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(54) ELECTRICAL INSULATING OIL COMPOSITIONS AND PREPARATION THEREOF

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(57) **ABSTRACT**

An electrical insulating oil composition comprising a heavy reformate as an anti-gassing agent is provided with excellent gassing tendency. In one embodiment, the composition displays a gassing performance of <30 μ L per minute as measured according to ASTM D-2300-1976. In a second embodiment, the composition displays a gassing performance of <0 μ L per minute. In a third embodiment, the composition displays a negative gassing tendency as low as <-70 μ L per minute.

ELECTRICAL INSULATING OIL COMPOSITIONS AND PREPARATION THEREOF

TECHNICAL FIELD

[0001] The invention relates generally to electrical insulating oil compositions exhibiting improved gassing properties.

BACKGROUND

[0002] Electrical insulating oils (or sometimes called "electrical oils" or "transformer oils") are essential in the transmission of electrical power. They are manufactured to provide extremely low electrical conductivity, meaning with high resistance to passing an electric current. Also because transferring electricity generates a great deal of heat, electrical insulating oils are also required for their cooling capability. Due to the high performance requirements, specifications were developed to ensure that fluids from different manufacturers are interchangeable, including the American Society for Testing and Materials (ASTM), the International Electrotechnical Commission (IEC), the British Standard (BS) and the German specifications DIN 57370/VDE 0370.

[0003] Under electrical or thermal stress, dielectric liquids such as electrical insulating oils produce gas. The performance of oil cooled, insulated, or impregnated electrical equipment such as transformers, cables, or capacitors, is affected by the presence of these small gaseous bubbles, which can give rise to partial discharges and to eventual insulation breakdown. Therefore, the gassing properties of an electrical insulating oil, i.e. its tendency to absorb or evolve gases, have been recognized as a factor of major importance in characterizing electrical insulating oils. The transition from gas absorption to gas evolution can occur at different temperatures and electrical stresses for different oils.

[0004] IEC60296 has no requirement for gassing tendency of insulating oil. However, for special application, this standard suggests a number of maximum +5, as measured by test method IEC60628. ASTM D3487-00 (Re-approved 2006) has a limit of +30 as measured by ASTM D2300-00. In this test a 10,000 volt a.c. current is applied to two closely spaced electrodes, one being immersed in the transformer fluid under a hydrogen atmosphere. The amount of pressure elevation is an index of the amount of decomposition resulting from the electrical stress that is applied to the liquid. A pressure decrease, indicated by a negative pressure reading is indicative of a liquid which is stable under the corona forces and which is a net absorber of hydrogen.

[0005] U.S. Pat. No. 6,790,386 discloses a dielectric fluid comprising an iso-paraffinic base oil and hydrogen donor compound, which may be a substituted or partially saturated aromatic compound, e.g., saturated polyring aromatics, aklyated one ring aromatics, alkylated polyring aromatics, partially saturated alkylated polyring aromatics, and mixtures thereof.

[0006] Typically reformate is the largest process stream contributing benzene to the gasoline pool, making up about 75 to 80 vol. % of the benzene. It is readily available and less expensive than the anti-gassing compounds used in the prior art. There is still a need for electrical insulating oils exhibiting improved gassing tendency and aniline point meeting stan-

dard specifications, employing inexpensive and available petroleum resources such as heavy reformates.

SUMMARY OF THE INVENTION

[0007] In one embodiment, there is provided an electrical insulating oil composition in compliance with at least one of ASTM D 3487-2000 and IEC 60296-2003, the composition comprising: (a) a base oil selected from the group of a natural oil, a synthetic oil, a Fischer-Tropsch derived base oil, and mixtures thereof, (b) 0.001 to 10 wt % at least an additive selected from an additive package, an oxidation inhibitor, anti-gassing agent, pour point depressant, metal deactivator, metal passivator, anti-foaming agent, and mixtures thereof, and (c) a sufficient amount of a heavy reformate for the composition to have a gassing tendency of <30 μ L per minute as measured according to ASTM D-2300-2300.

[0008] In another aspect, there is provided an electrical insulating oil composition comprising 0.50 to 10 wt. % of a heavy reformate for the composition to have a gassing tendency of less than 0 μL per minute as measured according to ASTM D-2300-1976.

[0009] There is also provided a method to improve the gassing tendency of an electrical insulating oil composition comprising by blending into a base oil 0.50 to 10 wt. % of a heavy reformate for the composition to have a gassing tendency of $<-5 \,\mu$ L per minute as measured according to ASTM D-2300-1976.

DETAILED DESCRIPTION

[0010] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[0011] As used herein, the terms "electrical insulating oil," "transformer oil," "dielectric fluid," "transformer fluid" may be used interchangeably, referring to a composition that can be used for insulating/cooling power and distribution electrical equipment, and meeting electrical insulating oil specifications and testing protocol defined by the American Society for Testing and Materials (ASTM D3487-00 (Re-approved 2006)) and the European specifications 60296 as defined by the International Electrical Commission (IEC).

[0012] "Fischer-Tropsch derived" means that the product, fraction, or feed originates from or is produced at some stage by a Fischer-Tropsch process. As used herein, "Fischer-Tropsch base oil" may be used interchangeably with "FT base oil," "FTBO," "GTL base oil" (GTL: gas-to-liquid), or "Fischer-Tropsch derived base oil."

[0013] As used herein, "isomerized base oil" refers to a base oil made by isomerization of a waxy feed.

[0014] As used herein, a "waxy feed" comprises at least 40 wt % n-paraffins. In one embodiment, the waxy feed comprises greater than 50 wt % n-paraffins. In another embodiment, greater than 75 wt % n-paraffins. In one embodiment, the waxy feed also has very low levels of nitrogen and sulphur, e.g., less than 25 ppm total combined nitrogen and sulfur, or in other embodiments less than 20 ppm. Examples of waxy feeds include slack waxes, deoiled slack waxes, refined foots oils, waxy lubricant raffinates, n-paraffin waxes, NAO waxes, waxes produced in chemical plant processes, deoiled petroleum derived waxes, microcrystalline waxes, Fischer-Tropsch waxes, and mixtures thereof. In one embodiment, the waxy feeds have a pour point of greater than 50° C. In another embodiment, greater than 60° C.

[0015] As used herein, "pour point reducing blend component" refers to an isomerized waxy product with relatively high molecular weights and a specified degree of alkyl branching in the molecule, such that it reduces the pour point of lubricating base oil blends containing it. Examples of a pour point reducing blend component are disclosed in U.S. Pat. Nos. 6,150,577 and 7,053,254, and Patent Publication No. US 2005-0247600 A1. A pour point reducing blend component can be: 1) an isomerized Fischer-Tropsch derived bottoms product; 2) a bottoms product prepared from an isomerized highly waxy mineral oil, or 3) an isomerized oil having a kinematic viscosity at 100° C. of at least about 8 mm²/s made from polyethylene plastic.

[0016] As used herein, the "10 percent point" of the boiling range of a pour point reducing blend component refers to the temperature at which 10 weight percent of the hydrocarbons present within that cut will vaporize at atmospheric pressure. Similarly, the 90 percent point of the respective boiling ranges refers to the temperature at which 90 weight percent of the hydrocarbons present within that cut will vaporize at atmospheric pressure. For samples having a boiling range above 1000° F. (538° C.), the boiling range can be measured using the standard analytical method D-6352-04 or its equivalent. For samples having a boiling range below 1000° F. (538° C.), the boiling range distributions in this disclosure can be measured using the standard analytical method D-2887-06 or its equivalent. It will be noted that only the 10 percent point of the respective boiling range is used when referring to the pour point reducing blend component that is a vacuum distillation bottoms product, since it is derived from a bottoms fraction which makes the 90 percent point or upper boiling limit irrelevant.

[0017] "Kinematic viscosity" is a measurement in mm²/S of the resistance to flow of a fluid under gravity, determined by ASTM D445-06.

[0018] "Viscosity index" (VI) is an empirical, unit-less number indicating the effect of temperature change on the kinematic viscosity of the oil. The higher the VI of an oil, the lower its tendency to change viscosity with temperature. Viscosity index is measured according to ASTM D 2270-04.

[0019] Cold-cranking simulator apparent viscosity (CCS VIS) is a measurement in millipascal seconds, mPa·s to measure the viscometric properties of lubricating base oils under low temperature and high shear. CCS VIS is determined by ASTM D 5293-04.

[0020] The boiling range distribution of base oil, by wt %, is determined by simulated distillation (SIMDIS) according to ASTM D 6352-04, "Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700° C. by Gas Chromatography."

[0021] "Noack volatility" is defined as the mass of oil, expressed in weight %, which is lost when the oil is heated at 250° C. with a constant flow of air drawn through it for 60 min., measured according to ASTM D5800-05, Procedure B. **[0022]** Brookfield viscosity is used to determine the internal fluid-friction of a lubricant during cold temperature operation, which can be measured by ASTM D 2983-04.

[0023] "Pour point" is a measurement of the temperature at which a sample of base oil will begin to flow under certain carefully controlled conditions, which can be determined as described in ASTM D 5950-02.

[0024] "Auto ignition temperature" is the temperature at which a fluid will ignite spontaneously in contact with air, which can be determined according to ASTM 659-78.

[0025] "Ln" refers to natural logarithm with base "e."

[0026] "Traction coefficient" is an indicator of intrinsic lubricant properties, expressed as the dimensionless ratio of the friction force F and the normal force N, where friction is the mechanical force which resists movement or hinders movement between sliding or rolling surfaces. Traction coefficient can be measured with an MTM Traction Measurement System from PCS Instruments, Ltd., configured with a polished 19 mm diameter ball (SAE AISI 52100 steel) angled at 220 to a flat 46 mm diameter polished disk (SAE AISI 52100 steel). The steel ball and disk are independently measured at an average rolling speed of 3 meters per second, a slide to roll ratio of 40 percent, and a load of 20 Newtons. The roll ratio is defined as the difference in sliding speed between the ball and disk divided by the mean speed of the ball and disk, i.e. roll ratio=(Speed1–Speed2)/((Speed1+Speed2)–/2).

[0027] As used herein, "consecutive numbers of carbon atoms" means that the base oil has a distribution of hydrocarbon molecules over a range of carbon numbers, with every number of carbon numbers in-between. For example, the base oil may have hydrocarbon molecules ranging from C22 to C36 or from C30 to C60 with every carbon number in-between. The hydrocarbon molecules of the base oil differ from each other by consecutive numbers of carbon atoms, as a consequence of the waxy feed also having consecutive numbers of carbon atoms. For example, in the Fischer-Tropsch hydrocarbon synthesis reaction, the source of carbon atoms is CO and the hydrocarbon molecules are built up one carbon atom at a time. Petroleum-derived waxy feeds have consecutive numbers of carbon atoms. In contrast to an oil based on poly-alpha-olefin ("PAO"), the molecules of an isomerized base oil have a more linear structure, comprising a relatively long backbone with short branches. The classic textbook description of a PAO is a star-shaped molecule, and in particular tridecane, which is illustrated as three decane molecules attached at a central point. While a star-shaped molecules is theoretical, nevertheless PAO molecules have fewer and longer branches that the hydrocarbon molecules that make up the isomerized base oil disclosed herein.

[0028] "Molecules with cycloparaffinic functionality" mean any molecule that is, or contains as one or more substituents, a monocyclic or a fused multicyclic saturated hydrocarbon group.

[0029] "Molecules with monocycloparaffinic functionality" mean any molecule that is a monocyclic saturated hydrocarbon group of three to seven ring carbons or any molecule that is substituted with a single monocyclic saturated hydrocarbon group of three to seven ring carbons.

[0030] "Molecules with multicycloparaffinic functionality" mean any molecule that is a fused multicyclic saturated hydrocarbon ring group of two or more fused rings, any molecule that is substituted with one or more fused multicyclic saturated hydrocarbon ring groups of two or more fused rings, or any molecule that is substituted with more than one monocyclic saturated hydrocarbon group of three to seven ring carbons.

[0031] Molecules with cycloparaffinic functionality, molecules with monocycloparaffinic functionality, and molecules with multicycloparaffinic functionality are reported as weight percent and are determined by a combination of Field Ionization Mass Spectroscopy (FIMS), HPLC-UV for aromatics, and Proton NMR for olefins, further fully described herein. **[0032]** Oxidator BN measures the response of a lubricating oil in a simulated application. High values, or long times to adsorb one liter of oxygen, indicate good stability.

[0033] Oxidator BN can be measured via a Dornte-type oxygen absorption apparatus (R. W. Dornte "Oxidation of White Oils," Industrial and Engineering Chemistry, Vol. 28, page 26, 1936), under 1 atmosphere of pure oxygen at 340° F., time to absorb 1000 ml of O₂ by 100 g. of oil is reported. In the Oxidator BN test, 0.8 ml of catalyst is used per 100 grams of oil. The catalyst is a mixture of soluble metal-naphthenates simulating the average metal analysis of used crankcase oil. The additive package is 80 millimoles of zinc bispolypropylenephenyldithiophosphate per 100 grams of oil.

[0034] Molecular characterizations can be performed by methods known in the art, including Field Ionization Mass Spectroscopy (FIMS) and n-d-M analysis (ASTM D 3238-95 (Re-approved 2005)). In FIMS, the base oil is characterized as alkanes and molecules with different numbers of unsaturations. The molecules with different numbers of unsaturations may be comprised of cycloparaffins, olefins, and aromatics. If aromatics are present in significant amount, they would be identified as 4-unsaturations. When olefins are present in significant amounts, they would be identified as 1-unsaturations. The total of the 1-unsaturations, 2-unsaturations, 3-unsaturations, 4-unsaturations, 5-unsaturations, and 6-unsaturations from the FIMS analysis, minus the wt % olefins by proton NMR, and minus the wt % aromatics by HPLC-UV is the total weight percent of molecules with cycloparaffinic functionality. If the aromatics content was not measured, it was assumed to be less than 0.1 wt % and not included in the calculation for total weight percent of molecules with cycloparaffinic functionality. The total weight percent of molecules with cycloparaffinic functionality is the sum of the weight percent of molecules with monocyclopraffinic functionality and the weight percent of molecules with multicycloparaffinic functionality.

[0035] Molecular weights are determined by ASTM D2503-92 (Reapproved 2002). The method uses thermoelectric measurement of vapour pressure (VPO). In circumstances where there is insufficient sample volume, an alternative method of ASTM D2502-94 may be used; and where this has been used it is indicated.

[0036] Density is determined by ASTM D4052-96 (Reapproved 2002). The sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the cange in the mass of the tube is used in conjunction with calibration data to determine the density of the sample. [0037] Weight percent olefins can be determined by proton-NMR according to the steps specified herein. In most tests, the olefins are conventional olefins, i.e. a distributed mixture of those olefin types having hydrogens attached to the double bond carbons such as: alpha, vinylidene, cis, trans, and trisubstituted, with a detectable allylic to olefin integral ratio between 1 and 2.5. When this ratio exceeds 3, it indicates a higher percentage of tri or tetra substituted olefins being present, thus other assumptions known in the analytical art can be made to calculate the number of double bonds in the sample. The steps are as follows: A) Prepare a solution of 5-10% of the test hydrocarbon in deuterochloroform. B) Acquire a normal proton spectrum of at least 12 ppm spectral width and accurately reference the chemical shift (ppm) axis, with the instrument having sufficient gain range to acquire a signal without overloading the receiver/ADC, e.g., when a 30 degree pulse is applied, the instrument having a minimum signal digitization dynamic range of 65,000. In one embodiment, the instrument has a dynamic range of at least 260,000. C) Measure the integral intensities between: 6.0-4.5 ppm (olefin); 2.2-1.9 ppm (allylic); and 1.9-0.5 ppm (saturate). D) Using the molecular weight of the test substance determined by ASTM D 2503-92 (Reapproved 2002), calculate: 1. The average molecular formula of the saturated hydrocarbons; 2. The average molecular formula of the olefins; 3. The total integral intensity (=sum of all integral intensities); 4. The integral intensity per sample hydrogen (=total integral/number of hydrogens in formula); 5. The number of olefin hydrogens (=Olefin integral/integral per hydrogen); 6. The number of double bonds (=Olefin hydrogen times hydrogens in olefin formula/2); and 7. The wt % olefins by proton NMR=100 times the number of double bonds times the number of hydrogens in a typical olefin molecule divided by the number of hydrogens in a typical test substance molecule. In this test, the wt % olefins by proton NMR calculation procedure, D, works particularly well when the percent olefins result is low, less than 15 wt %.

[0038] Weight percent aromatics in one embodiment can be measured by HPLC-UV. In one embodiment, the test is conducted using a Hewlett Packard 1050 Series Quaternary Gradient High Performance Liquid Chromatography (HPLC) system, coupled with a HP 1050 Diode-Array UV-V is detector interfaced to an HP Chem-station. Identification of the individual aromatic classes in the highly saturated base oil can be made on the basis of the UV spectral pattern and the elution time. The amino column used for this analysis differentiates aromatic molecules largely on the basis of their ringnumber (or double-bond number). Thus, the single ring aromatic containing molecules elute first, followed by the polycyclic aromatics in order of increasing double bond number per molecule. For aromatics with similar double bond character, those with only alkyl substitution on the ring elute sooner than those with naphthenic substitution. Unequivocal identification of the various base oil aromatic hydrocarbons from their UV absorbance spectra can be accomplished recognizing that their peak electronic transitions are all redshifted relative to the pure model compound analogs to a degree dependent on the amount of alkyl and naphthenic substitution on the ring system. Quantification of the eluting aromatic compounds can be made by integrating chromatograms made from wavelengths optimized for each general class of compounds over the appropriate retention time window for that aromatic. Retention time window limits for each aromatic class can be determined by manually evaluating the individual absorbance spectra of eluting compounds at different times and assigning them to the appropriate aromatic class based on their qualitative similarity to model compound absorption spectra.

[0039] HPLC-UV Calibration. In one embodiment, HPLC-UV can be used for identifying classes of aromatic compounds even at very low levels, e.g., multi-ring aromatics typically absorb 10 to 200 times more strongly than singlering aromatics. Alkyl-substitution affects absorption by 20%. Integration limits for the co-eluting 1-ring and 2-ring aromatics at 272 nm can be made by the perpendicular drop method. Wavelength dependent response factors for each general aromatic class can be first determined by constructing Beer's Law plots from pure model compound mixtures based on the nearest spectral peak absorbances to the substituted aromatic analogs. Weight percent concentrations of aromatics can be calculated by assuming that the average molecular weight for each aromatic class was approximately equal to the average molecular weight for the whole base oil sample.

[0040] NMR analysis. In one embodiment, the weight percent of all molecules with at least one aromatic function in the purified mono-aromatic standard can be confirmed via longduration carbon 13 NMR analysis. The NMR results can be translated from % aromatic carbon to % aromatic molecules (to be consistent with HPLC-UV and D 2007) knowing that 95-99% of the aromatics in highly saturated base oils are single-ring aromatics. In another test to accurately measure low levels of all molecules with at least one aromatic function by NMR, the standard D 5292-99 (Reapproved 2004) method can be modified to give a minimum carbon sensitivity of 500:1 (by ASTM standard practice E 386) with a 15-hour duration run on a 400-500 MHz NMR with a 10-12 mm Nalorac probe. Acorn PC integration software can be used to define the shape of the baseline and consistently integrate.

[0041] Extent of branching refers to the number of alkyl branches in hydrocarbons. Branching and branching position can be determined using carbon-13 (13C) NMR according to the following nine-step process: 1) Identify the CH branch centers and the CH₃ branch termination points using the DEPT Pulse sequence (Doddrell, D. T.; D. T. Pegg; M. R. Bendall, Journal of Magnetic Resonance 1982, 48, 323ff.). 2) Verify the absence of carbons initiating multiple branches (quaternary carbons) using the APT pulse sequence (Patt, S. L.; J. N. Shoolery, Journal of Magnetic Resonance 1982, 46, 535ff.). 3) Assign the various branch carbon resonances to specific branch positions and lengths using tabulated and calculated values known in the art (Lindeman, L. P., Journal of Qualitative Analytical Chemistry 43, 1971 1245ff; Netzel, D. A., et. al., Fuel, 60, 1981, 307ff). 4) Estimate relative branching density at different carbon positions by comparing the integrated intensity of the specific carbon of the methyl/ alkyl group to the intensity of a single carbon (which is equal to total integral/number of carbons per molecule in the mixture). For the 2-methyl branch, where both the terminal and the branch methyl occur at the same resonance position, the intensity is divided by two before estimating the branching density. If the 4-methyl branch fraction is calculated and tabulated, its contribution to the 4+methyls is subtracted to avoid double counting. 5) Calculate the average carbon number. The average carbon number is determined by dividing the molecular weight of the sample by 14 (the formula weight of CH_2). 6) The number of branches per molecule is the sum of the branches found in step 4.7) The number of alkyl branches per 100 carbon atoms is calculated from the number of branches per molecule (step 6) times 100/average carbon number. 8) Estimate Branching Index (BI) by ¹H NMR Analysis, which is presented as percentage of methyl hydrogen (chemical shift range 0.6-1.05 ppm) among total hydrogen as estimated by NMR in the liquid hydrocarbon composition. 9) Estimate Branching proximity (BP) by ¹³C NMR, which is presented as percentage of recurring methylene carbons-which are four or more carbons away from the end group or a branch (represented by a NMR signal at 29.9 ppm) among total carbons as estimated by NMR in the liquid hydrocarbon composition. The measurements can be performed using any Fourier Transform NMR spectrometer, e.g., one having a magnet of 7.0 T or greater. After verification by Mass Spectrometry, UV or an NMR survey that aromatic carbons are absent, the spectral width for the ¹³C NMR studies can be limited to the saturated carbon region, 0-80 ppm vs. TMS (tetramethylsilane). Solutions of 25-50 wt. % in chloroform-dl are excited by 30 degrees pulses followed by a 1.3 sec acquisition time. In order to minimize non-uniform intensity data, the broadband proton inverse-gated decoupling is used during a 6 sec delay prior to the excitation pulse and on during acquisition. Samples are doped with 0.03 to 0.05 M Cr (acac)₃ (tris(acetylacetonato)-chromium (III)) as a relaxation agent to ensure full intensities are observed. The DEPT and APT sequences can be carried out according to literature descriptions with minor deviations described in the Varian or Bruker operating manuals. DEPT is Distortionless Enhancement by Polarization Transfer. The DEPT 45 sequence gives a signal all carbons bonded to protons. DEPT 90 shows CH carbons only. DEPT 135 shows CH and CH₂ up and CH₂ 180 degrees out of phase (down). APT is attached proton test, known in the art. It allows all carbons to be seen, but if CH and CH₃ are up, then quaternaries and CH₂ are down. The branching properties of the sample can be determined by ¹³C NMR using the assumption in the calculations that the entire sample was iso-paraffinic. The unsaturates content may be measured using Field Ionization Mass Spectroscopy (FIMS).

[0042] In one embodiment, the electrical insulating composition comprises a heavy reformate as an anti-gassing agent and optional additives in a matrix of base oil.

[0043] Base Oil Component: Base oils suitable for use in formulating electrical insulating oil compositions are selected from any of the synthetic or natural oils or mixtures thereof, e.g., any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines.

[0044] Examples of natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) and mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale are also suitable. Further, oils derived from a gas-to-liquid process are also suitable.

[0045] In one embodiment, synthetic oils for use in the electrical insulating composition include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); polyalphaolefins such as poly(1-hexenes), poly-(1-octenes), poly(1-decenes), etc. and mixtures thereof, alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, di-nonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyl, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0046] In one embodiment, the synthetic oil for use in the electrical insulating composition is selected from the group of alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc. Examples include oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxy-alkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_{3-8} fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

[0047] In another embodiment, the synthetic oil is selected from esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.). Examples include dibutyl adipate, di(2ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like. Examples of esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0048] In one embodiment, the base oil is a poly-alphaolefin (PAO). Typically, the poly-alpha-olefins are derived from monomers having from about 4 to about 30, or from about 4 to about 20, or from about 6 to about 16 carbon atoms. Examples of useful PAOs include those derived from octene, decene, mixtures thereof, and the like, e.g., 4 cSt at 100° C. poly-alpha-olefins, 6 cSt at 100° C. poly-alpha-olefins, and mixtures thereof. In another embodiment, the base oil comprises mixtures of mineral oil with the foregoing poly-alphaolefins.

[0049] In one embodiment, the base oil comprises at least an isomerized base oil which the product itself, its fraction, or feed originates from or is produced at some stage by isomerization of a waxy feed from a Fischer-Tropsch process ("Fischer-Tropsch derived base oils"). In another embodiment, the base oil comprises at least an isomerized base oil made from a substantially paraffinic wax feed ("waxy feed").

[0050] Fischer-Tropsch derived base oils are disclosed in U.S. Pat. Nos. 6,080,301, 6,090,989, 6,165,949, 7,018,525, 7,083,713, U.S. application Ser. Nos. 11/400,570, 11/535, 165 and 11/613,936, and US Patent Publication Nos. US2004/0079678A1, US20050133409, US20060289337, US 2006/0289337, US2006/0201851, US2006/0016721, US2006/0016724, US2006/0076267, US2006/020185, US2006/013210, US2005/0241990, US2005/0077208, US2005/0139513, US2005/0139514, US2005/0133409, US2005/0133407, US2005/0261147, US2005/0261146, US2005/0261145, and US2004/0159582. Fischer-Tropsch process is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms including a light reaction product and a waxy reaction product, with both being substantially paraffinic.

[0051] In one embodiment the isomerized base oil has consecutive numbers of carbon atoms and has less than 10 wt % naphthenic carbon by n-d-M. In yet another embodiment the isomerized base oil made from a waxy feed has a kinematic viscosity at 100° C. between 1.5 and 3.5 mm²/S.

[0052] In one embodiment, the isomerized base oil is made by a process in which the hydroisomerization dewaxing is performed at conditions sufficient for the base oil to have: a) a weight percent of all molecules with at least one aromatic functionality less than 0.30; b) a weight percent of all molecules with at least one cycloparaffinic functionality greater than 10; c) a ratio of weight percent molecules with monocycloparaffinic functionality to weight percent molecules with multicycloparaffinic functionality greater than 20 and d) a viscosity index greater than 28×Ln (Kinematic viscosity at 100° C.)+80.

[0053] In another embodiment, the isomerized base oil is made from a process in which the highly paraffinic wax is hydroisomerized using a shape selective intermediate pore size molecular sieve comprising a noble metal hydrogenation component, and under conditions of 600-750° F. (315-399° C.) In the process, the conditions for hydroisomerization are controlled such that the conversion of the compounds boiling above 700° F. (371° C.) in the wax feed to compounds boiling below 700° F. (371° C.) is maintained between 10 wt % and 50 wt %. A resulting isomerized base oil has a kinematic viscosity of between 1.0 and $3.5 \text{ mm}^2/\text{s}$ at 10° C. and a Noack volatility of less than 50 weight %. The base oil comprises greater than 3 weight % molecules with cycloparaffinic functionality and less than 0.30 weight percent aromatics.

[0054] In one embodiment the isomerized base oil has a Noack volatility less than an amount calculated by the following equation: $1000 \times (\text{Kinematic Viscosity at } 100^{\circ} \text{ C.})^{-2.7}$. In another embodiment, the isomerized base oil has a Noack volatility less than an amount calculated by the following equation: 900×(Kinematic Vicosity at 100° C.)^{-2.1}. In a third embodiment, the isomerized base oil has a Kinematic Vicosity at 100° C. of >1.808 mm²/S and a Noack volatility less than an amount calculated by the following equation: 1.286+ 20 $(kv100)^{-1.5}$ +551.8 e^{kv100} , where kv100 is the kinematic viscosity at 10° C. In a fourth embodiment, the isomerized base oil has a kinematic viscosity at 100° C. of less than 4.0 mm²/s, and a wt % Noack volatility between 0 and 100. In a fifth embodiment, the isomerized base oil has a kinematic viscosity between 1.5 and 4.0 mm²/s and a Noack volatility less than the Noack volatility calculated by the following equation: 160-40 (Kinematic Viscosity at 100° C.).

[0055] In one embodiment, the isomerized base oil has a kinematic viscosity at 100° C. in the range of 2.4 and 3.8 mm²/s and a Noack volatility less than an amount defined by the equation: $900\times$ (Kinematic Viscosity at 100° C.)^{-2.8}–15). For kinematic viscosities in the range of 2.4 and 3.8 mm²/s the equation: $900\times$ (Kinematic Viscosity at 100° C.)^{-2.8}–15) provides a lower Noack volatility than the equation: 160-40 (Kinematic Viscosity at 100° C.)

[0056] In one embodiment, the isomerized base oil is made from a process in which the highly paraffinic wax is hydroisomerized under conditions for the base oil to have a kinematic viscosity at 100° C. of 3.6 to 4.2 mm²/s, a viscosity index of greater than 130, a wt % Noack volatility less than 12, a pour point of less than -9° C.

[0057] In one embodiment, the isomerized base oil has an auto-ignition temperature (AIT) greater than the AIT (° C.) defined by equation: $1.6\times$ (Kinematic Viscosity at 40° C., in mm²/s)+300. In a second embodiment, the base oil as an AIT of greater than 329° C. and a viscosity index greater than 28×Ln (Kinematic Viscosity at 100° C., in mm²/s)+100.

[0058] In one embodiment, the isomerized base oil has a relatively low traction coefficient, specifically, its traction coefficient is less than an amount calculated by the equation: traction coefficient= $0.009 \times Ln$ (kinematic viscosity in mm²/S)-0.001, wherein the kinematic viscosity in the equation is the kinematic viscosity during the traction coefficient measurement and is between 2 and 50 mm²/S. In one embodiment, the isomerized base oil has a traction coefficient of less than 0.023 (or less than 0.021) when measured at a kinematic

viscosity of 15 mm²/s and at a slide to roll ratio of 40%. In another embodiment the isomerized base oil has a traction coefficient of less than 0.017 when measured at a kinematic viscosity of 15 mm²/s and at a slide to roll ratio of 40%. In another embodiment the isomerized base oil has a viscosity index greater than 150 and a traction coefficient less than 0.015 when measured at a kinematic viscosity of 15 mm²/s and at a slide to roll ratio of 40 percent.

[0059] In some embodiments, the isomerized base oil having low traction coefficients also displays a higher kinematic viscosity and higher boiling points. In one embodiment, the base oil has a traction coefficient less than 0.015, and a 50 wt % boiling point greater than 565° C. (1050° F.). In another embodiment, the base oil has a traction coefficient less than 0.011 and a 50 wt % boiling point by ASTM D 6352-04 greater than 582° C. (1080° F.).

[0060] In some embodiments, the isomerized base oil having low traction coefficients also displays unique branching properties by NMR, including a branching index less than or equal to 23.4, a branching proximity greater than or equal to 22.0, and a Free Carbon Index between 9 and 30. In one embodiment, the base oil has at least 4 wt % naphthenic carbon, in another embodiment, at least 5 wt % naphthenic carbon by n-d-M analysis by ASTM D 3238-95 (Reapproved 2005).

[0061] In one embodiment, the isomerized base oil is produced in a process wherein the intermediate oil isomerate comprises paraffinic hydrocarbon components, and in which the extent of branching is less than 7 alkyl branches per 100 carbons, and wherein the base oil comprises paraffinic hydrocarbon components in which the extent of branching is less than 8 alkyl branches per 100 carbons and less than 20 wt % of the alkyl branches are at the 2 position. In one embodiment, the FT base oil has a pour point of less than -8° C.; a kinematic viscosity at 100° C. of at least 3.2 mm²/s; and a Viscosity Index greater than a viscosity index calculated by the equation of =22×Ln (Kinematic Viscosity at 100° C.)+132.

[0062] In one embodiment, the base oil comprises greater than 10 wt. % and less than 70 wt. % total molecules with cycloparaffinic functionality, and a ratio of weight percent molecules with monocycloparaffinic functionality to weight percent molecules with multicycloparaffinic functionality greater than 15.

[0063] In one embodiment, the isomerized base oil has an average molecular weight between 600 and 1100, and an average degree of branching in the molecules between 6.5 and 10 alkyl branches per 100 carbon atoms. In another embodiment, the isomerized base oil has a kinematic viscosity between about 8 and about $25 \text{ mm}^2/\text{s}$ and an average degree of branching in the molecules between 6.5 and 10 alkyl branches per 100 carbon atoms.

[0064] In one embodiment, the isomerized base oil is obtained from a process in which the highly paraffinic wax is hydroisomerized at a hydrogen to feed ratio from 712.4 to 3562 liter H_2 /liter oil, for the base oil to have a total weight percent of molecules with cycloparaffinic functionality of greater than 10, and a ratio of weight percent molecules with monocycloparaffinic functionality to weight percent molecules with multicycloparaffinic functionality of greater than 15. In another embodiment, the base oil has a viscosity index greater than an amount defined by the equation: 28×Ln (Kinematic viscosity at 100° C.)+95. In a third embodiment, the base oil comprises a weight percent aromatics less than 0.30; a weight percent of molecules with cycloparaffinic function-

ality greater than 10; a ratio of weight percent of molecules with monocycloparaffinic functionality to weight percent of molecules with multicycloparaffinic functionality greater than 20; and a viscosity index greater than $28 \times \text{Ln}$ (Kinematic Viscosity at 100° C.)+110. In a fourth embodiment, the base oil further has a kinematic viscosity at 100° C. greater than 6 mm²/s. In a fifth embodiment, the base oil has a weight percent aromatics less than 0.05 and a viscosity index greater than $28 \times \text{Ln}$ (Kinematic Viscosity at 100° C.)+95. In a sixth embodiment, the base oil has a weight percent aromatics less than 0.30, a weight percent molecules with cycloparaffinic functionality greater than the kinematic viscosity at 100° C., in mm²/s, multiplied by three, and a ratio of molecules with multicycloparaffinic functionality to molecules with multicycloparaffinic functionality greater than 15.

[0065] In one embodiment, the isomerized base oil contains between 2 and 10% naphthenic carbon as measured by n-d-M. In one embodiment, the base oil has a kinematic viscosity of 1.5- 3.0 mm^2 /s at 100° C. and 2-3% naphthenic carbon. In another embodiment, a kinematic viscosity of 1.8- 3.5 mm^2 /s at 100° C. and 2.5-4% naphthenic carbon. In a third embodiment, a kinematic viscosity of 3- 6 mm^2 /s at 100° C. and 2.7-5% naphthenic carbon. In a fourth embodiment, a kinematic viscosity of 10- 30 mm^2 /s at 100° C. and greater than 5.2% naphthenic carbon.

[0066] In one embodiment, the isomerized base oil has an average molecular weight greater than 475; a viscosity index greater than 140, and a weight percent olefins less than 10. The base oil improves the air release and low foaming characteristics of the mixture when incorporated into the electrical insulating oil composition.

[0067] Unrefined, refined and re-refined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the base oil. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment.

[0068] In one embodiment, the electrical insulating oil composition employs a base oil that consists of at least one of the isomerized base oils described above. In another embodiment, the composition consists essentially of at least a Fischer-Tropsch base oil. In yet another embodiment, the composition employs at least a Fischer-Tropsch base oil and optionally 5 to 95 wt. % of at least another type of oil, e.g., conventionally used mineral oils, synthetic hydrocarbon oils or synthetic ester oils, or mixtures thereof depending on the application.

[0069] In one embodiment, the isomerized base oil is a FT base oil having a kinematic viscosity at 100° C. between 1.5 mm²/s and 4.5 mm²/S; a kinematic viscosity at 40° C. between 5 mm²/s and 20 mm²/s; CCS viscosity below 4000 mPa·s at -40° C. and below 2300 mPa·s at -35° C.; pour point in the range of -20 and -60° C.; molecular weight of 250-475; density in the range of 0.780 to 0.820; paraffinic carbon in the range of 93-97%; naphthenic carbon in the range of 3-7%; Oxidator BN of 30 to 60 hours; and Noack volatility in wt. % of 8 to 90 as measured by ASTM D5800-05 Procedure B.

[0070] Anti-gassing Agent—Heavy Reformate: In one embodiment, the electrical insulating composition comprises a sufficient amount of heavy reformate as an anti-gassing agent for improved gas absorption properties. Low gassing performance is important because, if hydrogen is evolved due to electrical stress, a liquid having low gassing tendency tends to absorb the evolved hydrogen and thereby reduce the chances of an explosion.

[0071] In one embodiment, a sufficient amount of heavy reformate is added to reduce the gassing tendency to +30 μ L/min. or less, in another embodiment to 15 μ L/min. or less, in a third embodiment to 5 μ L/min. or less, according to ASTM Test Method D2300-00. In one embodiment, this sufficient amount is 0.10 to 15 wt. %. In a second embodiment, this amount is 0.25 to 10 wt. %. In a third embodiment, from 0.50 to 5 wt. %.

[0072] In yet another embodiment, a sufficient amount of heavy reformate is added for the electrical insulating oil to have a negative gassing tendency according to ASTM Test Method D2300-00, i.e., for a value of $-5 \,\mu$ L/min. or less; in another embodiment, a value of $-10 \,\mu$ L/min. or less; in a third embodiment a value of $-20 \,\mu$ L/min. or less; and in a fourth embodiment a value of $-30 \,\mu$ L/min. or less. This sufficient amount ranges from 0.10 to 15 wt. % in one embodiment, from 0.5 to 7 wt. % in another embodiment, and 1 to 5 wt. % in a third embodiment.

[0073] As used herein, "heavy reformate" is defined as the heavy fraction obtained from a catalytic reformer comprising C_8 aromatics, C_9 aromatics, C_{10} aromatics, and heavier components. In one embodiment, the heavy reformate has a boiling range of 300 to 500° F. (148-260° C.). Boiling range for reformate can be measured using ASTM D2887-06a. In another embodiment, the heavy reformate has a Research Octane Number (RON) of 95 to 105. RON or octane rating is a measure of how resistant gasoline is to premature detonation (knocking). It is measured relative to a mixture of 2,2,4-trimethylpentane (an octane) and n-heptane. For example, an 87-octane gasoline has the same knock resistance as a mixture of 87% isooctane and 13% n-heptane. RON can be measured using ASTM D2699-07.

[0074] In one embodiment, the heavy reformate contains ethyltoluenes, propylbenzenes, trimethylbenzenes, and indane, and has a very low level of olefins (alkenes).

[0075] In another embodiment, the feedstock contains an average methyl group/benzene ring mole ratio of 1.4, with a composition as follows: paraffins/napthlenes (0.5 wt. %); C8 aromatics (0.3 wt. %), C₈ aromatics (0.3 wt. %), toluene (65.3 wt. %), trimethylbenzenes (23.6 wt. %), ethyltoluenes (6.7 wt. %), propylbenzenes and indame (1.3 wt. %), tetramethylbenzenes (2.1 wt. %).; and C₁₀ aromatics (0.2 wt. %).

[0076] Besides the heavy reformate, other anti-gassing compounds in the prior art may be added to the composition. Examples include anti-gassing compounds from the group consisting of alkyl substituted or unsubstituted, partially saturated poling aromatics (e.g. polyaromatics with some degree of saturation), alkylated one ring aromatics (e.g. alkylated benzenes), or alkylated polyring aromatics. In other examples, the additional anti-gassing additive may be any compound or mixture of compounds, which is a hydrogen donor other than an unsubstituted aromatic compound, e.g., a bicyclic, partially saturated, aromatic compound, or an alkylated benzene compound. Examples of such bicyclic, partially saturated compounds include di- and tetra-hydronaphthalene compounds, alkylated hydronaphthalene compounds such as an alkylated tetrahydronaphthalene. In yet another embodiment, the additional anti-gassing agent is selected from dihydrophenanthrene, phenyl ortho xylyl ethane, alkylated benzenes, Dowtherm RPT[™] (tetrahydro-5-(1-phenylethyl)-naphthalene), acenapthene, tetrahydronaphthalene, alkylated tetrahydronaphthalenes, and tetrahydroquinoline.

[0077] In yet another embodiment, the additional anti-gassing additive is a polyarylalkane compound, e.g., commercially available from Elf Atochem S.A. or anti-gassing aromatic(s) other than phenolic compounds either comprising one or more labile hydrogen atom or comprising diaryls, which may or may not comprise one or more labile hydrogen atoms. Examples include, but are not necessarily limited to diaryls and agents having from 9 to 11 carbon atoms selected from the group of alkyl-substituted aromatic compounds, alkyl substituted, partially saturated aromatic compounds, and combinations thereof. In another embodiment, the composition comprises an anti-gassing agent selected from the group consisting of alkyl substituted or unsubstituted biphenyl and alkyl substituted or unsubstituted diaryl alkanes.

[0078] Additional Components: In one embodiment, the electrical insulating composition further contains at least another additive such as pour point depressants, metal deactivators, anti-foaming agents, anti-oxidants (oxidation inhibitors), additives for corrosive sulphur and static electricfication (metal passivators), anti-foaming agents, dyes, markers, biocides, antistatic additives, and other additives known in the art, in a sufficient amount to provide the desired effects. In one embodiment, this sufficient amount is 0.001 to 10 wt. %.

[0079] In another embodiment, in an amount of 0.005 to 6 wt. %. In one embodiment, the electrical insulating oil composition comprises from 0.10 to 5.0 wt. % of a pour point depressant capable of lowering the pour point to below the lowest temperature expected for the climate in which the electrical insulating oil is to be used. This would normally be a temperature of -30° C. to -40° C. In one embodiment, the pour point depressant is an alkylated polystyrene. Other illustrative pour point depressants include esters of maleic anhydride-styrene copolymers, polymethacrylates, polyacrylates, polyacrylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers, olefin copolymers, fumeric acid esters, polymethacrylate chemicals such as Acryloid[™] 155C made by RohmMax, and mixtures thereof.

[0080] In another embodiment, electrical insulating oil composition further comprises a pour point reducing blend component as a pour point depressant. In one embodiment, the pour point reducing blend component is an isomerized Fischer-Tropsch derived vacuum distillation bottoms product, which is a high boiling syncrude fraction isomerized under controlled conditions to give a specified degree of alkyl branching in the molecule. Syncrude prepared from the Fischer-Tropsch process comprises a mixture of various solid, liquid, and gaseous hydrocarbons. When the Fischer-Tropsch waxes are converted into Fischer-Tropsch base oils by various processes, such as by hydroprocessing and distillation, the base oils produced fall into different narrow-cut viscosity ranges. The bottoms that remains after recovering the lubricating base oil cuts from the vacuum column is generally unsuitable for use as a lubricating base oil itself and is usually recycled to a hydrocracking unit for conversion to lower molecular weight products.

[0081] In one embodiment, the pour point reducing blend component is an isomerized Fischer-Tropsch derived vacuum distillation bottoms product having an average molecular

weight between 600 and 1100 and an average degree of branching in the molecules between 6.5 and 10 alkyl branches per 100 carbon atoms. Generally, the higher molecular weight hydrocarbons are more effective as pour point reducing blend components than the lower molecular weight hydrocarbons. In one embodiment, a higher cut point in a vacuum distillation unit which results in a higher boiling bottoms material is used to prepare the pour point reducing blend component. The higher cut point also has the advantage of resulting in a higher yield of the distillate base oil fractions. In one embodiment, the pour point reducing blend component is an isomerized Fischer-Tropsch derived vacuum distillation bottoms product having a pour point that is at least 3° C. higher than the pour point of the distillate base oil it is blended with.

[0082] In one embodiment, the 10 percent point of the boiling range of the pour point reducing blend component that is a vacuum distillation bottoms product is between about 850° F. -1050° F. (454-565° C.). In another embodiment, the pour point reducing blend component is derived from either Fischer-Tropsch or petroleum products, having a boiling range above 950° F. (510° C.), and contains at least 50 percent by weight of paraffins. In yet another embodiment the pour point reducing blend component has a boiling range above 1050° F. (565° C.)

[0083] In another embodiment, the pour point reducing blend component is an isomerized petroleum derived base oil containing material having a boiling range above about 1050° F. In one embodiment, the isomerized bottoms material is solvent dewaxed prior to being used as a pour point reducing blend component. The waxy product further separated during solvent dewaxing from the pour point reducing blend component were found to display excellent improved pour point depressing properties compared to the oily product recovered after the solvent dewaxing.

[0084] In one embodiment, the pour point reducing blend component has an average degree of branching in the molecules in the range of 6.5-10 alkyl branches per 100 carbon atoms. In another embodiment, the pour point reducing blend component has an average molecular weight between 600-1100. In a third embodiment, between 700-1000. In one embodiment, the pour point reducing blend component has a kinematic viscosity at 100° C. of 8-30 mm²/s, with the 10% point of the boiling range of the bottoms falling between about 850-1050° F. In yet another embodiment, the pour point reducing blend component has a kinematic viscosity at 100° C. of 15-20 mm²/s and a pour point of -8 to -12° C.

[0085] In another embodiment, the pour point reducing blend component is an isomerized oil having a kinematic viscosity at 100° C. of at least about 8 mm²/s and made from polyethylene plastic. In another embodiment the pour point reducing blend component is made from waste plastic. In yet another embodiment the pour point reducing blend component is made from a process comprising: pyrolysis of polyethylene plastic, separating out a heavy fraction, hydrotreating the heavy fraction, catalytic isomerizing the hydrotreated heavy fraction, and collecting the pour point reducing blend component having a kinematic viscosity at 100° C. of at least about 8 mm²/S. In one embodiment, the pour point reducing blend component derived from polyethylene plastic has a boiling range above 1050° F. (565° C.), or even a boiling range above 1200° F. (649° C.).

[0086] Since metal, specifically copper, is always present in the electrical environment, metal deactivators can be added to the composition in an amount from 0.10 to less than 1.5%.

Examples include benzotriazole derivatives to reduce the catalytic activity of copper in electrical apparatus. In some embodiments, the deactivator is a benzotriazole derivative, e.g., a triazole derivative, N,N-bis(2-Ethylhexyl)-1H-1,2,4-triazole-1 methanamine such as IRGAMET 30 from Ciba Geigy.

[0087] In one embodiment, the electrical oil insulating composition further comprises 0.01 wt. % to 3.0 wt. % of at least an antioxidant to improve oxidation stability of the dielectric liquid, thereby minimizing the development of oil sludge and acidity during storage, processing, and service. Minimizing oxidation minimizes electrical conduction and metal corrosion, maximizes system life, maximizes electrical breakdown strength, and ensures satisfactory heat transfer. Examples of antioxidants include but are not limited to hindered phenols, cinnamate type phenolic esters, and alkylated diphenylamines. In one embodiment, the antioxidants are selected from the group consisting of 2,6-ditertiary-butyl para-cresol, 2,6-ditertiary butylphenol, and combinations thereof. An example is a combination of 2,6-ditertiary-butyl para-cresol and 2,6-ditertiary butylphenol. Other examples include but are not limited to, phenol type (phenolic) oxidation inhibitors, e.g., 2,6-di-tert-butyl-4-ethylphenol, 4'-methvlene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-4,4'methylene-bis(4-methyl-6-tert-butylphenol), butylidene-bis(3-methyl-6-tert-butylphenol), 4.4'isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6dimethylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,2'-5methylene-bis(4-methyl-6-cyclohexylphenol), 2.4dimethyl-6-tert-butyl-phenol, 2,6-di-tert-1-dimethylaminop-cresol, 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-10butylbenzyl)-sulfide, alkylated diphenylamine, bis(3,5-ditert-butyl-4-hydroxybenzyl), phenyl-alpha-naphthylamine, and alkylated-alpha-naphthylamine. Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and 15-methylenebis(dibutyldithiocarbamate).

[0088] One example of an oxidation inhibitor is AdditinTM RC 9308 manufactured by Rhein Chemie Rheinau GmbH, Germany, containing ca. 1.5 wt-% of C12-C14-t-alkylamines (CAS number 68955-53-3), ca. 4 wt-% of tolyltriazol (CAS number 29385-43-1), and ca. 3.4 wt-% tributyl phosphate (CAS number 126-73-8). This substance contains, besides the antioxidant, also a corrosion inhibitor. Other applicable additives are RC 7110 and RC 6301 by the same manufacturer, or mixtures including RC 7110+RC 9308 and RC 7110+RC 6301.

[0089] In one embodiment, the electrical insulating oil composition comprises from 0.001 to 1 wt. % of a triazole derivative metal deactivator and 0.05 to 1 wt. % of a phenolic anti-oxidant. In a second embodiment, the composition comprises from 0.003 to 0.8 wt. % of a copper deactivator and to 0.10 to 0.50 wt. % of a solid phenolic anti-oxidant.

[0090] In one embodiment the electrical insulating oil composition comprises (i) from 0.05 to 3.0 wt. % of at least one hindered phenol antioxidant, and (ii) from 0.01 to 1.5 wt. % of a metal deactivator. Examples of hindered phenolic antioxidants include 2,6 di-tert-butylphenol, 2,6 di-tert-butylparacresol and mixtures thereof. In one embodiment, the metal deactivator is a tolyltriazole metal deactivator such as 1,2,3

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tolyltriazole. Examples include a reaction product of a tolyltriazole and an alkylated diphenyl amine.

[0091] In one embodiment, the electrical insulating oil comprises an additive package containing at least one of the above additive materials, specifically designed for improved pour point, improved cooling properties, and improved dielectric stability.

[0092] Method for Making: The anti-gassing agent and other additives used in formulating the electrical insulating oil composition can be blended into the base oil matrix individually or in various sub-combinations. In one embodiment, all of the components are blended concurrently using an additive concentrate (i.e., additives plus a diluent, such as a hydrocarbon solvent). The use of an additive concentrate takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate.

[0093] In another embodiment, the electrical insulating oil composition is prepared by mixing the base oil matrix with the anti-gassing agent, optional additives or additive package (s) at an appropriate temperature, such as approximately 60° C., until homogeneous.

[0094] Properties: The electrical insulating composition meets relevant specifications for physical, electrical, and chemical properties for electrical oils provided by ASTM D 3487-2000 (Re-approved 2006) as well as IEC 60296-2003.

[0095] In one embodiment, the composition displays excellent oxidation resistance and low gassing tendency with a gassing tendency of $<30 \,\mu$ L per minute as measured according to ASTM D-2300-1976 and a rotary pressure vessel oxidation stability (RPVOT) value of at least 400 minutes as measured according to ASTM D 2272-02. In one embodiment, the composition has a gassing tendency of $<20 \,\mu$ L per minute. In another embodiment, the composition has an RPVOT of at least 500 minutes.

[0096] In one embodiment for use in specific applications including but not limited to sealed capacitors and oil filed cables requiring the use of gas absorbing oils, the composition displays a negative gassing value of less than $-40 \,\mu\text{L}$ per minute in one embodiment, less than $-30 \,\mu\text{L}$ per minute in a second embodiment, less than $-10 \,\mu\text{L}$ per minute in a third embodiment, and less than $0 \,\mu\text{L}$ per minute in a fourth embodiment.

[0097] In one embodiment, the electrical insulating oil composition is readily biodegradable, with the OECD 301D level ranging from 60 to 95%. In one embodiment, the electrical insulating oil composition has a kinematic viscosity at 40° C. of 10-14 mm²/s and an OECD 301D biodegrability of >=60%. In a second embodiment, the composition has a kinematic viscosity at 40° C. of less than 10 mm²/s and an OECD 301D biodegrability of >=80%. In a third embodiment, the composition has a kinematic viscosity at 40° C. of less than 8 mm²/s and an OECD 301D biodegrability of >=90%.

[0098] In one embodiment, the composition displays an excellent sulphur corrosion property, with a sulphur content of less than 10 ppm. In a second embodiment, the composition has a sulphur content of less than 5 ppm. In a third embodiment, less than 1 ppm.

[0099] In one embodiment when subjected to the acid sludge test (ASTM D2440), the composition produces a % sludge by mass at 72 hours of 0.15 or less and a 72 hour "total acid number" or "TAN" of 0.5 or less (mg of KOH/g).

[0100] In one embodiment, the electrical insulating oil composition meets all ASTM physical property requirements for electrical oils include, but are not necessarily limited to: a color of about 0.5 or less, as measured using ASTM D1500-04a; a flash point of 145° C. or greater, as measured using ASTM D92-05a; an interfacial tension of 40 dynes/cm or more at 25° C. as measured using ASTM D971-99a; a pour point of less than -40° C., as measured using ASTM D92-05a; a relative density of 0.91 or less, according to ASTM D1298-99a (Re-approved 2005); a visual examination of clear and bright, according to ASTM D1524-94 (Re-approved 2004); and, a viscosity of less than 76 mm²/S or less at 0° C., less than 12.0 mm²/s at 40° C., and from about 3.0 mm²/S or less at 100° C., as measured by ASTM D445-06.

[0101] In one embodiment, the electrical insulating oil composition also meets the electrical property requirements for electrical oils, including but not necessarily limited to the ASTM requirements of: a dielectric breakdown voltage of 30 kV or more at 60 Hz by disc electrodes, according to ASTM D877-02e1; a dielectric breakdown voltage of 20 kV or more at 60 Hz and a 1.02 mm (0.040-inch) gap using new oil by ASTM D1816-04; a dielectric breakdown voltage impulse of 145 kV or more at 25° C. using a needle-to-sphere grounded 25.4 mm (1-inch) gap, according to ASTM D3300-00 (Reapproved 2006), and a power factor at 60 Hz of 0.05% or less at 25° C. and of 0.30% or less at 100° C. using ASTM D924-04.

[0102] In one embodiment, the electrical insulating oil composition also meets the chemical property requirements for electrical oils, including but not necessarily limited to the ASTM requirements of: an oxidation inhibitor content of 0.08 wt. % or less, and for Type II oils of 0.3 wt. % or less as measured using ASTM D2668-02e1 (incorporated herein by reference), or where the oxidation inhibitor is 2.6-ditertiary butyl cresol, as measured using ASTM D1473-80 (incorporated herein by reference); a low content of elemental sulfur and thermally unstable sulfur-bearing compounds to prevent corrosion of certain metals such as copper and silver in contact with the dielectric liquid, according to ASTM D1274-95 (2000) (previously incorporated herein by reference); 35 ppm or less water according to ASTM D1533-00 (2005) (incorporated herein by reference); a neutralization number of 0.03 mg KOH/g or less, using Test Method ASTM D-974-02 (incorporated herein by reference); and a non-detectible polychlorinated biphenyl (PCB) content, or a content of less than 1 ppm, as measured using ASTM D4059-00 (2005)e1 (incorporated herein by reference).

[0103] Applications: In one embodiment, the electrical insulating oil is used to insulate, cool, and lubricate high voltage electrical equipment such as power and distribution transformers, circuit breakers (switches), capacitors (condensers), and insulating cables. In another embodiment, the composition is used in cable applications, regulators, and rectifiers within electrical power systems. In a third embodiment, the oil is used in medical equipment (X-Ray, MRI), and in industrial and academic R&D applications (sonar, etc.). Moving parts include a transmission, a hydrostatic transmission, a gear box, a drive, a hydraulic system, etc.

[0104] The following Examples are given as non-limitative illustration of aspects of the present invention.

[0105] Unless specified otherwise, the components in the examples are as follows:

 $[010\hat{G}]$ Unless specified otherwise, the compositions are prepared by mixing the components in the amounts indicated in the Examples. The components used in the Examples are listed below.

[0107] GTL XXL and GTL-XL are Fischer-Tropsch derived base oils from Chevron Corporation of San Ramon, Calif., having the properties shown in Table 1.

TABLE 1

Properties	GTL XXL	GTL-XL
Kinematic Viscosity @ 40° C., cSt	6.31	10.45
Kinematic Viscosity @ 100° C., cSt	2.032	2.86
Viscosity Index	118	125
Pour Point, ° C.	-57	-33
Oxidator BN	42.82	57.86
Saybolt color		28
Molecular Weight, gm/mol	320	350
Density, gm/ml	0.7956	0.8049
Sulfur, ppm	<1	<0.1
Nitrogen, ppm	<0.1	<0.1
Noack, wt. %	81.9	34.1
Aromatics (HPLC-UV), wt. %	0.00226	0
COC Flash Point, ° C.	168	202
COC Flash Point, ° F.	334	396

[0108] BHT or butylated hydroxytoluene is an anti-oxidant readily available from a number of commercial sources.

[0109] THN or 1,2,3,4-Tetrahydronaphthalene is an antigassing agent typically used in the prior art.

[0110] SureSolTM 150 is an aromatic specialty solvents from Koch Chemical Co., Corpus Christi, Tex., commonly used as an anti-gassing agent in the prior art.

[0111] JET fuel is a special grade of petroleum product with a flash point of 125° F. (52° C.), used for jet aircraft, commercially available from a number of sources, and commonly used as an anti-gassing agent in the prior art.

[0112] "Heavy Reformate" used in the Examples is a product stream from a refinery of Chevron Corporation, having the following properties: Average Molecular Weight=127.1; API Gravity=29.3; Specific Gravity=0.8802; RON of 102.7; Aromatics content of 92.30 vol. %; Saturates content of 7.7 vol. %; and the following individual compounds of 0.5 vol. % and higher: 1,2,4-Trimethylbenzene at 20.78 vol. %; 1-Methyl,2-Ethyl-benzene at 13.52 vol. %; 1,3,5-Trimethylbenzene at 6.81 vol. %; Cyclopentane (C10) at 6.42 vol. %; 1,2-Dimethyl,4-Ethyl-benzene at 6.15 vol. %; 1-Methyl,2-Ethyl-benzene at 4.32 vol. %; 1,2,3-Trimethylbenzene at 3.67 vol. %; n-Propylbenzene at 3.46 vol. %; 1-Methyl,3-Propyl-benzene at 2.88 vol. %; 1-Methyl,4-Propyl-benzene at 2.83 vol. %; 1,3-Diethylbenzene at 2.30 vol. %; 1,2,3,5-Tetramethylbenzene at 2.18 vol. %; 1,3-Dimethyl,4-Ethyl-benzene at 2.05 vol. %; 1,4-Dimethyl,2-Ethyl-benzene at 2.04 vol. %; Naphthalene at 1.80 vol. %; 1,2,4,5-Tetramethylbenzene at 1.62 vol. %; Indan at 1.11 vol. %; Methylindane B at 0.98 vol. %; 2-Methylnapthalene at 0.92 vol. %; 1-Methyl,2-Propyl-benzene at 0.87 vol. %; 1,2-Dimethyl, 3-Ethyl-benzene at 0.70 vol. %; Cumene at 0.66 vol. %; Methylindane at 0.58 vol. %; Tetralin at 0.55 vol. %; and m-Cymene at 0.54 vol. %.

Examples 1-13

[0113] A number of electrical insulating compositions having components as listed in Table 2 were formulated and their properties were measured. The examples incorporating embodiments with the heavy reformate as anti-gassing agents show excellent negative gassing properties compared to the anti-gassing agents of the prior art, with some examples showing values of $<-70 \mu$ L per minute (measured by Doble Engineering). The examples also exhibit excellent aniline point property, e.g., of 219.6 and 223, well above the minimum 60 limit required for transformer oils; pour point less than then -40° C. maximum limit; kinematic viscosity of less than 3 cSt for 100° C. and less than 11 for 40° C.

Examples 14-15

[0114] The testing for degradation by micro-organisms and assessment of the toxicity of materials to micro-organism is an important indication of the biodegradability a material for use as an electrical insulating oil. The biodegradation of the material can be monitored by a variety of parameters such as CO2 evolution, oxygen consumption and removal of organic carbon or by compound specific methods. One standard test is OECD 301D (closed bottle test), wherein the limit for "readily" biodegradable is >=60% and the limit for moderately or inherently biodegradable is 20%.

[0115] The isomerized base oils GTL XL and GTL XXL were subject to OECD 301D (closed bottle test). Sample GTL XXL with a kinematic viscosity at 40° C. of 6.3 mm²/S shows an OECD 301D of 93%. Sample GTL XL with a kinematic viscosity at 40° C. of 11.16 mm²/s shows an OECD 301D of 80%.

TABLE 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
GTL XXL	97.8	97.8	99.3	98.8	98.8	95.8	91.8	97.8	95.8	91.8	97.3	94.8	89.8
BHT	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tetrahydronaphthalene	2.0				1.0								
SureSol 150	_	2.0	_	_	_	4.0	8.0	_	_	_	_	_	_
Jet	_	_	_	_	_	_	_	2.0	4.0	8.0	_	_	_
Heavy Reformate	_	_	0.5	1.0	_	_		_	_	_	2.5	5.0	10.0
Kinematic Viscosity	1.981	1.964	1.964	1.930	2.002	1.904	1.790	1.996	1.968	1.923	1.946	1.938	1.748
@100° C., cSt													
Kinematic Viscosity	6.098	6.065	6.028	5.740	6.214	5.785	5.243	6.182	6.050	5.820	6.004	5.790	5.323
@40° C., cSt													
Viscosity Index	_	_	_	_	115	_	_	_	_	_	_		
Pour Point, ° C.	-51	—	-59	-57	-53	-56	_	_		-59	-59	_	_
Cloud Point, ° C.	-33	-31	-33	-35	-35	-34	-36	-32	-33.6	-34	-33	-34	-35
COC Flash, ° C.	154	150	168	136	160	138	138	162	168	150	152	126	100
COC Flash, ° F.	309.2	302	334.4	276.8	320	280.4	280.4	323.6	334.4	302	305.6	258.8	212

TABLE 2-continued

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
ASTM D1500 Color °API Gravity @60/60° F.	0.0 44.8	0.0 45.1	0.0 45.2	0.0 44.9	0.0 45.1	0.0 44.8	0.0 44	0.0 45.1	0.0 44.8	0.0 44.2	0.0 45.1	0.0 44.7	0.0 44
Aniline Point Neutralization Number	221.3 <0.03	<0.03	223 <0.03	219.6 <0.03	_	_	_	_	_	_	_	_	_
Karl Fischer Water Appearance	15 C&B	13 C&B	13 C&B	12 C&B	_	_	_	_	_	_	_		_
ASTM D2300 Gassing Tendency (3 tests)	-40.7	-15.6	-31.8	-49.7	2.2	-56.4	-59.7	43.0	36.3	32.4	-65.3	-70.3	-100.0
• • • •	-37.9 -39.3	-15.8 -15.7	-29.4 -30.6	-53.2 -51.5	2.8 2.5	-55.9 -56.0	-60.0 -59.9	40.0 41.5	32.8 34.6	30.0 31.2	-68.6 -67.0	-62.6 -66.5	-89.8 -94.9

*C&B Clear and Bright

[0116] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0117] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

[0118] All citations referred herein are expressly incorporated herein by reference.

1. An electrical insulating oil composition in compliance with at least one of ASTM D 3487-2000 and IEC 60296-2003, the composition comprising

- (a) a base oil comprising at least one of a natural oil, a synthetic oil, an isomerized base oil, and mixtures thereof,
- (b) 0.001 to 10 wt % at least an additive selected from an additive package, an oxidation inhibitor, anti-gassing agent, pour point depressant, metal deactivator, metal passivator, anti-foaming agent, and mixtures thereof, and
- (c) a sufficient amount of a heavy reformate for the composition to have a gassing tendency of $<30 \,\mu$ L per minute as measured according to ASTM D-2300-2300.

2. The composition of claim **1**, wherein the sufficient amount of heavy reformate is 0.10 to 15 wt. % based on the total weight of the composition.

3. The composition of claim **2**, wherein the sufficient amount of heavy reformate is 0.50 to 10 wt. % based on the

total weight of the composition, for the composition to have a gassing tendency of $<30 \ \mu$ L per minute as measured according to ASTM D-2300-1976.

4. The composition of claim 3, wherein the sufficient amount of heavy reformate is 0.50 to 15 wt. % based on the total weight of the composition, for the composition to have a gassing tendency of <0 μ L per minute as measured according to ASTM D-2300-1976.

5. The composition of claim 4, wherein the sufficient amount of heavy reformate is 1 to 15 wt. % for the composition to have a gassing tendency of $<-30 \ \mu$ L per minute as measured according to ASTM D-2300-1976.

6. The composition of claim **1**, wherein the heavy reformate has a boiling range of 300 to 500° F. (148-260° C.) and a Research Octane Number (RON) of 95 to 105.

7. The electrical insulating oil composition of claim 1, wherein the electrical insulating oil displays a rotary pressure vessel oxidation stability (RPVOT) value of at least 400 minutes as measured according to ASTM D 2272-02.

8. The electrical insulating oil composition of claim **7**, wherein the electrical insulating oil displays a rotary pressure vessel oxidation stability (RPVOT) value of at least 500 minutes as measured according to ASTM D 2272-02.

9. The composition of claim **1**, wherein the base oil is selected from the group of a mineral oil, a vegetable oil, an oligomer of an alphaolefin, an ester, an oil derived from a gas-to-liquid process, a Fischer-Tropsch derived base oil, and mixtures thereof.

10. The composition of claim **9**, wherein the base oil comprises at least an isomerized base oil and 5 to 95 wt. % of at least one of a mineral oil, a vegetable oil, an oligomer of an alphaolefin, an ester, an oil derived from a gas-to-liquid process, and mixtures thereof.

11. The electrical insulating oil composition of claim **1**, wherein the lubricating base oil consists essentially of at least an isomerized base oil having a biodegradability of at least 60% as measured according to OECD **301D**.

12. The electrical insulating oil composition of claim **11**, wherein the lubricating base oil consists essentially of at least an isomerized base oil having a biodegradability of at least 90% as measured according to OECD **301D**.

13. The electrical insulating oil composition of claim 1, wherein the lubricating base oil comprises an isomerized base oil having an auto-ignition temperature in ° C. (AIT) greater than an AIT in ° C. defined by: $1.6 \times (\text{kinematic viscosity at } 40^{\circ} \text{ C}, \text{ in mm}^2/\text{s})+300.$

14. The electrical insulating oil composition of claim 1, wherein the lubricating base oil comprises an isomerized base oil having a traction coefficient less than an amount calcu-

lated by: $0.009 \times Ln$ (kinematic viscosity in mm²/S)-0.001, wherein the kinematic viscosity is the viscosity of the oil during the measurement of the traction coefficient.

15. The electrical insulating oil composition of claim 1, wherein the lubricating base oil comprises an isomerized base oil having a Kinematic Vicosity at 100° C. of >1.808 mm²/s and a Noack volatility less than an amount calculated by the following equation: 1.286+20 (kv100)^{-1.5}+551.8 e^{-kv100}, where kv100 is the Kinematic Viscosity at 100° C.

16. The electrical insulating oil composition of claim 1, wherein the additive is a pour point depressant selected from the group of pour point reducing blend components; polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; terpolymers of dialkylfumarates, vinyl esters of fatty acids, and alkyl vinyl ethers; and mixtures thereof.

17. The electrical insulating oil composition of claim 1, wherein the additive is an antioxidant selected from the group consisting of phenolics, aromatic amines, compounds containing sulfur and phosphorus, organosulfur compounds, organophosphorus compounds, and mixtures thereof.

18. The electrical insulating oil composition of claim **1**, wherein the additive is a metal deactivator selected from the group consisting of triazoles, benzotriazoles, tolyltriazole, tolyltriazole derivatives, and mixtures thereof.

19. The electrical insulating oil composition of claim **1**, wherein the lubricating base oil has a sulfur content of less than 10 ppm.

20. An electrical equipment comprising the electrical insulating oil composition of claim **1** for cooling and/or insulating.

21. A medical equipment comprising the electrical insulating oil composition of claim **1** for cooling and/or insulating.

22. A method for improving the gassing tendency of an electrical insulating oil composition for the composition to have a gassing tendency of $<-30 \,\mu$ L per minute as measured according to ASTM D-2300-197, the method comprising the step of adding 1 to 15 wt. % of a heavy reformate to a mixture of (a) a base oil selected from the group of a natural oil, a synthetic oil, a Fischer-Tropsch derived base oil, and mixtures thereof, and (b) 0.001 to 10 wt % at least an additive selected from an additive package, an oxidation inhibitor, anti-gassing agent, pour point depressant, metal deactivator, metal passivator, anti-foaming agent, and mixtures thereof.

23. The method of claim 22, wherein 0.50 to 15 wt % of the heavy reformate is added to the mixture for the composition to have a gassing tendency of <0 μ L per minute as measured according to ASTM D-2300-197.

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