(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 100 946 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
16.09.2009 Bulletin 2009/38

(21) Application number: **08163865.2**

(22) Date of filing: **08.09.2008**

(51) Int Cl.:
C10M 107/02 *(2006.01)* ***C10M 171/00*** *(2006.01)*
C10N 20/02 *(2006.01)* *C10N 40/30* *(2006.01)*

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK RS

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(54) Oil formulations

(57) Use of a Fischer-Tropsch derived base oil component in a refrigerator oil formulation, for the purpose of increasing the energy efficiency of a temperature modifying and/or controlling system in which the formulation is, or is intended to be, used. The Fischer-Tropsch derived base oil component may be a light base oil having a kinematic viscosity at 100 °C (VK 100) of from 1.2 to 5 centistokes. The system may in particular be a cooling appliance or component thereof. Also provided is a refrigerator oil formulation containing a Fischer-Tropsch derived light base oil component which has a VK 100 of from 1.2 to 5 centistokes.

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Description

Field of the invention

[0001] This invention relates to refrigerator oil formulations and their preparation, and to the use of certain types of base oil in refrigerator oil formulations.

Background to the invention

[0002] It is known to use mineral base oils as lubricants in cooling and other climate control systems, including as refrigerator oils in refrigerator or freezer compressor systems. Such oils are for instance commonly used in refrigerators and freezers which run on the refrigerant R600a (isobutane), in particular in Europe and increasingly also in Asia and other regions of the world.

[0003] Since compressors for appliances such as refrigerators are hermetically sealed units, the lubricants introduced into them remain there throughout the lifetime of the appliance, and are therefore required to provide reliable lubrication during that period.

[0004] It is desirable for a refrigerator oil to have a low viscosity, so as to reduce the energy consumption of the compressor system. Energy consumption is becoming increasingly important, not only due to increased environmental awareness amongst consumers but also as a result of increasingly stringent legislation. Within the European Union, for example, electrical appliances such as refrigerators and freezers have been required since 1998 to carry a rating indicative of their energy efficiency, with the lowest energy consumption Class A appliances inevitably enjoying a greater market share than other less efficient appliances.

[0005] Lower oil viscosities can be particularly desirable for efficient operation during the low temperature regions of the compression/evaporation cycle. This is why naphthenic mineral base oils, which have very low pour points, tend to be preferred for use as refrigerator oils.

[0006] Too low a viscosity in a refrigerator oil can however increase wear in the compressor. The choice of a mineral derived base oil for use as a refrigerator oil can often therefore involve a compromise between the various properties desired of it. For example, a chosen base oil may have a relatively low viscosity, which would be beneficial during the low temperature part of the operational cycle, but this could result in increased wear during other parts of the cycle. Conversely, a higher viscosity oil, which could reduce wear, might correspondingly increase energy consumption and/or impair performance in particular during the cold part of the refrigeration cycle.

[0007] It would therefore be desirable to provide refrigerator oil formulations which could overcome or at least mitigate the above described problems, in particular which had suitable viscosities at both the low and the high temperature ranges of their intended use and/or which could improve the energy efficiency of an appliance in which they were used.

Statements of the invention

[0008] According to a first aspect of the present invention, there is provided the use of a Fischer-Tropsch derived base oil component in a refrigerator oil formulation, for the purpose of increasing the energy efficiency of a temperature modifying and/or controlling system in which the formulation is, or is intended to be, used.

[0009] The system may in general terms be any system for modifying and/or controlling the temperature of, in particular for cooling, an environment. It may for example be an air conditioning system or a heat pump. It will typically be a cooling appliance such as a refrigerator, freezer, chilled or frozen storage cabinet or combination thereof. It may be a component part of such an appliance, in particular a compressor or fluid pump. The refrigerator oil formulation will typically be used as a lubricant in such an appliance or component, suitably within a closed circulation loop.

[0010] In the present context, the term "refrigerator oil formulation" is thus used to denote any lubricant oil formulation suitable for use in a temperature modifying and/or controlling system, in particular the compressor of a cooling appliance such as a refrigerator or freezer. The system may be for domestic, medical, mobile or industrial use. In an embodiment of the invention, the refrigerator oil formulation is adapted and/or intended for use in a refrigerator or freezer, in particular a refrigerator.

[0011] It has surprisingly been found that when a Fischer-Tropsch derived base oil is used as a lubricant in such a system, the energy consumption of the system, during its operation, can be reduced. In other words, the Fischer-Tropsch derived base oil appears to contribute to improved energy efficiency.

[0012] Moreover in the higher temperature region of its use (for example at around 100 °C) a Fischer-Tropsch derived base oil component can be chosen to have a viscosity comparable to that of a typical mineral derived refrigerator oil, yet at lower temperatures the viscosity of the Fischer-Tropsch derived oil can be significantly lower than that of the mineral oil. This in turn, as described above, can have beneficial effects during the cold part of the refrigeration cycle. As a result, a refrigerator oil formulation prepared according to the invention is more likely to function efficiently throughout the service life of an appliance in which it is used, thus allowing increased intervals between oil servicing for non-hermetically sealed systems.

[0013] Fischer-Tropsch derived base oils tend to exhibit better low temperature behaviour than many mineral base oils. They also tend to have high viscosity indices (which provide a measure of the temperature dependence of their viscosity) compared to their mineral derived counterparts. They can therefore be used, in accordance with the invention, to reduce compressor energy consumption at higher temperatures, yet because of their relatively high viscosity indices, can provide proportionately lower viscosities during the cold parts of their operational cycles.

[0014] In the present context, the term "Fischer-Tropsch derived" means that a material is, or derives from, a synthesis product of a Fischer-Tropsch condensation process, typically a Fischer-Tropsch derived wax. The term "non-Fischer-Tropsch derived" may be interpreted accordingly. A Fischer-Tropsch derived base oil component will therefore be a hydrocarbon stream of which a substantial portion, except for added hydrogen, is derived directly or indirectly from a Fischer-Tropsch condensation process.

[0015] A Fischer-Tropsch derived product may also be referred to as a GtL (or GTL) product.

[0016] A Fischer-Tropsch derived base oil component is therefore prepared via a Fischer-Tropsch condensation process. This process is a reaction which converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons:

$$n(CO + 2H_2) = (-CH_2-)_n + nH_2O + \text{heat},$$

in the presence of an appropriate catalyst and typically at elevated temperatures (eg, 125 to 300 °C, preferably 175 to 250 °C) and/or pressures (eg, 5 to 100 bar, preferably 12 to 50 bar). Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired.

[0017] The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane. In general the gases which are converted into liquid fuel components using Fischer-Tropsch processes can include natural gas (methane), LPG (eg, propane or butane), "condensates" such as ethane, synthesis gas (CO/hydrogen) and gaseous products derived from coal, biomass and other hydrocarbons.

[0018] Thus, a Fischer-Tropsch derived base oil component may be a component derived from a gas to liquid synthesis (sometimes referred to as a GtL component). Alternatively it may be a component derived from an analogous Fischer-Tropsch synthesis which for instance converts biomass or coal to liquid (sometimes referred to generically as an XtL component). In the context of the present invention a Fischer-Tropsch derived base oil component is preferably, although not necessarily, a GtL component.

[0019] The Fischer-Tropsch process can be used to prepare a range of hydrocarbon fuels, including LPG, naphtha, kerosene and gas oil fractions. Of these, the gas oils have been used in middle distillate fuel compositions such as in particular automotive diesel fuels, typically in blends with petroleum derived gas oils. The heavier fractions can yield, following hydroprocessing and vacuum distillation, a series of base oils having different distillation properties and viscosities, which are useful as lubricating base oil stocks. These base oils have a wide range of uses, including as lubricants, as dielectric fluids (for example electrical oils or transformer oils), as hydraulic fluids (for example in shock absorbers) and as process oils for instance in elastomer production.

[0020] WO-A-02070627 and WO-A-02070629 describe processes for preparing iso-paraffinic base oils from a wax made by a Fischer-Tropsch process. The products of such a process include, inter alia, a gas oil and a base oil stream having a nominal kinematic viscosity at 100 °C (VK 100) of about 4 centistokes, which is suitable for use in lubricant formulations. They also include a so-called "light" base oil, of VK 100 from about 2 to 3 centistokes, which has boiling points between the final boiling point of the gas oil and the initial boiling point of the 4 centistoke base oil.

[0021] Fischer-Tropsch derived base oils tend to have excellent low temperature properties, for example low pour points, and relatively good oxidation stability. They are also attractive because of the relatively simple process used to make them as compared to similar oils prepared from mineral crude sources. Thus the use of a Fischer-Tropsch derived base oil in a refrigerator oil formulation, in accordance with the present invention, can bring additional advantages.

[0022] These improvements may in turn make possible the use of lower levels of performance enhancing additives such as antioxidants and cold flow additives, thus reducing production costs. In cases a refrigerator oil formulation prepared according to the invention may be entirely free of such additives. Moreover the use of a Fischer-Tropsch derived base oil can itself serve to reduce production costs, since such base oils tend to be cheaper to produce than their mineral derived counterparts.

[0023] Fischer-Tropsch derived oils are also known to be more readily biodegradable than mineral ones, and to have high purity. They can provide a "cleaner" alternative to mineral derived base oils, and as a result may be more suitable for inclusion in refrigerator oil formulations which are intended to be used in environmentally sensitive areas, in marine or other outdoor or off-road applications, or for example in machinery handling sensitive consumer products such as foods, cosmetics or pharmaceuticals. This is likely to be particularly true of refrigerator oil formulations which contain no, or only low levels of, additives, as may be possible in accordance with the present invention.

[0024] In the present context, the term "Fischer-Tropsch derived" means that a material is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The term "non-Fischer-Tropsch derived" may be interpreted accordingly. A Fischer-Tropsch derived base oil component will therefore be a hydrocarbon stream of which a substantial portion, except for added hydrogen, is derived directly or indirectly from a Fischer-Tropsch condensation process.

[0025] Hydrocarbon products may be obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by fractionation of Fischer-Tropsch synthesis products or from hydrotreated Fischer-Tropsch synthesis products. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, eg, GB-B-2077289 and EP-A-0147873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0583836 describes a two step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon product. The desired fraction(s) may subsequently be isolated for instance by distillation.

[0026] Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in US-A-4125566 and US-A-4478955.

[0027] Typical catalysts for the Fischer-Tropsch synthesis of paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII of the periodic table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0 583 836 (pages 3 and 4).

[0028] An example of a Fischer-Tropsch process is the SMDS (Shell Middle Distillate Synthesis) described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al, paper delivered at the 5th Synfuels Worldwide Symposium, Washington DC, November 1985; see also the November 1989 publication of the same title from Shell International Petroleum Company Ltd, London, UK. This process (also sometimes referred to as the Shell "Gas-To-Liquids" or "GtL" technology) produces middle distillate range products by conversion of a natural gas (primarily methane) derived synthesis gas into a heavy long chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions. Base oils, having a range of viscosities and including both light and heavier fractions, may also be produced by such a process.

[0029] By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived oil has essentially no, or undetectable levels of, sulphur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from the synthesis gas feed. This can bring additional benefits to refrigerator oil formulations prepared in accordance with the present invention. In particular, low nitrogen levels can help improve formulation stability in systems in which oxygen might be present.

[0030] Further, the Fischer-Tropsch process as usually operated produces no or virtually no aromatic components. The aromatics content of a Fischer-Tropsch derived oil, suitably determined by ASTM D-4629, will typically be below 1 wt%, preferably below 0.5 wt% and more preferably below 0.1 wt%.

[0031] Generally speaking, Fischer-Tropsch derived hydrocarbon products have relatively low levels of polar components, in particular polar surfactants, for instance compared to mineral derived fuels. Such polar components may include for example oxygenates, and sulphur and nitrogen containing compounds. A low level of sulphur in a Fischer-Tropsch derived product is generally indicative of low levels of both oxygenates and nitrogen containing compounds, since all are removed by the same treatment processes.

[0032] The Fischer-Tropsch derived base oil component used in a refrigerator oil formulation according to the invention suitably has a kinematic viscosity at 100 °C (VK 100, for instance measured using the standard test method ASTM D-445) of 35 centistokes or lower, suitably 30 or 25 or 20 centistokes or lower. It may have a VK 100 of 1 centistoke or greater, more typically 1.2 or 1.5 or 2 centistokes or greater, for example from 2 to 15 centistokes or from 2 to 10 or 2 to 8 centistokes. Suitable Fischer-Tropsch derived base oil components may for example be those which have a VK 100 of approximately 3 or 4 or 8 centistokes, in particular those having a VK 100 of approximately 3 or 4 centistokes. However, both lighter and heavier base oils (including the so-called "extra heavy base oils", of VK 100 typically greater than 8 centistokes, more typically at least 10 or 13 or 15 or 17 centistokes and in cases at least 20 centistokes) may be used in a refrigerator oil formulation in accordance with the invention.

[0033] A Fischer-Tropsch derived base oil component suitably has a viscosity index (for instance measured using the standard test method ASTM D-2270) of 110 or greater, more typically 115 or 120 or greater, for example from about 115 to 125. In cases its viscosity index may be up to 150 or 145.

[0034] For use in the present invention, a Fischer-Tropsch derived base oil component suitably has a pour point (for instance measured using the standard test method ASTM D-5950) of -10 °C or lower, for example -15 °C or lower, or in cases -20 or -30 or -35 °C or lower, or even -40 or -45 °C or lower.

[0035] A Fischer-Tropsch derived base oil component for use in the present invention suitably comprises, and in some cases consists essentially of, a light base oil, as described in more detail below.

[0036] In general, however, the base oil component may be selected from both light and heavier base oils, depending in part on the refrigerant with which it is combined. It may therefore have a VK 100 (ASTM D-445) of from 1 to 35 centistokes, as described above, more typically of from 2 to 15 or from 2 to 10 centistokes, in cases from 2 to 8 centistokes. If for example the refrigerator oil formulation is to be used in a system containing ammonia and/or carbon dioxide as the refrigerant, then a higher viscosity base oil such as of VK 100 around 4 to 10 centistokes (typically around 6 to 8 centistokes, for example around 8 centistokes) might be suitable. For use with hydrofluorocarbon and in particular hydrocarbon refrigerants, lighter base oils such as those having a VK 100 around 2 to 5 centistokes (typically around 3 centistokes) might be more appropriate. Higher viscosity base oils may also be appropriate for use in more powerful systems such as for example shop or factory cooling systems.

[0037] A Fischer-Tropsch derived light base oil is a base oil which is derived from a Fischer-Tropsch derived wax, and is suitably a base oil cut which has a boiling range between the initial boiling point of a 4 centistoke base oil and the final boiling point of a gas oil. Typically, it will be a 340 to 400 °C cut, or a 350 to 400 °C cut, from a full range dewaxing of a Fischer-Tropsch waxy raffinate.

[0038] Such a light base oil will suitably have a VK 100 (ASTM D-445) of from 1.2 to 5 centistokes, or from 1.5 or 2 to 5 centistokes, preferably from 2.1 to 3.5 centistokes, more preferably from 2.5 to 3 centistokes.

[0039] It will suitably have a kinematic viscosity at 40 °C (VK 40, also measured by ASTM D-445) of from 3 to 12 centistokes, suitably from 5 to 12 centistokes or from 7 to 11 centistokes.

[0040] It will suitably have a viscosity index (ASTM D-2270) of from 105 to 124, preferably greater than 120, more preferably from 121 to 123.

[0041] The pour point of the light base oil (ASTM D-5950) is preferably -39 °C or lower, more preferably -40 or -42 or -45 °C or lower.

[0042] A Fischer-Tropsch derived light base oil component for use in the present invention is suitably obtained by hydrocracking a paraffinic, conveniently Fischer-Tropsch derived, wax and preferably dewaxing the resultant waxy raffinate for instance by solvent or more preferably catalytic dewaxing. The paraffinic wax may be a slack wax. The raffinate can be distilled to produce a number of different products, including a lower boiling dewaxed gas oil, a light base oil stream having a VK 100 of around 2 to 4 centistokes, a heavy base oil stream having a VK 100 of about 4 to 8 centistokes, typically around 8 centistokes, and an "extra heavy" base oil stream having a VK 100 of around 8 to 30 or 8 to 25 centistokes, typically about 20 centistokes. The base oil component used in the present invention may in particular be derived from the light stream.

[0043] Since the base oil component used in the present invention is derived from a Fischer-Tropsch wax, it will be largely paraffinic in nature, and will typically contain a major proportion of iso-paraffins. Suitably, the base oil is a paraffinic base oil having a total paraffin content of at least 80 wt%, preferably at least 85 or 90 wt%. It suitably has a saturates content (as measured by IP-368) of greater than 98 wt%, preferably greater than 99 wt%, more preferably greater than 99.5 wt%. It may comprise a series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms, where n is from 20 to 35. Preferably it has an n-paraffin content of 0.5 wt% or less, more preferably of 0.1 wt% or less, in cases of zero (ie, its i:n ratio will typically be extremely high).

[0044] The base oil component preferably has a content of naphthenic compounds of from 0 to 20 wt%, more preferably of from 1 to 20 or from 1 to 10 wt%.

[0045] The content of naphthenic compounds in a Fischer-Tropsch derived base oil component, and the presence of the desired continuous series of iso-paraffins, may be measured by the Field Ionisation Mass Spectrometry (FIMS) technique. According to this technique, an oil sample is firstly separated into a polar (aromatic) phase and a non-polar (saturates) phase by the high performance liquid chromatography (HPLC) method IP 368/01 but using pentane instead of hexane as the mobile phase. The aromatic and saturates fractions are then analysed using for instance a Finnigan MAT90 mass spectrometer equipped with a FD/FI interface, the FI (a "soft" ionisation technique) being used to determine hydrocarbon types in terms of carbon number and hydrogen deficiency.

[0046] The emitter/source block is thereby preferably operated at ambient temperature to avoid any over-expression of unsaturated compounds.

[0047] The type classification of compounds in mass spectrometry is determined by the characteristic ions formed and is normally classified by "z number". This is given by the general formula for all hydrocarbon species: C_nH_{2n+z}. Because the saturates phase is analysed separately from the aromatic phase it is possible to determine the content of the different iso-paraffins having the same stoichiometry or n-number. The results from the mass spectrometer can be processed using commercially available software (for example Poly 32, available from Sierra Analytics LLC, 3453 Dragoo Park Drive, Modesto, California GA95350 USA) to determine the relative proportions of each hydrocarbon type.

[0048] A Fischer-Tropsch derived base oil component for use in a formulation according to the invention, which preferably contains the above described continuous series of iso-paraffins, is suitably obtained by hydroisomerisation of a paraffinic wax, preferably followed by some type of dewaxing, such as solvent or catalytic dewaxing. The paraffinic wax may be a slack wax. More preferably the paraffinic wax is a Fischer-Tropsch derived wax, because of its purity and high paraffinic content, as well as the fact that such waxes result in a product containing a continuous series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms in the desired molecular weight range.

[0049] Examples of Fischer-Tropsch processes which can be used to prepare the Fischer-Tropsch derived base oil are the so-called commercial Slurry Phase Distillate technology of Sasol, the Shell Middle Distillate Synthesis process referred to above and the "AGC-21" Exxon Mobil process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-4943672, US-A-5059299, WO-A-9934917 and WO-A-9920720. Typically the products of these Fischer-Tropsch syntheses will comprise hydrocarbons having from 1 to 100 or even more than 100 carbon atoms. Such products will comprise normal paraffins, iso-paraffins, oxygenated components and unsaturated components.

[0050] Where a base oil is one of the desired iso-paraffinic products it may be advantageous to use a relatively heavy Fischer-Tropsch derived feed. Such a feed suitably contains at least 30 wt%, preferably at least 50 wt% and more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio in the feed of compounds having at least 60 carbon atoms to those having at least 30 but fewer than 60 carbon atoms is preferably at least 0.2, more preferably at least 0.4 and most preferably at least 0.55.

[0051] Preferably the Fischer-Tropsch derived feed comprises a C_{20+} fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955. Such a Fischer-Tropsch derived feed can be obtained by any process which yields a suitably heavy product as described above. An example of a suitable Fischer-Tropsch process is described in WO-A-9934917.

[0052] A Fischer-Tropsch derived base oil will contain no or very few sulphur and nitrogen containing compounds. This is typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limits, which are currently 5 mg/kg for sulphur and 1 mg/kg for nitrogen respectively.

[0053] In its broadest sense, the present invention embraces the use, in a refrigerator oil formulation for the purpose of increasing the energy efficiency of a temperature modifying and/or controlling system, of a paraffinic base oil component, in particular a light base oil component, having one or more of the above described properties, whether or not the base oil component is actually Fischer-Tropsch derived.

[0054] However the process used to prepare the base oil component will conveniently comprise a Fischer-Tropsch synthesis, a hydroisomerisation step and an optional pour point reducing step, wherein the hydroisomerisation and optional pour point reducing steps are performed by:

(a) hydrocracking/hydroisomerising a Fischer-Tropsch product, and

(b) isolating from the product of step (a) a base oil or base oil intermediate fraction, or more preferably separating the product of step (a) into at least (i) one or more distillate fuel fractions and (ii) a base oil or base oil intermediate fraction.

[0055] The base oil is again preferably a light base oil, as described above, although other base oil fractions may also be used in a refrigerator oil formulation in accordance with the invention, depending in part on the refrigerant it is to be used with.

[0056] If the viscosity and pour point of the base oil obtained in step (b) are as desired no further processing is necessary and the oil can be used directly in a refrigerator oil formulation. If required, however, the pour point of a base oil intermediate fraction may be further reduced in a step (c) by means of solvent or more preferably catalytic dewaxing.

[0057] A desired viscosity of base oil may be obtained by isolating (by means of distillation) a product having a suitable boiling range and corresponding viscosity, from an intermediate base oil fraction or from a dewaxed oil. The distillation may be a vacuum distillation step.

[0058] The hydroconversion/hydroisomerisation reaction of step (a) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art, examples of which are described in more detail below. The catalyst may in principle be any catalyst known in the art to be suitable for isomerising paraffinic molecules. In general, suitable hydroconversion/hydroisomerisation catalysts are those comprising a hydrogenation component supported on a refractory oxide carrier, such as amorphous silica-alumina (ASA), alumina, fluorided alumina, molecular sieves (zeolites) or mixtures of two or more of these.

[0059] Preferred catalysts for use in the hydroconversion/hydroisomerisation step (a) include those comprising platinum and/or palladium as the hydrogenation component. A very much preferred hydroconversion/hydroisomerisation catalyst comprises platinum and palladium supported on an amorphous silica-alumina (ASA) carrier. The platinum and/or palladium is suitably present in an amount of from 0.1 to 5.0 wt%, more suitably from 0.2 to 2.0 wt%, calculated as the element and based on the total weight of the carrier. If both elements are present, the weight ratio of platinum to palladium may vary within wide limits, but is suitably in the range of from 0.05 to 10, more suitably from 0.1 to 5. Examples of suitable noble metal on ASA catalysts are, for instance, disclosed in WO-A-9410264 and EP-A-0582347. Other suitable noble metal-based catalysts, such as platinum on a fluorided alumina carrier, are disclosed in eg, US-A-5059299 and WO-A-9220759.

[0060] A second type of suitable hydroconversion/hydroisomerisation catalyst includes those comprising at least one Group VIB metal, preferably tungsten and/or molybdenum, and at least one non-noble Group VIII metal, preferably nickel and/or cobalt, as the hydrogenation component. Either or both metals may be present as an oxide, a sulphide or a combination thereof. The Group VIB metal is suitably present in an amount of from 1 to 35 wt%, more suitably from 5 to 30 wt%, calculated as the element and based on the total weight of the carrier. The non-noble Group VIII metal is suitably present in an amount of from 1 to 25 wt%, preferably from 2 to 15 wt%, calculated as the element and based on the total weight of the carrier. A hydroconversion catalyst of this type, which has been found particularly suitable, is one comprising nickel and tungsten supported on fluorided alumina.

[0061] The above non-noble metal based catalysts are preferably used in their sulphided form. In order to maintain the sulphided form of the catalyst during use some sulphur needs to be present in the feed, for example at least 10 mg/kg or more preferably from 50 to 150 mg/kg of sulphur.

[0062] A preferred catalyst, which can be used in a non-sulphided form, comprises a non-noble Group VIII metal, eg, iron or nickel, in conjunction with a Group IB metal, e.g. copper, supported on an acidic support. Copper is preferably present to suppress hydrogenolysis of paraffins to methane. The catalyst preferably has a pore volume in the range from 0.35 to 1.10 ml/g as determined by water absorption, a surface area of from 200 to 500 m^2/g as determined by BET nitrogen adsorption, and a bulk density of from 0.4 to 1.0 g/ml. The catalyst support is preferably made of an amorphous silica-alumina wherein the alumina may be present within a range of from 5 to 96 wt%, preferably from 20 to 85 wt%. The silica content of such a support, as SiO_2, is preferably from 15 to 80 wt%. The support may also contain small amounts, for example from 20 to 30 wt%, of a binder such as alumina, silica, a Group IVA metal oxide, a clay, magnesia, etc, preferably alumina or silica.

[0063] The preparation of amorphous silica-alumina microspheres has been described by Ryland, Lloyd B., Tamele, M.W. and Wilson, J.N., in "Cracking Catalysts", Catalysis: Volume VII, Ed. Paul H. Emmett, Reinhold Publishing Corporation, New York, 1960, pp. 5-9. The catalyst may be prepared by co-impregnating the metals from solutions onto the support, drying at 100 to 150 °C and calcining in air at 200 to 550 °C. The Group VIII metal may be present in an amount of about 15 wt% or less, preferably from 1 to 12 wt%, whilst the Group IB metal is usually present in a lower amount: for example the weight ratio of the Group IB metal to the Group VIII metal may be from about 1:2 to about 1:20. A typical catalyst is specified below:

Ni, wt%	2.5-3.5
Cu, wt%	0.25-0.35
Al_2O_3-SiO_2 wt%	65- 75
Al_2O_3 (binder) wt%	25-30
Surface area	290-325 m^2/g
Pore volume	(Hg)0.35-0.45 ml/g
Bulk density	0.58-0.68 g/ml.

[0064] Another class of suitable hydroconversion/hydroisomerisation catalysts includes those based on molecular sieve type materials, suitably comprising at least one Group VIII metal component, preferably Pt and/or Pd, as the hydrogenation component. Suitable zeolitic and other aluminosilicate materials, then, include Zeolite beta, Zeolite Y, Ultra Stable Y, ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-48, MCM-68, ZSM-35, SSZ-32, ferrierite, mordenite and silica-aluminophosphates such as SAPO-11 and SAPO-31. Examples of suitable hydroconversion/hydroisomerisation catalysts are, for instance, described in WO-A-9201657. Combinations of these catalysts are also possible.

[0065] Suitable hydroconversion/hydroisomerisation processes are those involving a first step wherein a zeolite beta or ZSM-48 based catalyst is used and a second step wherein a ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-48, MCM-68, ZSM-35, SSZ-32, ferrierite or mordenite based catalyst is used. Of the latter group ZSM-23, ZSM-22 and ZSM-48 are preferred. Examples of such processes are described in US-A-20040065581, which discloses the use of a first step catalyst comprising platinum and zeolite beta and a second step catalyst comprising platinum and ZSM-48.

[0066] Combination processes in which the Fischer-Tropsch product is first subjected to a first hydroisomerisation step using an amorphous catalyst comprising a silica-alumina carrier as described above, followed by a second hydroisomerisation step using a catalyst which comprises a molecular sieve, have also been identified as preferred processes by which to prepare a base oil component for use in the present invention. Preferably the first and second hydroisomerisation steps are performed in series flow. More preferably the two steps are performed in a single reactor comprising beds of the above amorphous and/or crystalline catalysts.

[0067] In step (a) the Fischer-Tropsch feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperature will typically be in the range from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range from 10 to 250 bar and preferably from 20 to 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

[0068] The conversion in step (a), defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is suitably at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt% and more preferably not more than 65 wt%. The feed as used in the above definition is the total hydrocarbon feed to step (a), thus including any optional recycle of a high boiling fraction which may be obtained in step (b).

[0069] In step (b) the product of step (a) is preferably separated into one or more distillate fuel fractions and a base oil or base oil precursor fraction having the desired viscosity. If the pour point of the base oil or precursor is not in the desired range it may be further reduced by means of a dewaxing step (c), preferably by catalytic dewaxing. In such an embodiment it may be a further advantage to dewax a wider boiling fraction of the product of step (a). From the resulting dewaxed product the desired, typically light, base oil component and optionally other oils having desired viscosities can then be isolated for instance by distillation. Dewaxing is preferably performed by catalytic dewaxing, as for example described in WO-A-02070627, which publication is hereby incorporated by reference (see in particular page 8 line 27 to page 11 line 6 for examples of suitable dewaxing conditions and catalysts). The final boiling point of the feed to the dewaxing step (c) may be the final boiling point of the product of step (a) or lower if desired. Typically, the feed to the catalytic dewaxer will comprise C_{18} to C_{40} hydrocarbons.

[0070] Prior to use in a refrigerator oil formulation, for instance after a dewaxing step (c), the base oil component may be subjected to one or more further treatments such as hydrofinishing, as described for example at page 11 line 7 to page 12 line 12 of WO-A-02070627.

[0071] A suitable process for the simultaneous production of both a Fischer-Tropsch derived gas oil and a Fischer-Tropsch derived light base oil is for instance that described in WO-A-02070627.

[0072] A refrigerator oil formulation prepared according to the invention may contain up to 100% of the Fischer-Tropsch derived base oil component. It may contain up to 99 or 98 or 95 wt% of the Fischer-Tropsch derived base oil component. It may for example contain 25 wt% or greater of the Fischer-Tropsch derived base oil component, or 30 or 40 or 50 or 60 wt% or greater, or in cases 70 or 80 wt% or greater. In cases, 60 wt% or greater may be preferred, as may 70 or 80 wt% or greater.

[0073] The formulation may contain, in addition to the Fischer-Tropsch derived base oil component, one or more solvents, for example selected from alkylbenzenes, alkylnaphthalines, esters, ethers, polyalkyleneglycols, mineral oils and mixtures thereof. It may contain one or more additives such as for example antioxidants, which again may be combined with suitable solvent(s).

[0074] The Fischer-Tropsch derived base oil component may be the only base oil component in a refrigerator oil formulation prepared according to the invention. Alternatively, it may be used in combination with one or more additional base oil components. The preferred properties (in particular viscosities) of such additional base oil components may be as described above for the Fischer-Tropsch derived base oil component, although this may not necessarily be the case. They may be Fischer-Tropsch derived or non-Fischer-Tropsch derived. Thus the formulation may additionally contain one or more mineral derived base oil components, for example of the type which are conventionally used in refrigerator oil formulations. In accordance with the invention, a Fischer-Tropsch derived base oil component may be used either wholly or partially to replace a non-Fischer-Tropsch derived base oil component in a refrigerator oil formulation, for the purpose of increasing the energy efficiency of a temperature modifying and/or controlling system, and/or for one or more of the advantages described below. This can allow greater flexibility in the formulation of refrigerator oils.

[0075] In embodiments of the invention, the overall formulation may contain less than 20 wt%, in cases less than 10 wt%, of such additional base oil components. In cases it might not contain any naphthenic base oil components, or might contain only a low quantity (for example 10 wt% or less) of naphthenic base oil components.

[0076] Examples of additional base oil components include mineral based paraffinic and naphthenic type base oils and synthetic base oils, for example esters, poly alpha olefins, polyalkylene glycols, ethers, alkylbenzenes, alkyl-napthhalenes and the like, and mixtures thereof. Of these, esters can be beneficial in order to improve the biodegradability of a refrigerator oil formulation. The content of an additional ester base oil, if present, may be from 1 to 30 wt% of the lubricant oil component of the formulation, more preferably from 5 to 25 wt%. Suitable esters are those derivable by reacting an aliphatic mono, di and/or poly carboxylic acid with isotridecyl alcohol under esterification conditions. Examples of such compounds are the isotridecyl ester of octane-1,8-dioic acid, 2-ethylhexane-1,6 dioic acid and dodecane-1,12-dioic acid. Preferably the ester is a so-called pentaerythritol tetrafattyacid ester (PET ester), as made by esterification of pentaerythritol (PET) with branched or linear fatty acids, preferably C_6-C_{10} acids. Such an ester may contain di-PET as an impurity.

[0077] It has however been found especially advantageous to use a Fischer-Tropsch derived base oil component as substantially the sole base oil component in a refrigerator oil formulation in accordance with the invention. By "substantially" in this context is meant that more than 60 wt%, preferably more than 70 or 80 or 90 or 95 wt% and most preferably

100 wt% of any base oil components in the formulation are Fischer-Tropsch derived base oils (preferably light base oils) as described above, or at least base oils having the preferred properties described above.

[0078] A refrigerator oil formulation prepared according to the invention may additionally contain a gas oil component, in particular a Fischer-Tropsch derived gas oil. It may for example contain a GtL gas oil, which may be prepared using Fischer-Tropsch processes analogous to those described above. Typically the formulation might contain 1% w/w or higher of such gas oil components, or 2 or 5 or 10% w/w or higher. It might contain up to 20 or 25 or 40 or 50% w/w of such gas oil components, in cases up to 60 or 70 or 80 or 90 or 95% w/w.

[0079] In cases, a Fischer-Tropsch derived gas oil may be used in the present invention in place of the Fischer-Tropsch derived base oil. Thus, an aspect of the invention provides the use of a Fischer-Tropsch derived gas oil as a refrigerator oil and/or in a refrigerator oil formulation, suitably although not necessarily for the purpose of increasing the energy efficiency of a temperature modifying and/or controlling system in which the formulation is, or is intended to be, used.

[0080] The hydrocarbon components of a Fischer-Tropsch derived gas oil will typically have boiling points within the typical diesel fuel ("gas oil") range, ie, from about 150 to 400 °C or from 170 to 370 °C. It will suitably have a 90% v/v distillation temperature of from 300 to 370 °C.

[0081] A Fischer-Tropsch derived gas oil will typically have a density from 0.76 to 0.79 g/cm^3 at 15 °C; a cetane number (ASTM D-613) greater than 70, suitably from 74 to 85; a kinematic viscosity (ASTM D-445) from 2 to 4.5, preferably from 2.5 to 4.0, more preferably from 2.9 to 3.7, centistokes at 40 °C; and a sulphur content (ASTM D-2622) of 5 mg/kg or less, preferably of 2 mg/kg or less.

[0082] A refrigerator oil formulation prepared according to the invention may contain a mixture of two or more Fischer-Tropsch derived base oil components. It may for example contain a mixture of a Fischer-Tropsch derived light base oil, of the type defined above, having for example a VK 100 of from about 2 to 3 centistokes, and a higher viscosity Fischer-Tropsch derived base oil, for instance having a VK 100 of around 4 centistokes or in cases higher. In such cases, the concentrations quoted above for the Fischer-Tropsch derived base oil component apply *mutatis mutandis* to a mixture of Fischer-Tropsch derived base oil components.

[0083] A refrigerator oil formulation prepared according to the invention suitably has a VK 100 (ASTM D-445) of 1.2 centistokes or greater. In cases, where the formulation is based on a Fischer-Tropsch derived light base oil, the VK 100 of the formulation may be from 1.2 to 4 centistokes, or from 2 to 3 centistokes.

[0084] The density of the formulation at 15 °C (for example ASTM D-4052) may be from 805 to 825 kg/m^3, or from 810 to 820 kg/m^3.

[0085] Its flash point (measured for example using the COC method) may be 175 or 180 °C or greater, for example from 175 to 195 °C or from 180 to 190 °C.

[0086] It suitably has a low sulphur content, for example 10 ppmw (parts per million by weight) or less. Sulphur contents may be measured using the standard test method ASTM D-2622.

[0087] The formulation may contain other components in addition to the Fischer-Tropsch derived base oil component. It may for example contain one or more base oil additives of the type which are conventional for use in refrigerator oil formulations, for instance additives to enhance its oxidation resistance (antioxidant additives), its resistance to rust through the action of water on steel (rust or corrosion inhibitors), its anti-wear and extreme pressure characteristics (for example anti-wear additives), its cold flow properties (for example pour point depressants), its viscosity or viscosity index, its friction characteristics, its fretting characteristics, its high temperature resistance, its foaming properties and/or its adhesiveness or tackiness. It may contain one or more additives selected from pour point depressants, viscosity index improvers and seal swell agents.

[0088] The concentration of each such additive in the refrigerator oil formulation is preferably up to 2 wt%, for example from 0.1 or 0.2 to 2 or 1.5 wt%, preferably below 1.5 or 1 or 0.8 or 0.5 wt%. (All additive concentrations quoted in this specification refer, unless otherwise stated, to active matter concentrations by mass. Further, all concentrations, unless otherwise stated, are quoted as percentages of the overall refrigerator oil formulation.)

[0089] For example, a refrigerator oil formulation may contain one or more anti-wear or extreme pressure additives such as aryl or alkyl thiophosphates or ZDDPT, at concentrations of for example from 0.1 to 2 wt%. It may contain one or more antioxidants such as phenols or amines, at concentrations of for example from 0.1 to 1.5 wt%. It may contain one or more corrosion inhibitors such as dicarboxylates or sulphonates, at concentrations of for example from 0.1 to 0.5 wt%. It may contain one or more pour point depressants such as polyacrylates or polyolefin copolymers (eg, styrene-butylene/isoprene copolymers), at concentrations of for example from 0.1 to 0.8 wt%. It may contain one or more antifoam agents, either silicon- or non-silicon-based, at concentrations of for example from 1 to 500 mg/kg.

[0090] A refrigerator oil formulation may in cases contain one or more friction modifiers such as molybdenum components, esters or fatty acid/alcohol derivatives, at concentrations of for example from 0.1 to 2 wt%. It may contain one or more lubricity additives such as esters, at concentrations of for example from 0.1 to 2 wt%. It may contain one or more viscosity index improvers such as polyacrylates or polyolefin copolymers (eg, styrene-butylene/isoprene copolymers, at concentrations of for example from 0.1 to 10 wt%. It may contain one or more detergent or dispersant additives, at concentrations of for example 0.1 wt% or greater.

[0091] If desired one or more additive components, such as those listed above, may be co-mixed - preferably together with suitable diluent(s) - in an additive concentrate, and the additive concentrate may then be dispersed into the Fischer-Tropsch derived base oil component, and/or into any other component of the formulation, in order to prepare a refrigerator oil formulation in accordance with the invention.

[0092] Due to the beneficial effects of incorporating the Fischer-Tropsch derived base oil component, a refrigerator oil formulation prepared according to the invention may contain lower levels of additives than other more conventional, in particular mineral oil-based, refrigerator oil formulations. It may for instance contain lower levels of viscosity index improvers and/or antioxidants. A formulation prepared according to the invention may for example contain 50,000 ppmw or less of additives, in cases 40,000 or 30,000 or 20,000 or 10,000 ppmw or less, or even 5,000 or 2,000 or 1,000 ppmw or less. In an embodiment, the formulation contains substantially no additives (by which is meant it contains less than 100 ppmw of additives), and is ideally additive-free.

[0093] In accordance with the invention, a Fischer-Tropsch derived base oil component may be used as a refrigerator oil in a system which contains a refrigerant. During operation of the system, the refrigerant and refrigerator oil formulation are likely to mix to at least some extent.

[0094] The refrigerant may for example be selected from ammonia; carbon dioxide; dimethyl ether; hydrofluorocarbons (HFCs) such as R134a; hydrocarbons such as isobutane (R600a), propane (R290), butane (R600) and propene (R1270); hydrochlorofluorocarbons (HCFCs); and mixtures thereof.

[0095] It may in particular be a hydrocarbon refrigerant such as isobutane (R600a) and/or propane (R290), more particularly isobutane.

[0096] According to the invention, a Fischer-Tropsch derived base oil component may in particular be used to reduce the energy consumption rate of a temperature modifying and/or controlling system. Instead or in addition it may be used to increase the ratio of the energy output rate of the system to its energy consumption rate.

[0097] In accordance with the invention, the energy consumption rate of a system may be assessed in any suitable way, for example using the standard test method EN 153 ("Methods of measuring the energy consumption of electric mains operated household refrigerators, frozen food storage cabinets, food freezers and their combinations, together with associated characteristics"). In general the assessment will involve measuring the amount of energy consumed by the system during a fixed period of time (for example over a period of 24 hours).

[0098] A reduction in energy consumption rate is suitably measured over several operational cycles, suitably two or more or five or more or ten or more. It may for instance be measured over a 24 hour period of operation.

[0099] In the context of the first aspect of the invention, "reducing" the energy consumption rate of a system embraces any degree of reduction compared to the energy consumption rate of the system before the Fischer-Tropsch derived base oil component is incorporated into the refrigerator oil formulation, or compared to that of the system - or of an otherwise analogous system - when running on a refrigerator oil formulation containing no, or a lower concentration of, Fischer-Tropsch derived base oil components. This may for example involve adjusting the energy consumption rate of the system, by means of the Fischer-Tropsch derived base oil component, in order to meet a desired target.

[0100] The reduction may for example be of 5% or greater, preferably 8 or 10% or greater, more preferably 15% or 18% or greater, compared to the energy consumption rate of the system before the Fischer-Tropsch derived base oil component is incorporated into the refrigerator oil formulation, or to that of the system - or of an otherwise analogous system - when running on a refrigerator oil formulation containing no, or a lower concentration of, Fischer-Tropsch derived base oil components.

[0101] "Increasing" the energy output/consumption rate ratio of a system embraces any degree of increase compared to the energy output/consumption rate ratio of the system before the Fischer-Tropsch derived base oil component is incorporated into the refrigerator oil formulation, or compared to that of the system - or of an otherwise analogous system - when running on a refrigerator oil formulation containing no, or a lower concentration of, Fischer-Tropsch derived base oil components. This may for example involve adjusting the energy output/consumption rate ratio of the system, by means of the Fischer-Tropsch derived base oil component, in order to meet a desired target.

[0102] In addition to its use for the purpose of increasing the energy efficiency of a system running on a refrigerator oil formulation into which it is incorporated, the Fischer-Tropsch derived base oil component may be used for one or more of the following purposes:

i) improving the oxidation stability of the formulation;
ii) improving the cold flow properties of the formulation;
iii) improving the biodegradability of the formulation;
iv) improving the compatibility of the formulation with one or more component parts of the system, for example with plastics and/or elastomeric components;
v) improving the mechanical stability of the formulation, for instance its performance under or after applied stress.

[0103] The above properties typically need to be monitored and adjusted in order for a refrigerator oil formulation to meet current performance specifications, and/or to satisfy consumer demand. For example, a certain level of cold flow performance (for example, a maximum pour point) may be desirable to meet relevant specifications, as may a certain level of stability against oxidation. According to the present invention, such standards may all be achievable simultaneously, often with reduced levels of or even no additives present, due to the inclusion of the Fischer-Tropsch derived base oil component.

[0104] In the context of the present invention, "use" of a Fischer-Tropsch derived base oil component in a refrigerator oil formulation means incorporating the base oil component into the formulation, optionally as a blend (ie, a physical mixture) with one or more additional base oil components and optionally with one or more additives such as those described above.

[0105] Such use may also embrace supplying a Fischer-Tropsch derived base oil component together with instructions for its use in a refrigerator oil formulation to achieve the purpose(s) of the first aspect of the invention, for instance to achieve a desired target energy consumption rate in a system running on the formulation.

[0106] The use may involve running a temperature modifying and/or controlling system, in particular a cooling appliance, using within it a refrigerator oil formulation which contains the Fischer-Tropsch derived base oil component.

[0107] A second aspect of the present invention provides the use of a refrigerator oil formulation containing a Fischer-Tropsch derived base oil component, in particular a formulation which has been prepared according to the first aspect of the invention, in a temperature modifying and/or controlling system such as a cooling appliance, for the purpose of increasing the energy efficiency of the system.

[0108] In this context, "use" of a refrigerator oil formulation in a system means introducing the formulation into the system, or into a component of the system such as a compressor; and/or running the system when it contains the formulation.

[0109] A third aspect of the invention provides a temperature modifying and/or controlling system such as a cooling appliance, in particular a refrigerator or freezer or component thereof, which contains a refrigerator oil formulation which has been prepared according to the first aspect of the invention. The oil formulation will typically be contained within a (potentially sealed) component of the system, for example a compressor.

[0110] According to a fourth aspect, the invention provides a method for manufacturing a temperature modifying and/or controlling system such as a cooling appliance, which method involves introducing into the system a refrigerator oil formulation which has been prepared according to the first aspect of the invention. The formulation will typically be introduced into a (potentially sealed) component of the system, for example a compressor. It may be introduced for one or more of the purposes referred to above in connection with the first aspect of the invention, in particular to reduce the energy consumption rate of the system or of a component thereof.

[0111] A fifth aspect provides a method for repairing or otherwise modifying a temperature modifying and/or controlling system such as a cooling appliance, which method involves introducing into the system a refrigerator oil formulation prepared according to the first aspect of the invention. Again the formulation will typically be introduced into a (potentially sealed) component of the system, for example a compressor, or within a new component part which is itself introduced into the system in order to repair or modify it. The formulation may be introduced for one or more of the purposes referred to above in connection with the first aspect of the invention, in particular to reduce the energy consumption rate of the system or of a component thereof.

[0112] A sixth aspect of the invention provides a method of running a temperature modifying and/or controlling system, in particular a cooling appliance such as a refrigerator or freezer, which method involves the use, as a refrigerator oil in the system or in a component thereof, of a refrigerator oil formulation which has been prepared according to the first aspect of the invention. The refrigerator oil formulation may be used in the system so as to provide one or more of the advantages described above.

[0113] According to a seventh aspect, the invention provides a refrigerator oil formulation containing a Fischer-Tropsch derived light base oil.

[0114] An eighth aspect provides the use of a Fischer-Tropsch derived light base oil as a refrigerator oil, and/or in a refrigerator oil formulation. In this context, the light base oil may be used for one or more of the purposes which are described above in connection with the first to the sixth aspects of the invention.

[0115] In accordance with the seventh and eighth aspects of the invention, the Fischer-Tropsch derived light base oil may for example have a VK 100 of from 1 or 1.2 to 5 or from 1.5 to 5 or from 1 or 1.2 or 1.5 to 4 centistokes, or from 2 to 5 or 2 to 4 centistokes, preferably from 2.1 to 3.5 centistokes, more preferably from 2.5 to 3 centistokes.

[0116] Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other moieties, additives, components, integers or steps.

[0117] Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

[0118] Preferred features of each aspect of the invention may be as described in connection with any of the other aspects.

[0119] Other features of the present invention will become apparent from the following examples. Generally speaking the invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith.

[0120] Moreover unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

[0121] The following example illustrates the properties and performance of a refrigerator oil formulation in accordance with the invention.

Example

[0122] A refrigerator oil formulation prepared according to the invention was compared with an otherwise analogous formulation containing a mineral derived base oil.

[0123] The formulation according to the invention, RO-1, contained a blend of 53 wt% of a Fischer-Tropsch derived light base oil BO-1, of VK 100 approximately 2 centistokes, and 36 wt% of a second Fischer-Tropsch derived base oil BO-2, of VK 100 approximately 4 centistokes.

[0124] The two base oils BO-1 and BO-2 (both ex-Shell) had the properties shown in Table 1 below. They had been prepared using Fischer-Tropsch processes analogous to those described above.

Table 1

Property	*Test method*	*Units*	*BO-1*	*BO-2*
Appearance	By eye	N/A	Clear & bright; water white	Clear & bright; water white
Kinematic viscosity at 40 °C	ASTM D-445	centistokes	7.889	17.25
Kinematic viscosity at 100 °C	ASTM D-445	centistokes	2.386	4.029
Viscosity index	ASTM D-2270		126	135
Density @ 15 °C	ASTM D-4052	kg/m^3	802.8	815.7
Pour point	ASTM D-5950	°C	-51	-30

[0125] The mineral-based formulation used as a comparison, RO-2, was sourced from Shell and contained a blend of primarily naphthenic mineral derived base oils.

[0126] The two formulations RO-1 and RO-2 had both been subjected to the same clay treatment steps (Pansil™ 100 (2*1, 5% clay treatment) and Tonsil™ 411 (1*1, 5% clay treatment)). Both contained the same additives, namely, 9 wt% of Infineum™ C 9308 (alkylbenzene solvent, ex Infineum) and 2 wt% of Durad™ 220 (triaryl phosphate; anti-wear additive ex Crompton).

[0127] The VK 100 (ASTM D-445) of the formulation according to the invention, RO-1, was 2.906 centistokes. That of the mineral-based formulation RO-2 was 2.976 centistokes. Thus the two formulations were approximately equivalent in viscosity at the reference temperature of 100 °C, chosen because this is the typical oil sump temperature of a hermetic compressor at its operation point. Both had been tailored to have a VK 100 of approximately 2.9 centistokes, similar to typical currently available naphthenic (mineral-based) refrigerator oils such as ISO VG 15.

[0128] The two formulations were used as lubricants in a commercially available Liebherr™ refrigerator equipped with an Embraco™ EMU 26 CLC compressor and containing the refrigerant R600a (isobutane). Their effects on the energy consumption of the appliance were then determined using the standard test procedure EN 153 ("Methods of measuring the energy consumption of electric mains operated household refrigerators, frozen food storage cabinets, food freezers and their combinations, together with associated characteristics").

[0129] The initial fill lubricant for the test appliance was a standard mineral-based refrigerator oil, ISO VG 10.

[0130] The test procedure was as follows.

[0131] The refrigerator compressor was flushed with, and then filled with, the oil formulation under test, either RO-1 or RO-2. It was then loaded with the refrigerant R600a. The room temperature, temperature measurement method, energy consumption measurement method and test duration were fixed according to EN 153. In this case, however, the temperature and the energy consumption needed to be adjusted because the room temperature could not be fixed to

the required temperature variance as required by EN 153.
The test conditions were:

Room temperature:	25 °C
Average refrigerator inside temperature:	5 °C
Test duration:	24 h + time until last test cycle ends (one cycle = compressor run time + compressor off time (time until compressor re-starts))

Temperature measured once per minute

[0132] Energy consumption measured throughout the test.

[0133] The results, in the form of energy consumption data measured according to EN 153, are shown in Tables 2 and 3 below. Table 2 contains the data obtained using the refrigerator oil according to the invention, RO-1, whilst Table 3 contains the data for the mineral-based formulation RO-2.

Table 2

RO-1 Test number	Tm [°C]	Energy consumption in 24 hours [kWh]
1	4.53	0.6963
2	4.92	0.6411
3	4.68	0.6787
4	4.78	0.6714
5	4.97	0.6515
6	5.54	0.6568
7	5.35	0.6396
8	5.66	0.6279
9	5.88	0.6106
10	5.83	0.6254
11	4.62	0.6978
12	4.73	0.6819
13	4.76	0.6808
14	4.92	0.6701
15	5.31	0.6600
16	5.57	0.6167
17	5.72	0.6277
18	5.40	0.6456
19	3.48	0.7721

Table 3

RO-2 Test number	Tm [°C]	Energy consumption in 24 hours [kWh]
1	3.34	0.93
2	3.80	0.93
3	4.63	0.87
4	4.49	0.89

(continued)

RO-2 Test number	Tm [°C]	Energy consumption in 24 hours [kWh]
5	5.17	0.80
6	5.81	0.73
7	4.69	0.87
8	4.50	0.92
9	4.78	0.84
10	5.96	0.71
11	5.55	0.73
12	5.31	0.76
13	5.23	0.79
14	5.49	0.77
15	5.64	0.77
(Tm = average refrigerator inside temperature during the 24 hour test period.)		

[0134] In order to compare the energy consumption rates of the test appliance when running on the two oils, in accordance with EN 153, it is necessary to adjust the recorded measurements since EN 153 requires measurement at a 5 °C average refrigerator inside temperature and a room temperature of 25 °C, during a 24 hour test cycle.

[0135] By plotting the Table 2 and Table 3 data points graphically, it is possible to derive an estimation of the energy consumption, during 24 hours, at a refrigerator inside temperature of 5 °C. On this basis, the energy consumption when using the mineral derived oil RO-2 was approximately 0.81 kWh, whilst when using the formulation of the invention, RO-1, it was approximately 0.66 kWh. This equates to a reduction of 18.5% in energy consumption when using the invented refrigerator oil formulation as compared to the more conventional mineral derived oil.

[0136] EN 153 further requires a calculation by interpolation of temperature/energy data. This is because the test requires a refrigerator inside temperature of exactly 5 °C and an outside room temperature of exactly 25 °C. In practice, these temperatures cannot be kept uniform over a 24 hour period, especially the inside temperature which varies with the compressor working cycle. Thus, energy consumption values have to be interpolated from two measured results observed at inside temperatures as close as possible to 5 °C.

[0137] The results of this interpolation, for the oils RO-1 and RO-2 respectively, are shown in Tables 4 and 5 below. The results obtained at refrigerator inside temperatures closest to 5 °C were used for this purpose.

Table 4

Test numbers chosen for interpolation	Interpolated energy consumption at 5 °C [kWh]
2,15	0.6450
5,7	0.6506
14,18	0.6750
4,6	0.6672

Table 5

Test numbers chosen for interpolation	Interpolated energy consumption at 5°C [kWh]
9,5	0.8163
7,13	0.8232
3,12	0.8100

[0138] The Table 4 and 5 data provide further evidence of the reduced energy consumption, and hence the improved efficiency, of the test appliance when running on the refrigerator oil formulation prepared according to the present invention.

Claims

1. Use of a Fischer-Tropsch derived base oil component in a refrigerator oil formulation, for the purpose of increasing the energy efficiency of a temperature modifying and/or controlling system in which the formulation is, or is intended to be, used.

2. Use of a refrigerator oil formulation containing a Fischer-Tropsch derived base oil component, in a temperature modifying and/or controlling system, for the purpose of increasing the energy efficiency of the system.

3. Use according to claim 1 or claim 2, wherein the Fischer-Tropsch derived base oil component has a kinematic viscosity at 100 °C (VK 100) of from 1.2 to 5 centistokes.

4. Use according to any one of the preceding claims, wherein the system is a cooling appliance or component thereof.

5. A temperature modifying and/or controlling system, containing a refrigerator oil formulation which has been prepared according to any one of the preceding claims.

6. A method for manufacturing a temperature modifying and/or controlling system, which method involves introducing into the system a refrigerator oil formulation which has been prepared according to any one of claims 1 to 4.

7. A method for repairing or otherwise modifying a temperature modifying and/or controlling system, which method involves introducing into the system a refrigerator oil formulation which has been prepared according to any one of claims 1 to 4.

8. A method of operating a temperature modifying and/or controlling system, which method involves the use in the system of a refrigerator oil formulation which has been prepared according to any one of claims 1 to 4.

9. A refrigerator oil formulation containing a Fischer-Tropsch derived light base oil component which has a VK 100 of from 1.2 to 5 centistokes.

10. A temperature modifying and/or controlling system, which contains a refrigerator oil formulation according to claim 9.

11. A method for manufacturing, or for repairing or otherwise modifying a temperature modifying and/or controlling system, which method involves introducing into the system a refrigerator oil formulation according to claim 9.

12. Use of a Fischer-Tropsch derived light base oil component, having a VK 100 of from 1.2 to 5 centistokes, in a refrigerator oil formulation.

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EUROPEAN SEARCH REPORT

Application Number
EP 08 16 3865

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Place of search	Date of completion of the search	Examiner
Munich	8 December 2008	Greß, Tobias

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X : particularly relevant if taken alone
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