

ALKYLAROMATIC LUBRICANT FLUIDS

FIELD

[0001] The present disclosure relates to novel alkylaromatic compositions useful as lubricant basestocks and additives. More particularly, the compositions of the present disclosure are quaternary-substituted alkylaromatic compositions that have improved thermo- and oxidative stability prepared by alkylating aromatics with vinylidene-containing olefins. The present disclosure also relates to processes for producing alkylaromatic compositions that employ acidic alkylation catalysts.

BACKGROUND

[0002] A lubricant is a substance capable of reducing friction, heat and wear when introduced as a film between solid surfaces. Efforts to improve upon the performance of mineral oil based lubricants have been the focus of important research and development activities in the petrochemical industry for over 50 years. Maintenance of friction reducing properties, extended useful life in terms of thermal and oxidative stability and wear protection, improved viscosity index and pour point equal to or better than mineral oil are performance areas where research and development activities have occurred. These efforts have led to the introduction of a number of synthetic fluids including polyalpha-olefin (PAO) synthetics primarily made by oligomerization of alpha-olefins or 1-alkenes. Synthetic fluids is a term that can describe materials useful as lubricants, heat transfer agents, and corrosion inhibition among other uses. PAO synthetic fluids compositions are saturated hydrocarbons and thus are less polar than mineral oil based compositions that can contain polar moieties including aromatics. To improve the solvency and dispersancy of PAO type fluids, a polar co-basestock is added to the composition to help dissolve polar additives of the composition and sludge during usage. A polar co-basestock such as ester or alkylaromatics is

used in amounts of about 3 to about 50 weight percent of the basestock composition. The polar co-basestock could introduce undesirable side effects such as hydrolytic instability if an ester co-basestock is used or poorer low temperature properties, reduced cleanliness properties if typical alkylaromatic co-basestocks are used. Finished synthetic lubricants are often formulated with additives to enhance their properties for specific applications. Additives that are commonly used can include oxidation inhibitors, dispersants, detergents, rust inhibitors, antiwear agents, extreme pressure agents, metal passivators, pour point depressants, viscosity index (VI) improvers, and the like. Thus formulated fluids are compositions comprising a number of components, the largest volume component being the fluid basestock. Adding to the complexity of formulating lubricating oils is the trend to ever higher oil performance standards dictated by the increasing complexity of newer equipment and engines. There is a continuing need to improve the suite of properties of the fluid basestock to provide improved performance of the formulated products in all areas required including thermal and oxidative stability.

[0003] Alkylaromatic compounds have been known for many years. For example, US Patent No. 6,491,809 (Briot et al.) discloses the alkylation of aromatic compounds (e.g., benzene, toluene, cumene) by alkylating agents (e.g., olefins, alcohol, halides) for producing aromatic monoalkyls whose grafted aliphatic chain comprises a carbon number that is selected from 2 to 20 carbons. US Patent No. 6,429,345 (Joly et al.) discloses a process for producing at least one compound selected from 2-, 3-, 4-, 5- and 6-phenylalkanes by alkylating benzene using at least one olefin containing at least 9 carbon atoms per molecule, in the presence of a catalyst comprising at least one zeolite with structure type EUO, at least partially in its acid form and at least one matrix. US Patent No. 5,254,274 (Ho et al.) discloses alkylating aromatic compounds with C₂₀-C₁₃₀₀ olefinic oligomers using an acidic alkylation catalyst to produce

alkylated aromatic products, usually alkylaromatic hydrocarbons. Additional discussions of alkylaromatics and other synthetic lubricants can be found in L.R. Rudnick and R.L. Shubkin's *Synthetic Lubricants and High-Performance Functional Fluids*, Marcel Dekker, Inc., NY (1999).

[0004] PAOs can be produced by reacting an olefin feed in the presence of a catalyst such as AlCl_3 , BF_3 , or promoted BF_3 . Processes for the production of PAOs are disclosed, for example, in the following patents: U.S. Pat. Nos. 3,149,178; 3,382,291; 3,742,082; 3,769,363; 3,780,128; 4,172,855; and 4,956,122. Novel PAO lubricant compositions in which little double bond isomerization is found has resulted in different classes of high viscosity index PAO (HVI-PAO). In one class of HVI-PAO, reduced chromium catalyst is reacted with an alpha-olefin monomer. Such PAOs are described in U.S. Pat Nos. 4,827,073; 4,827,064; 4,967,032; 4,926,004; and 4,914,254.

[0005] Recently patents describe HVI-PAOs compositions prepared by contacting one or more alpha-olefins monomers having 3 to 24 carbons atoms with a transition metal compound, an anion activator and an alkyl aluminum compound. The novel compositions conform to the unique specificity of the HVI-PAO oligomerization reaction in that little double bond isomerization occurs. Such HVI-PAOs are described in PCT Patent Publication Nos. WO2007011462 A1 and WO2007011832 A1.

[0006] Novel compositions of low viscosity PAOs can also be prepared from metallocene catalysts as taught in U.S. Patents 5,688,887 and 6,043,401 and PCT Patent Publication No. WO2007011973 A1. Separation of the low molecular weight material, representing non-lube range molecular weight material, is necessitated to control product volatility and viscosity. As

oligomerization conditions are changed to produce the lower viscosity products of lower average molecular weight, the non-lube range dimer or light end fraction increases. The increase in dimer by-product yield represents a substantial economic burden on the overall process to produce useful lower viscosity lubricant in the process.

[0007] Accordingly, there is a need for improved processes for the manufacture of the alkylaromatic fluid compositions as well as alkylaromatic fluid compositions that have improved thermal and oxidative stability. There is also a need for novel processes to utilize the by-products from the metallocene process to produce novel synthetic lubricant fluids.

SUMMARY

[0008] The present disclosure relates to an alkylaromatic compositions comprising an aromatic moiety other than unsubstituted naphthalene; and an alkyl moiety having a carbon atom number in the range between 12 to 40, wherein said alkyl moiety is attached to said aromatic moiety such that at least 25 mol% of the benzylic carbons are quaternary.

[0009] The present disclosure also includes a process for the preparation of an alkylaromatic compound comprising: contacting at least one an aromatic compound and a mono-olefin having a carbon atom number in the range between 12 to 40 in the presence of an acidic alkylation catalyst under alkylation conditions, wherein at least 50 mol% of the mono-olefin structure comprises a vinylidenyl structure and thereby producing said alkylaromatic compound having at least 25 mol% of benzylic carbons that are quaternary.

[0010] The present disclosure also provides a process for the utilization of the by-product from the metallocene process to produce a novel synthetic lubricant fluid.

[0011] Accordingly, the present disclosure provides useful alkylaromatic fluid compositions that have thermal and oxidative stability.

[0012] In addition, the present disclosure provides useful lubricant additives from aromatics alkylation by using vinylidene containing low molecular weight olefins as the alkylating agent.

[0013] These and other features and attributes of the disclosed alkylaromatic compositions suitable as liquid lubricant compositions or additives and processes for the preparation of the alkylaromatic compositions of the present disclosure and their advantageous applications and/or uses will be apparent from the detailed description which follows.

DETAILED DESCRIPTION

[0014] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art. It has been discovered that a new synthetic basestock with significantly improved lubricating properties can be produced by reacting aromatics with vinylidene-containing olefins. This new base stock may be produced in such a manner such that a significant amount of the alkylated aromatic is quaternary substituted alkylaromatic.

[0015] In some embodiments, the mono-olefin may be derived from the non-lubricant of metallocene-catalyzed alpha olefin polymerization process. Mono-

olefins derived in other manners with a significant amount of vinylidene may also be advantageous.

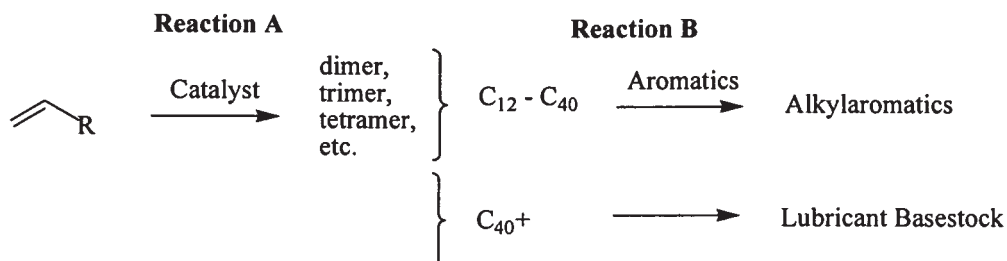
[0016] Also suitable for use in the processes disclosed herein are refinery feedstocks or effluents. Olefins suitable for the preparation of the dimers or mixtures of dimers, trimers and the like contain from about 3 to 20 carbons, such as 1-propylene, 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, and 1-hexadecene or branched olefins such as 4-methyl-1-pentene or mixtures thereof. The mono-olefin is a vinylidene with a carbon atom number less than 30 and may be a mixture of olefins with a significant amount of vinylidenes or trisubstituted olefins. Generally, at least 50 mol% , or at least 55 mol%, or at least 60 mol%, or at least 65 mol%, of the mono-olefin structure comprises a vinylidenyl structure.

[0017] The aromatic compound may be benzene, naphthalene, furan, thiophene, anthracene, phenanthrene, pyrrole, indole, benzothiophene, dibenzothiophene, benzofuran, dibenzofuran, phenoxathiin, thianthrene, biphenyl, pyrene, and mixtures thereof, each of which can be optionally substituted.

[0018] In further preferred embodiments, the aromatic compound may be toluene, o-, or p-xylene, hydroxylbenzene, alkoxybenzene such as methoxy or ethoxybenzene, thioanisole, diphenylether, diphenylmethane, bisphenol-A, bisphenol sulfide, diphenyl sulfide, naphthalene, methylnaphthalene, methoxynaphthalene, ethoxynaphthalene, methylnaphthal sulfide, ethyl naphthylsulfide, or mixtures thereof. In more preferred embodiments the aromatic compound may be substituted benzene or substituted naphthalene.

Process and Product

[0019] The general process according to the present disclosure is as follows:



In the present disclosure, aromatic hydrocarbons, including substituted aromatic hydrocarbons, are alkylated with olefins containing a significant amount of vinylidene substitution (generally, at least 50 mol% , or at least 55 mol%, or at least 60 mol%, or at least 65 mol%, of the mono-olefin structure includes vinylidene). These can be from the non-lube range oligomers made during the metallocene-low viscosity alpha olefin polymerization process (reaction A). The olefins used in the alkylation have a significant amount of vinylidene isomers. Other processes to make vinylidene containing olefins are also included within the scope of the present disclosure. The solid state acid catalysts such as zeolites or Friedel Crafts alkylation catalysts such as AlCl_3 or BF_3 are used to catalyze the alkylation. The resulting novel compositions contain a significant amount of quaternary substitution at the benzylic carbon. The compositions exhibit excellent additive solubilizing properties.

Olefin

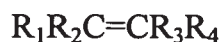
[0020] For the purpose of preparing alkylaromatic compositions suitable as liquid lubricant compositions or additive of the present disclosure, a thermally and oxidatively stable composition can be obtained with an alkylaromatic composition with a significant amount of quaternary benzylic carbon atoms and total side chain carbon content between 12 and 40 carbon atoms. For example, selected compositions can be prepared by a high activity zeolite catalyst, a one

or two ring aromatic substrate, and a vinylidene olefin that is a by-product from the metallocene-catalyzed alpha-olefin polymerization process. The metallocene-catalyzed PAO process consists of the oligomerization of 1-alkenes in contact with a metallocene type catalyst. A characteristic of the oligomerization reaction from which these vinylidene olefin by-products are produced is the production of mixtures of dialkyl vinylidenic and 1,2 dialkyl or trialkyl mono-olefin oligomers as determined by infrared and NMR analysis. The processes of the present disclosure result in a significant proportion of unhydrogenated dimerized 1-alkene, or alpha-olefin having a vinylidenyl structure as follows:



where R_1 and R_2 are alkyl groups. Other olefinic compositions having 12 to 40 carbon atoms may be used in the processes of the present disclosure, including olefin oligomers from the acid or metallocene catalyzed oligomerization of alkenes including, for example, propylene and/or butenes and/or pentenes. The presence of vinylidene-containing trimers or higher order are also advantageous. Other processes that form olefinic precursors enriched in vinylidenes can also be used. The reaction of alpha olefins with Ziegler catalysts, such as triisobutyl aluminum, form vinylidene-containing dimers (see CA Patent No. 1,034,967). A process to dimerize alpha olefins with cyclopentadienyl zirconium dichloride or hafnium metallocene, an aluminoxane with or without an trialkyl aluminum cocatalyst, resulted in the selective formation of vinylidene-containing dimers (See US Patents No. 4,658,078 and 5,087,788, incorporated herein by reference).

[0021] Other mono olefins with the following substitution patterns where R_1 , R_2 , and R_3 are alkyl groups and R_4 is a hydrogen or an alkyl group, having a total of 12 to 40 carbon atoms may be used to obtain alkylated aromatics with quaternary substitution:



Generally, at least 50 mol% , or at least 55 mol%, or at least 60 mol%, or at least 65 mol%, of the mono-olefin structure comprises a vinylidenyl structure for the inventive processes disclosed herein.

Alkylation

[0022] Acidic catalysts capable of affecting alkylation of aromatics with olefins include acidic halides (Lewis acids), protonic acids (Bronsted acids), cation exchange resins, Friedel Crafts catalysts, and solid acids including zeolites.

[0023] Thus, while numerous acids catalytically promote the alkylation of aromatics with olefins, the present disclosure exhibits that for the purpose of preparing alkylaromatic compositions that are useful as liquid lubricant compositions and additives, high activity zeolites may be effective. Non-limiting exemplary high activity zeolites with surface acidity useful for preparing alkylaromatic compositions that are useful as liquid lubricant compositions and additives include, but are not limited to, MCM-22, MCM-36, MCM-49, MCM-56, ITQ-1, ITQ-3 and any combination thereof. U.S. Patents No. 4,954,325; 5,229,341; 5,236,575; 5,362,697; 6,077,498, and 6,500,404; herein incorporated by reference in their entirety, respectively disclose MCM-22, MCM-36, MCM-49, MCM-56, ITQ-1, ITQ-3.

[0024] Non-limiting exemplary Lewis acids include aluminum chloride, aluminum bromide, iron (III) chloride, zinc chloride, boron trifluoride and others. Non-limiting exemplary Bronsted acids include sulfuric acid, nitric acid, hydrochloric acid, hydrofluoric acid, phosphoric acid and others.

[0025] Aromatic compounds which may be used in the present disclosure include substituted and unsubstituted one and two ring aromatics and mixtures thereof. Advantageously, the aromatic moiety is at least one chosen from:

benzene, toluene, xylenes, ethylbenzene and naphthalene. Suitable aromatic compounds include, but are not limited to, substituted or unsubstituted benzene, substituted or unsubstituted naphthalene, substituted or unsubstituted furan, substituted or unsubstituted thiophene, substituted or unsubstituted anthracene, substituted or unsubstituted phenanthrene, substituted or unsubstituted pyrrole, substituted or unsubstituted indole, substituted or unsubstituted benzothiophene, substituted or unsubstituted dibenzothiophene, substituted or unsubstituted benzofuran, substituted or unsubstituted dibenzofuran, substituted or unsubstituted phenoxanthiin, substituted or unsubstituted thianthrene, substituted or unsubstituted biphenyl, substituted or unsubstituted pyrene, bisphenol A, bisphenol sulfide, anisole, thioanisole, diphenyl oxide, diphenyl sulfide, diphenylmethane, their substituted analogs, and mixtures thereof. A substituted naphthalene is a particularly advantageous aromatic compound for the invention compounds and processes disclosed herein. A less advantaged aromatic compound for the invention compositions and processes disclosed herein is an unsubstituted naphthalene compound.

[0026] In further advantageous embodiments, the aromatic compound is benzene, toluene, o-, m- or p-xylene, hydroxybenzene, alkoxybenzene such as methoxy or ethoxybenzene, thioanisole, diphenylether, diphenylmethane, diphenyl sulfide, naphthalene, methylnaphthalene, methoxynaphthalene, ethoxynaphthalene, methylnaphthyl sulfide, ethyl naphthylsulfide, bisphenol-A, bisphenol sulfide or a mixture thereof.

[0027] The aromatic compound can be substituted. Suitable substituent groups include alkyl, hydroxy, alkoxy such as methoxy or ethoxy, aryloxy such as phenoxy, alkylthio such as methanethio, arylthio such as phenylthio, and aralkyl such as benzyl. Thus, in some advantageous embodiments the aromatic

compound is a mono-substituted benzene, for example toluene, or a disubstituted benzene, for example para-, meta- or ortho-xylene.

[0028] The amount of catalyst charged to a reactor relative to the olefinic material is 0.1% to 20%, preferably 0.5% to 5%. The mole ratio of aromatic compound e.g., benzene, naphthalene, 1,2,4-trimethylbenzene to olefin starting material is typically between 1:3 and 20:1, preferably 1:2 to 10:1, but depending on the degree of alkylation of the aromatic which is desired, the ratio may be altered accordingly.

[0029] Generally, when a zeolite catalytic process is used, the catalyst is charged in a slurry reactor. The reaction may be carried out in a fixed-bed continuous operation wherein the catalyst is in pellet or extruded form and packed in a tubular reactor heated to a desirable temperature. The feed is introduced at a specific weight hourly space velocity (WHSV) ranging from about 0.1 to about 20, preferably from about 0.5 to about 5, to achieve a high conversion. An effective reaction temperature for the preparation of the alkylaromatic compositions is, for example, between room temperature and 350 °C, advantageously between 75 °C and 350 °C. Above 200 °C, the catalyst may affect isomerization, therefore a more advantageous temperature is below 200°C. Preferred reaction conditions include a pressure of from about 1 to about 30 atmospheres, a preferred catalyst charge from about 1 wt% to about 5 wt% in a slurry reactor or a WHSV of about 0.2 to about 4 in a fixed bed continuous operation. The reactants can be in either the vapor phase or the liquid phase and can be neat, i.e., free from intentional admixture or dilution with other material, or they can be brought into contact with the catalyst composition with the aid of carrier gases or diluents such as , for example, hydrogen or nitrogen. The alkylation can be carried out as a batch-type reaction typically employing a closed, pressurized, stirred reactor with an inert gas blanketing system or in a

semi-continuous or continuous operation utilizing a fixed or moving bed catalyst system.

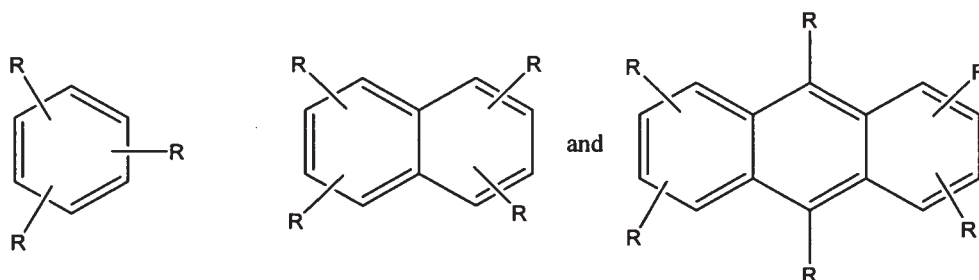
[0030] Generally, when a Friedel Crafts catalyst is used to affect the alkylation (US Patent 6,071,864), e.g., AlCl_3 or promoted BF_3 , process conditions may be carried out a temperature between -30 and 350 °C, typically at a temperature between 30 °C and 90 °C with a pressure typically between 700 and 7000 kPA. As conditions become more severe the Friedel Crafts catalysts causes isomerization of the vinylidene olefin so that the alkylaromatic product will contain a decreased amount of quaternary substituted alkylated aromatic. The alkylation can be carried out as a batch-type reaction typically employing a closed, pressurized, stirred reactor with an inert gas blanketing system or in a semi-continuous or continuous operation.

[0031] In the present disclosure, any means of separation that will provide a useful liquid alkylaromatic composition may be utilized. One example of a useful separation scheme following the alkylation of an aromatic is to use an excess of the lighter boiling hydrocarbon, for example, an aromatic and run the alkylation experiment until all of the olefin (vinylidene or other C_{12} - C_{40} olefin) has been consumed. Then the liquid composition can be separated from the acidic zeolite by ordinary means such as gravity separation or filtration and the unreacted aromatic can be separated from the liquid composition by vacuum distillation and recycled. In the general case of a Friedel Crafts catalyst, the reaction mixture can be quenched with a dilute acid or base solution, washed with water and dried as described in US Patents 5,254,274 and 6,071,864. Although the product of the alkylation has reduced bromine number compared to the starting olefin, mild hydrotreating of residual olefin or dimer co-product is an option.

[0032] This will provide the alkylaromatic composition useful as a liquid lubricant or additive.

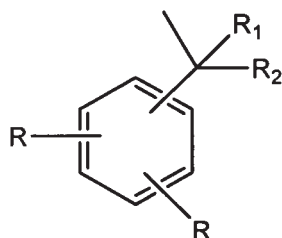
Composition

[0033] The alkylaromatic products may have the following non-limiting



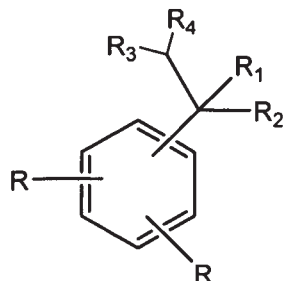
structures:

wherein a significant portion of at least one R group is the radical $R_2R_3CCH_3$ and wherein R has from about 6 to 40 carbons, or 12 to 40 carbons, or 16 to 24 carbons and R_2 and R_3 are alkyl groups. For example:



The amount of quaternary substituted aromatic was estimated from assignments determined by NMR DEPT experiments. In particular, the alkyl moiety attached to the aromatic moiety may be such that at least 25 mol% of the benzylic carbons are quaternary, or such that at least 30 mol% of the benzylic carbons are quaternary, or such that at least 35 mol% of the benzylic carbons are quaternary, or such that at least 40 mol% of the benzylic carbons are quaternary, or such that at least 50 mol% of the benzylic carbons are quaternary, or such that at least 70 mol% of the benzylic carbons are quaternary

Other aromatic structures that may be obtained using alternative olefins could result in quaternary substitution such as the general structure:



where R_1 , R_2 , and R_3 are alkyl groups and R_4 is a hydrogen or alkyl group.

[0034] Monoalkylated aromatics are the primary product disclosed herein, although multi-substituted aromatic compositions and olefin-olefin products may also be formed. The presence of non-quaternary alkylated aromatics are also present under the condition of isomerization of the olefin or the presence of non-vinylidene olefin reactants.

In the presence of a sufficiently strong acid catalyst, olefins may undergo skeletal rearrangement leading to tertiary carbocations (R_3C^+ , where R = alkyl) and that tertiary carbocations will alkylate aromatic substrates to produce a composition with a quaternary benzylic carbon adjacent to the aromatic ring. One of the advantages of the present disclosure is that alkylaromatic compositions having quaternary benzylic carbon at sufficiently high levels (defined as at least 25 mol% of the benzylic carbons are quaternary, or such that at least 30 mol% of the benzylic carbons are quaternary, or such that at least 35 mol% of the benzylic carbons are quaternary, or such that at least 40 mol% of the benzylic carbons are quaternary, or such that at least 50 mol% of the benzylic carbons are quaternary, or such that at least 70 mol% of the benzylic carbons are quaternary), such as to provide improved thermal and oxidative stability to the composition. An illustrative example of an alkylaromatic composition from the present disclosure having thermal and oxidative stability is

a composition where a significant amount (defined as at least 25 mol% of the benzylic carbons are quaternary, or such that at least 30 mol% of the benzylic carbons are quaternary, or such that at least 35 mol% of the benzylic carbons are quaternary, or such that at least 40 mol% of the benzylic carbons are quaternary, or such that at least 50 mol% of the benzylic carbons are quaternary, or such that at least 70 mol%) of the benzylic carbons are quaternary. The greater the thermal and oxidative stability of the alkylaromatic liquid lubricant composition the lower the requirement for additives to provide required thermal and oxidative stability.

[0035] More particularly, alkylaromatic compositions made from an aromatic moiety of unsubstituted naphthalene exhibit an oxidative stability as measured by RBOT of greater than 150, or greater than 155, or greater than 160, or greater than 165 minutes. Alkylaromatic compositions made from an aromatic moiety of toluene exhibit an oxidative stability as measured by RBOT of greater than 30, or greater than 35, or greater than 40, or greater than 45 minutes. In addition, alkylaromatic compositions made from an aromatic moiety of benzene exhibit an oxidative stability as measured by RBOT of greater than 20, or greater than 25, or greater than 30, or greater than 35 minutes. Generally, the greater the degree of branching and greater the chain length of the alkyl moiety yields a lower RBOT (poorer oxidative stability).

[0036] Another advantage of the alkylaromatic compositions of the present disclosure is that the pour point of the compositions formed herein is useful. Compositions including alkylaromatic compositions useful as liquid lubricant compositions must be liquid over a wide temperature range. The pour point is the lowest temperature at which a fluid will flow. The lower the pour point of a liquid lubricant composition, the lower the requirement for pour point depressant additives, which is advantageous. In particular, the disclosed alkylaromatic

compositions have pour points that are less than or equal to -30°C , or less than or equal to -35°C , or less than or equal to -40°C , or less than or equal to -45°C , or less than or equal to -50°C . Generally, the lower the degree of branching and the greater the chain length of the alkyl moiety yields a higher (less advantageous) pour point.

[0037] The following non-limiting examples are illustrative of the various embodiments of the present disclosure and the advantages thereto. It is within the ability of a person of ordinary skill in the art to select other variables from amongst the many known in the art without departing from the scope of the present disclosure. Accordingly, these examples shall serve to further illustrate the present disclosure, not to limit them.

EXAMPLES

Example 1

Preparation of Alkylated Naphthalene from 2-hexyl-1-decene and naphthalene

[0038] A solution of 200 g 2-hexyl-1-decene, 228 g naphthalene, 200 g decane (optional), and 10 g high activity zeolite catalyst (MCM-22) were heated under nitrogen to 125°C for 48 hours. The solution was cooled and filtered. The lubricant-range material was isolated from the mixture by distillation to remove any components boiling below 160°C at 1 millitorr vacuum. Yield: 231 g clear, nearly colorless fluid (74% based on olefin).

Example 2**Preparation of Alkylated Naphthalene from 2-octyl-1-dodecene and naphthalene**

[0039] The procedure was similar to Example 1 except that 250 g 2-octyl-1-dodecene was used. Yield: 268 g clear, bright yellow fluid (74% based on olefin).

Example 3**Preparation of Alkylated Naphthalene from 2-octyl-1-dodecene and naphthalene**

[0040] A solution of 250 g 2-octyl-1-dodecene, 114 g naphthalene, 200 g decane, and 15 g USY catalyst were heated under nitrogen to 175°C for 8 days. The solution was cooled and filtered. The lubricant-range material was isolated from the mixture by distillation to remove any components boiling below 160°C at 1 millitorr vacuum. Yield: 254 g clear, nearly colorless fluid (62% based on olefin).

Example 4**Preparation of Alkylated Naphthalene from 2-hexyl-1-decene and naphthalene**

[0041] 17.1 g Naphthalene and 50 mL hexanes were heated to 45 °C under N₂. BF₃.OEt₂ (5.0 mL) was added dropwise to naphthalene mixture. 20.0 g 2-hexyl-1-decene was added dropwise. Reaction was followed by GC. Upon completion (several days) the reaction mixture was quenched with 5% NaOH, washed with water until neutral and dried over sodium sulfate. The lubricant-range material was isolated from the mixture by distillation to remove any

components boiling below 160°C at 1 millitorr vacuum. Yield: 21 g clear fluid, 67% based on olefin.

Example 5

Preparation of Alkylated Toluene from 2-octyl-1-dodecene and toluene

[0042] 460 g Toluene, 140 g 2-octyl-1-dodecene, and crushed MCM-49 (4.0 g) were heated to reflux under N₂. The reaction was followed by GC. Upon completion, several days, the reaction mixture was cooled and filtered. The lubricant-range material was isolated from the mixture by distillation to remove any components boiling below 160°C at 1 millitorr vacuum. Yield: 155 g, 67% yield, based on olefin.

Example 6

Preparation of Alkylated Benzene from 2-decyl-1-tetradecene and benzene

[0043] 175 g Benzene, 140 g 2-decyl-1-tetradecene, and crushed MCM-49 (4.0 g) were heated to reflux under N₂. The reaction was followed by GC. Upon completion, several days, the reaction mixture was cooled and filtered. The lubricant-range material was isolated from the mixture by distillation to remove any components boiling below 160°C at 1 millitorr vacuum. Yield: 158 g clear colorless fluid, 91% yield, based on olefin.

Comparative Example 1

[0044] Comparative Example 1 is a commercial alkylated naphthalene made from 1-hexadecene, naphthalene, and USY catalyst. The majority of isomers are mono-alkylated with a mixture of alpha and beta naphthalene substitution.

Comparative Example 2

[0045] Comparative Example 2 is an alkylated toluene made from C20 internal olefins, toluene, and a Friedel Crafts catalyst. The majority of isomers are mono-alkylated with little quaternary substitution.

Table 1. Lube Properties of Vinylidene Alkylated Aromatics

Sample	Example 1	Example 2	Example 3	Comparative Example 1
Aromatic Group	Naphthalene	Naphthalene	Naphthalene	Naphthalene
Olefin	C16 vinylidene	C20 vinylidene	C20 vinylidene	C16 LAO
Catalyst	MCM-22	MCM-22	USY	USY
kV100°C, cSt	5.4	6.7	5.8	4.7
kV40°C, cSt	40.5	49.9	38.7	29
VI	26	67	69	65
Pour Point, °C	<-52.7	<-52.3	<-54.2	-39
Aniline Point, °C	37	54	49	34
B10 oxidation (40h@325F)				
sludge	nil	nil	trace	nil
D664-1, mg/gKOH	0.32	0.90	2.40	2.26
%Viscosity increase	2	15	17	13
Pb loss, wt%	0.6	4.66	13.9	14.3
RBOT, minutes	334	167	86	196
Noack Volatility, % loss	13.8	5.2	8.2	12.7
Quaternary isomer, mol% (NMR)	70	68	<10	NA

[0046] The olefins used to synthesize Examples 1-5 have a single branch at the vinylidene carbon and should be identical in structure to vinylidenes made via the metallocene processes. Examples 1, 2, 4, and 5 have 70, 68, and 72 %, respectively, of an isomer with a quaternary carbon alpha to the naphthalene or toluene ring. Example 3 provides an example of an alkylated naphthalene made

from a vinylidene which does not have a significant amount of quaternary substitution. The process of using high activity zeolites with acidity on the surface results in higher concentrations of quaternary substitution for bulky vinylidenes. Use of other acidic catalysts such as BF_3 etherate should result in high amounts of quaternary substitution.

[0047] Example 4 demonstrates that the BF_3 -etherate catalyst has similar selectivity with respect to quaternary substitution:

Table 2.

Sample	Example 4	Example 5	Example 6	Comparative Example 2
Aromatic Group	Naphthalene	Toluene	Benzene	Toluene
Olefin	C16 vinylidene	C20 vinylidene	C24 Vinylidene	C20 olefin
Catalyst	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	MCM-49	MCM-49	Friedel Crafts catalyst
$kV100^\circ\text{C}$, cSt	5.2	4.0	4.4	5.2
$kV40^\circ\text{C}$, cSt	34.8	20.0	19.9	32.1
<i>VI</i>	55	72	115	86
Pour Point, $^\circ\text{C}$	-54	-51	-30	-51
RBOT, minutes		45	31	20
Quaternary isomer, mol %	72	54	72	<5%

[0048] Examples 1 - 4 have much improved pour points (D5985 method) compared to Comparative Example 1, demonstrating that the branching improves pour points.

[0049] Example 1 can be directly compared to Comparative Example 1 since both lubricants have the same molecular weight. The RBOT (Rotary Bomb Oxidation Test, D2272 method) is 334 and 196 minutes, respectively, proving

that the quaternary carbon causes an improvement in the oxidation stability of the lubricant. Also, the B10 oxidation test (M334 method) demonstrates improvement of the acid number (0.32 vs. 2.26 mg/gKOH, D664-1 method), viscosity increase (2 vs. 13 wt%, D445-5 method) and Pb loss (0.6 vs. 14.3 wt%, D2272 method) during catalytic oxidation of Example 1 vs. Example 3.

[0050] Example 2, which is higher in molecular weight and viscosity than Example 1 and Comparative Example 1, also shows improved or equal B10 oxidation properties relative to Comparative Example 1, but not exceeding those of Example 1.

[0051] Example 3 demonstrates the loss of resistance to oxidation when there is little quaternary substitution due to isomerization of the vinylidene during the reaction. The USY catalyst was a poor alkylation catalyst for the alkylation of naphthalene with vinylidenes due to the bulk of the olefin. USY catalyst is an excellent alkylation catalyst for conventional alkylated naphthalenes for which linear alpha olefins are used. The result of this isomerization was poorer RBOT results compared to Comparative Examples 1, although their B10 oxidation results were similar.

[0052] Example 5 can be directly compared to Comparative Example 2 since both lubricants have the same molecular weight. The RBOT (Rotary Bomb Oxidation Test, D2272 method) is 45 and 20 minutes, respectively, proving that the quaternary carbon causes an improvement in the oxidation stability of the lubricant.

[0053] The resulting product was analyzed as summarized below. Oxidation stability was analyzed under the Rotating Bomb Oxidation Test (RBOT) and the B-10 oxidation test. The RBOT test protocol is described in ASTM D2272. The

B-10 oxidation test is used to evaluate mineral oil and synthetic lubricants either with or without additives. The evaluation is based on the resistance of the lubricant to oxidation by air under specified conditions as measured by the formation of sludge, the corrosion of a lead specimen, and changes in neutralization number and viscosity. In this method, the sample is placed in a glass oxidation cell together with iron, copper and aluminum catalysts and a weighed lead corrosion specimen. The cell and its contents are placed in a bath maintained at a specified temperature and a measured volume of dried air is bubbled through the sample for the duration of the test. The cell is removed from the bath and the catalyst assembly is removed from the cell. The oil is examined for the presence of sludge, the total acid number (TAN) (ASTM 664), and Kinematic Viscosity (kV) increase at 100° C (ASTM D445). The lead specimen is cleaned and weighed to determine the loss in weight.

Modeling Example 7

[0054] The products described in Examples 1 - 6 were made with a mono-olefin with a >95 mol% vinylidene content. The procedure for Example 1 resulted in 70 mol% quaternary isomer for alkylated aromatics. The procedure for Example 5 resulted in 54 mol % quaternary isomer. These numbers were used to calculate the theoretical yield for monoolefins with vinylidene contents of 50 - 65% as shown in Table 3 below.

Table 3.

Monolefin Vinylidene Content (mol %)	Theoretical Yield of Quaternary Isomer in Product (mol%)	
	<u>54%</u>	<u>70%</u>
50 %	27	35
60 %	32	42
65 %	35	45

[0055] Applicants have attempted to disclose all embodiments and applications of the disclosed subject matter that could be reasonably foreseen. However, there may be unforeseeable, insubstantial modifications that remain as equivalents. While the present disclosure has been described in conjunction with specific, exemplary embodiments thereof, it is evident that many alternations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure. Accordingly, the present disclosure is intended to embrace all such alterations, modifications, and variations of the above detailed description.

[0056] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted. When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

Claims

1. An alkylaromatic composition comprising:

an aromatic moiety other than unsubstituted naphthalene; and
an alkyl moiety having a carbon atom number in the range between 16 to 40, wherein said alkyl moiety is attached to said aromatic moiety such that at least 25 mol% of the benzylic carbons are quaternary.
2. The alkylaromatic composition of claim 1, wherein at least 35 mol%, preferably at least 70 mol %, of the benzylic carbons are quaternary.
3. The alkylaromatic composition of claim 1, wherein said aromatic moiety is toluene and optionally said composition has an oxidative stability, as measured by ASTM D2272, of greater than 30 minutes.
4. The alkylaromatic composition of claim 1, wherein said aromatic moiety is benzene and optionally said composition has an oxidative stability, as measure by ASTM D2272, of greater than 20 minutes.
5. The alkylaromatic composition of claim 1, wherein said composition has a pour point of less than or equal to -35°C, preferably less than or equal to -50°C.
6. A process for the preparation of an alkylaromatic compound comprising: contacting at least one aromatic moiety and a mono-olefin having a carbon atom number in the range between 16 to 40 in the presence of an acidic alkylation catalyst under alkylation conditions, wherein at least 50 mol% of the mono-olefin comprises a vinylidenyl structure, and thereby producing said alkylaromatic compound having at least 25 mol% of benzylic carbons that are quaternary.
7. The process according to claim 6, further comprising: separating and recovering said alkylaromatic compound.
8. The process according to claim 6, wherein said alkylaromatic compound has at least 65 mol% of benzylic carbons that are quaternary.
9. The process according to claim 6, wherein said acidic alkylation catalyst is chosen from zeolite catalysts, MCM-22, MCM-57, MCM-36, MCM-49, MCM-56, ITQ-1, and ITQ-3, or is a Friedel Craft catalyst chosen from BF₃, promoted BF₃, AlCl₃, SnCl₄, FeCl₃, and ZnCl₂.
10. The alkylaromatic composition of claim 1 wherein said aromatic moiety is chosen from benzene, toluene, xylenes, ethylbenzene, diphenyl sulfide, diphenyl oxide, and mixtures thereof.
11. The alkylaromatic composition of claim 1 wherein said aromatic moiety is chosen from substituted or unsubstituted benzene, substituted naphthalene, substituted or unsubstituted furan, substituted or unsubstituted thiophene, substituted or unsubstituted anthracene, substituted or unsubstituted phenanthrene, substituted or unsubstituted pyrrole, substituted or unsubstituted indole, substituted or unsubstituted benzothiophene, substituted or unsubstituted dibenzothiophene, substituted or unsubstituted benzofuran, substituted or unsubstituted dibenzofuran, substituted or unsubstituted phenoxanthiin, substituted or unsubstituted thianthrene, substituted or unsubstituted biphenyl, substituted or unsubstituted pyrene, bisphenol A, bisphenol sulfide, anisole, thioanisole, diphenyl oxide, diphenyl sulfide, diphenylmethane, and mixtures thereof.

12. The alkylaromatic composition of claim 1, wherein said aromatic moiety is chosen from toluene, o-, m- or p-xylene, hydroxybenzene, methoxy or ethoxybenzene, thioanisole, diphenylether, diphenylmethane, diphenyl sulfide, methylnaphthalene, methoxynaphthalene, ethoxynaphthalene, methylnaphthyl sulfide, ethyl naphthylsulfide, bisphenol-A, bisphenol sulfide and mixtures thereof.
13. The alkylaromatic composition of claim 1 or the process according to claim 6, wherein said mono-olefin has a carbon atom number in the range between 16 to 24.
14. The process according to claim 6, wherein said mono-olefin is derived from alkyl aluminum catalysts.
15. The process according to claim 14, wherein said alkyl aluminum catalyst is triisobutyl aluminum.
16. The process according to of claim 6, wherein said mono-olefin is derived from a metallocene-catalyzed alpha-olefin polymerization process.
17. The process according to claim 6, wherein said mono-olefin is derived from a vinylidene with a carbon atom number less than 40.
18. The process according to claim 17, wherein said vinylidene is chosen from 2-hexyl-1-decene, 2-octyl-1-dodecene, or 2-decyl-1-tetradecene, and mixtures thereof.
19. The process according to claim 6, wherein at least 65 mol% of the mono-olefin comprises a vinylidenyl structure.
20. The process according to claim 6, wherein said aromatic moiety is chosen from benzene, toluene, xylenes, ethylbenzene, naphthalene, diphenyl sulfide, diphenyl oxide, and mixtures thereof.
21. The process according to claim 6, wherein said aromatic moiety is chosen from substituted or unsubstituted benzene, substituted or unsubstituted naphthalene, substituted or unsubstituted furan, substituted or unsubstituted thiophene, substituted or unsubstituted anthracene, substituted or unsubstituted phenanthrene, substituted or unsubstituted pyrole, substituted or unsubstituted indole, substituted or unsubstituted benzothiophene, substituted or unsubstituted dibenzothiophene, substituted or unsubstituted benzofuran, substituted or unsubstituted dibenzofuran, substituted or unsubstituted phenoxanthiin, substituted or unsubstituted thianthrene, substituted or unsubstituted biphenyl, substituted or unsubstituted pyrene, bisphenol A, bisphenol sulfide, anisole, thioanisole, diphenyl oxide, diphenyl sulfide, diphenylmethane, and mixtures thereof.
22. The process according to claim 6, wherein said aromatic moiety is chosen from toluene, o-, m- or p-xylene, hydroxybenzene, methoxy or ethoxybenzene, thioanisole, diphenylether, diphenylmethane, diphenyl sulfide, naphthalene, methylnaphthalene, methoxynaphthalene, ethoxynaphthalene, methylnaphthyl sulfide, ethyl naphthylsulfide, bisphenol-A, bisphenol sulfide and mixtures thereof.