had the following make-up: 6 weight percent iron oxide particles, 2.5 weight percent Solsperse 27000 and 91.25 weight percent PAG oil. The iron oxide particle size was measured with a Microtrac® UPA (Microtrac®, Montgomeryville, Pa.) dynamic light scattering instrument after being diluted approximately 100/1 using the base oil as a diluent prior to measurement. The resultant slurry had a particle size with a D50 of 19 nanometers and a D90 of 156 nanometers and the dispersion composition was visually non-sedimenting over a period of several months.

Example 7

Thermal Conductivity Measurements

[0066] The thermal conductivities of dispersion compositions as prepared for Examples 4 and 5 were determined by measuring the density, heat capacity and thermal diffusivity as described previously. The thermal conductivity of the resultant slurry compositions as compared to the pure heat transfer medium is given in Table 1. Additionally, the thermal conductivity of a commercial aqueous nano silica dispersion, Ludox® TM-50 (Grace Davison, Columbia, Md.) was determined in the same manner and compared to the thermal conductivity of pure deionized water and also is listed in Table 1.

TABLE 1

Sample	Thermal conductivity ($mWm^{-1}K^{-1}$)	Percent improvement (over pure oil)
32-3MA POE oil	148.4	baseline
6.25 wt % Iron oxide in 32-3MA POE with 2.5 wt % Solsperse 21000, and 1.25 wt % AOT-100 (Example 4)	156.3	5.30%

TABLE 1-continued

Sample	Thermal conductivity ($mWm^{-1}K^{-1}$)	Percent improvement (over pure oil)
6.25 wt % Iron oxide in 32-3MA POE with 2.5 wt % Solsperse 27000 (Example 5)	162.7	9.60%
Deionized water	551	baseline
Ludox® TM-50 nano silica dispersion	691	25.4%

Example 8

Refrigeration System Operation with Dispersion Composition

[0067] A 15 cubic foot Frigidaire (Electrolux Home Products, Augusta, Ga.), chest type domestic freezer was instrumented and its performance was monitored and recorded for a period of several weeks. The freezer was monitored "as received" and thus containing a factory supplied ISO-22 (meaning approximate viscosity at 40° C. is equal to 22 centistokes) POE oil. Data recorded included freezer interior temperature, outside room temperature, and total power consumed by the freezer.

[0068] A dispersion of about 6 weight percent Nano Tek® copper oxide (Nanophase Technologies, Romeoville, Ill., average particle size as provided by manufacturer, calculated from BET surface area measurement, is 16-32 nanometers) in an Arctic EAL-22 POE oil (Exxon Mobil Corp, Fairfax, Va.) was prepared by milling in a beaker mill as described above in Example 5. The dispersant used was Tamol™ SN (Rohm & Haas, Philadelphia, Pa.), a polynaphthalene sulfonate. The slurry composition had the following make-up: 6.25 weight percent copper oxide particles, 1.6 weight percent Tamol™ SN dispersant and 92.15 weight percent POE oil The copper oxide particle size in the resultant slurry was determined utilizing a Lecotrac LT-100 light scattering instrument. The D50 was determined to be about 750 nanometers and the D90 was about 4700 nanometers (4.7 micrometers). It should be noted that the viscosity of the dispersion composition was about 20% higher than the viscosity of the base oil with no particles present.

[0069] The factory supplied POE oil was then removed from the freezer and replaced with a like volume of the above described copper oxide fine particle dispersion. The freezer was allowed to run for a period of seven months while it's cooling performance was monitored. The same data, freezer interior temperature, outside room temperature, and total power consumed by the freezer, was recorded as for the "as received" condition operation. At the end of the seven month test period, the copper oxide dispersion was removed from the system, and the system was flushed about ten times with pure POE oil, with one hour of operation for each flush in order to remove as much dispersion as possible. Finally, the freezer was re-charged with the pure base POE oil (the oil used to prepare the dispersion) with no particles present and allowed to run for two weeks in order to re-establish base line performance.

[0070] After the data was analyzed it was determined that the operation with the fine particle dispersion used about 0.7% less total energy than the base line operation mode. On the basis of viscosity alone (higher viscosity for the dispersion), one would expect more energy to be consumed, as it is well known within the domestic appliance industry that increasing the viscosity of the oil in a compressor will increase energy consumption.

[0071] Additionally, after the test unit was dismantled and inspected, no compressor wear and no pluggage of the capillary tube was observed. Nor was any other negative effect observed due to the operation of the system containing the fine particle dispersion. This test demonstrates successful operation of a freezer unit with no ill effects observed due to the presence of a fine particle dispersion and actually a small improvement in energy efficiency when the higher viscosity of the oil dispersion would have been expected to negatively effect energy efficiency.

What is claimed is:

1. A dispersion composition, said composition comprising fine particles of metal or metal oxide dispersed in a synthetic oil medium and optionally, at least one dispersant.

2. The composition of claim 1 wherein said metal oxide is selected from the group consisting of magnesium oxide, silicon dioxide, titanium dioxide, iron oxide, copper oxide, zinc oxide, zirconium oxide, stannic oxide, and cerium oxide.

3. The composition of claim 1 wherein said metal is selected from the group consisting of copper and silver.

4. The composition of claim 1 wherein said metal oxide is iron oxide and said synthetic oil is selected from the group consisting of polyol ester and polyalklyene glycol.

5. The composition of claim 4 wherein said iron oxide particles are present in an amount not greater than about 50 weight percent.

6. The composition of claim 4 wherein said iron oxide particles are present in an amount not greater than about 25 weight percent.

7. The composition of claim 4 wherein said iron oxide particles are present in an amount not greater than about 6 weight percent.

8. The composition of claim 5, 6, or **7** wherein said dispersant is present and is selected from the group consisting of anionic dispersants, non-ionic dispersants, and combinations thereof.

9. The composition of claim 5, 6, or **7** wherein at least one dispersant is present and is selected from the group consisting of sulfosuccinates, alkoxylated polyaromatics, 12-hydroxystearic acid, polyhydroxystearic acid and combinations thereof.

10. The composition of claim 4 wherein said dispersant is present in said composition at from about 1 weight percent to about 6 weight percent.

11. The composition of claim 4 wherein said dispersant is present in said composition at from about 1 weight percent to about 4 weight percent.

12. The composition of claim 1 wherein said metal oxide particles are iron oxide particles having a median particle size of about 30 nanometers or less, and wherein said dispersant is selected from the group consisting of sulfosuccinates, alkoxylated polyaromatics, 12-hydroxystearic acid, polyhydroxystearic acid and mixtures thereof.

13. A synthetic oil composition comprising fine particles of metal or metal oxide, and at least one dispersant, and having enhanced thermal conductivity based on the presence of the fine particles.

14. A method for preparing a dispersion composition comprised of fine particles of metal or metal oxide, synthetic oil and at least one dispersant, said method comprising combining said at least one dispersant with said synthetic oil, combining said fine particles of metal or metal oxide with the dispersant and synthetic oil combination to form a slurry, and providing the resultant slurry to a milling device to produce said dispersion composition.

15. The method of claim 14, said method further comprising providing the produced dispersion composition to a milling device until a median particle size of less than about 30 nanometers is obtained to produce a synthetic oil having enhanced thermal conductivity.

16. The method of claim 14 wherein said milling device is a ball mill or a media mill.

17. The method of claim 14 wherein said milling device is a media mill.

18. The method of claim 14 wherein said milling device is a media mill and wherein said milling device utilizes 0.2 millimeter diameter grinding media.

19. The method of claim 14 wherein said particles are a metal oxide selected from the group consisting of magnesium oxide, silicon dioxide, titanium dioxide, iron oxide, copper oxide, zinc oxide, zirconium oxide, stannic oxide, and cerium oxide.

20. The method of claim 14 wherein said fine particles are iron oxide particles and said synthetic oil is polyol ester or polyalkylene glycol.

21. The method of claim 19 wherein said dispersant is anionic, non-ionic, or a combination thereof.

22. The method of claim 19 wherein said dispersant is selected from the group consisting of sulfosuccinates, alkoxylated polyaromatics, 12-hydroxystearic acid, polyhydroxystearic acid and combinations thereof.

23. The method of claim 14 wherein said particles are iron oxide particles having a median particles size of about 30 nanometers or less, and wherein said dispersant is at least one selected from the group consisting of sulfosuccinates, alkoxylated polyaromatics, 12-hydroxystearic acid, polyhydroxystearic acid and mixtures thereof.

24. The method of claim 14 wherein said dispersion composition comprises metal oxide particles having a median particle size of less than about 50 nanometers.

25. The method of claim 14, said method further comprising combining said dispersion composition with a refrigerant composition.

26. A method of using a refrigeration oil having fine particle dispersion, said method comprising providing said refrigeration oil to a mechanical system to transfer heat from a heat source to a heat sink.

27. The method of claim 26 wherein said mechanical system is selected from the group consisting of a refrigeration apparatus, heating apparatus and air conditioning apparatus.

28. The method of claim 27 wherein said mechanical system is a heat pump, refrigerator, air conditioner, or secondary loop system.

29. The method of claim 27 wherein said method further comprises combining said refrigeration oil having fine particle dispersion with a refrigerant composition.

30. A method of using a heat transfer fluid dispersion composition comprising fine particles of metal or metal oxide dispersed in a heat transfer fluid selected from water, aliphatic alcohols, aliphatic glycols, silicones, hydrocarbons, fluorine-containing refrigerants, or non-fluorine containing refrigerants and at least one dispersant, said method comprising providing said heat transfer fluid dispersion composition to a mechanical system to transfer heat from a heat source to a heat sink.

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