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(54) Titre : NAPHTALENES ALKYLES UTILISES COMME MATIERES DE BASE LUBRIFIANTES SYNTHETIQUES ET DESTINES A AMELIORER LES PERFORMANCES ANTIOXYDATION D'AUTRES HUILES DE BASE LUBRIFIANTES

(54) Title: ALKYLATED NAPHTHALENES AS SYNTHETIC LUBRICANT BASE STOCKS AND THEIR USE TO IMPROVE THE ANTIOXIDATION PERFORMANCE OF OTHER LUBRICANT BASE OILS

(57) **Abrégé/Abstract:**

This invention relates to alkylated methylnaphthalenes and their utility in lubricant base stocks. In particular, the alkylated methylnaphthalenes of the present invention have unexpectedly superior thermal and oxidative properties and may be used to improve the performance characteristics of other lubricant base oils.

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(57) Abstract: This invention relates to alkylated methylnaphthalenes and their utility in lubricant base stocks. In particular, the alkylated methylnaphthalenes of the present invention have unexpectedly superior thermal and oxidative properties and may be used to improve the performance characteristics of other lubricant base oils.



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ALKYLATED NAPHTHALENES AS SYNTHETIC LUBRICANT BASE STOCKS AND THEIR USE TO IMPROVE THE ANTIOXIDATION PERFORMANCE OF OTHER LUBRICANT BASE OILS

FIELD OF THE INVENTION

[0001] This invention relates to alkylated methylnaphthalenes and their utility in synthetic lubricant base stocks.

BACKGROUND OF THE INVENTION

[0002] Alkylaromatic fluids have been proposed for use as certain types of functional fluids where good thermal and oxidative properties are required. For example, U.S. Pat. No. 4,714,794 (Yoshida) describes monoalkylated naphthalenes as having excellent thermal and oxidative stability, low vapor pressure and flash point, good fluidity and high heat transfer capacity and other properties which render them suitable for use as thermal medium oils. The use of a mixture of monoalkylated and polyalkylated naphthalenes as a base for synthetic functional fluids is described in U.S. Pat. No. 4,604,491 (Dressler). Pellegrini U.S. Pat. Nos. 4,211,665 and 4,238,343 describe the use of alkylaromatics as transformer oils.

[0003] The alkylated naphthalenes are usually produced by the alkylation of naphthalene or a substituted naphthalene in the presence of an acidic alkylation catalyst such as a Friedel-Crafts catalyst, for example, an acidic clay as described in Yoshida U.S. Pat. No. 4,714,794 or Dressler U.S. Pat. No. 4,604,491 or a Lewis acid such as aluminum trichloride as described in Pellegrini U.S. Pat. Nos. 4,211,665 and 4,238,343. The use of a catalyst described as a collapsed silica-alumina zeolite for the alkylation of aromatics such as naphthalene is disclosed in Boucher, U.S. Pat. No. 4,570,027. The use of

various zeolites including intermediate pore size zeolites such as ZSM-5 and large pore size zeolites such as zeolite L and ZSM-4 for the alkylation of various monocyclic aromatics such as benzene is disclosed in Young, U.S. Pat. No. 4,301,316.

[0004] In the formulation of functional fluids based on the alkyl naphthalenes, it has been found that the preferred alkyl naphthalenes are the mono-substituted naphthalenes since they provide the best combination of properties in the finished product. The mono-substituted naphthalenes possess fewer benzylic hydrogens than the corresponding di-substituted or poly-substituted versions and were said to have better oxidative stability and therefore form better functional fluids and additives. In addition, the mono-substituted naphthalenes have a kinematic viscosity in the desirable range of about 5-8 cSt (at 100°C) when working with alkyl substituents of about 14 to 18 carbon atoms chain length. Numerous work has been done to improve the selectivity to the desired mono-alkylated naphthalenes.

[0005] U.S. Pat. No. 5,034,563, Ashjian et al., which is incorporated by reference, teaches use of a zeolite containing a bulky cation. The use of, e.g., USY with cations having a radius of at least about 2.5 Angstroms increases selectivity for desired mono-alkylated products. Suitable zeolites include those containing hydrated cations of metals of Group IA, divalent cations, especially of Group IIA, and cations of the Rare Earths.

[0006] U.S. Pat. No. 5,177,284, Le et al., which is incorporated by reference, discusses the desirable properties of alkylated naphthalene fluids with higher alpha:beta ratios, including improved thermal and oxidative stability. Le et al. found that several parameters influenced the alpha:beta ratio of the alkylated

naphthalene products, including steaming the zeolite, lowering the alkylation temperature, or using an acid-treated clay.

[0007] U.S. Pat. No. 5,191,135 Dwyer et al., which is incorporated by reference, discloses the effect of co-feeding water for the alkylation reaction when using a large pore zeolite catalyst, such as zeolite Y. U.S. Pat. Nos. 5,191,134, and 5,457,254, incorporated by reference herein, disclose a similar alkylation process using MCM-41 and a mixed H/NH₄ catalyst, respectively.

[0008] As previously noted, the prior art taught that mono-substituted naphthalene is the most desirable component for synthetic lubricant base stock with optimized thermal and oxidative stability and viscometrics. Accordingly, the prior art taught processes to improve selectivity and achieve the desired mono-alkylated products. Di-alkyl naphthalenes were thought to have inferior lubricant properties because di-alkylation inhibits the naphthalene rings to neutralize the oxygen, peroxides or radicals. Alkylated naphthalenes with di- or tri-alkyl components were thought to have poor thermal and oxidative stabilities.

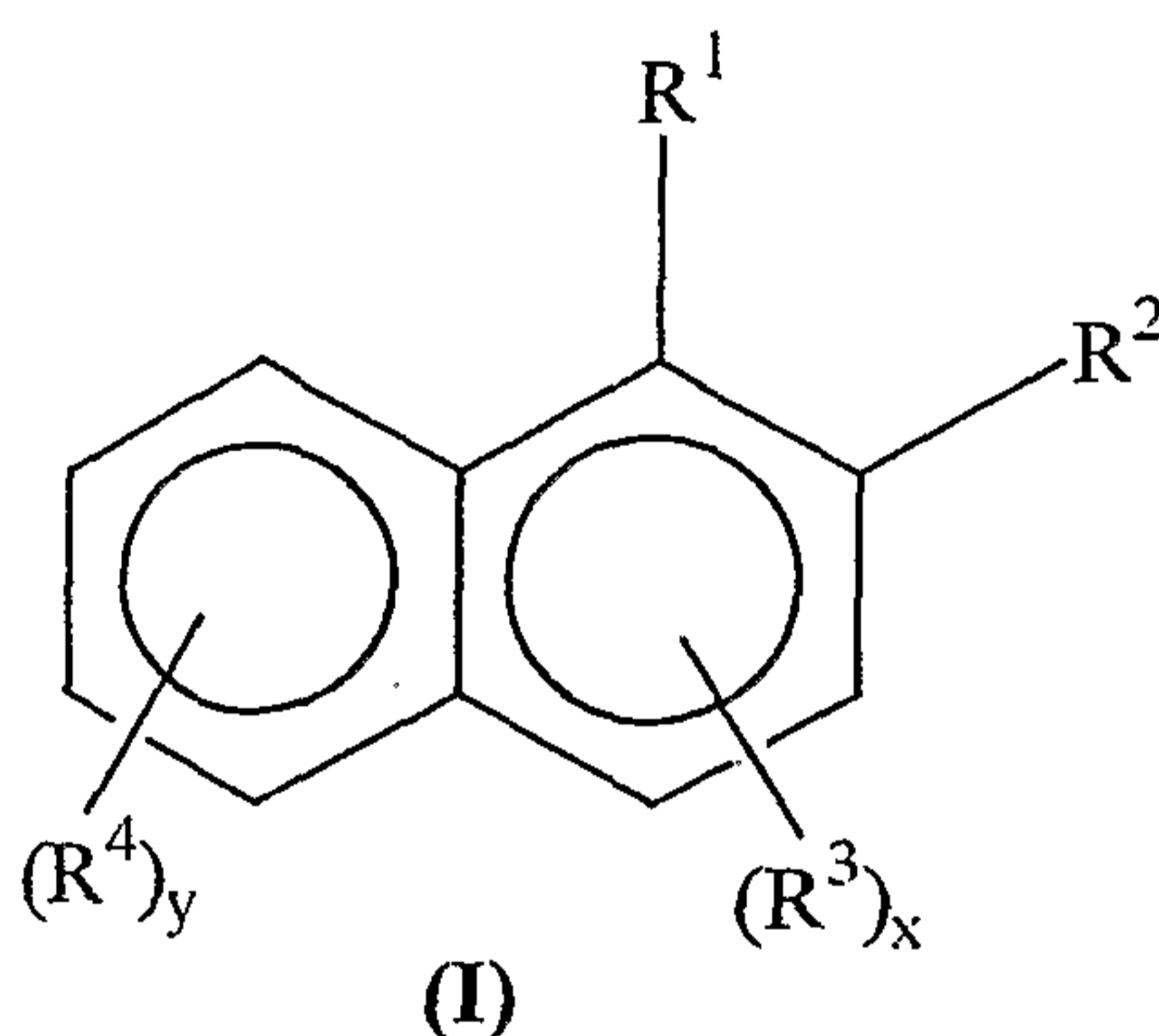
SUMMARY OF THE INVENTION

[0009] It has now been discovered that di-, tri-, or tetra-alkyl naphthalenes, in particular alkyl methylnaphthalenes, contrary to the teachings of the art, have superior thermal and oxidative properties, in many cases significantly better than mono-substituted naphthalenes.

[0010] Accordingly, the present invention extends the range of raw materials that can be used to produce synthetic base stock and establishes that alkyl

methylnaphthalenes have better oxidative stability than known alkyl naphthalene fluid.

[0011] The present invention includes di-, tri- or tetra-alkyl naphthalenes, preferably di-alkyl naphthalenes, as having utility as synthetic lubricant base stocks, blending stocks, or as additives for other base stock fluids or liquid fuels. The present invention includes a base oil comprising a mixture of monoalkylated and polyalkylated naphthalenes wherein the improvement comprises said base oil containing at least 20 wt% of an alkylated naphthalene selected from the group consisting of a compound or mixture of compounds of the following formula (I):



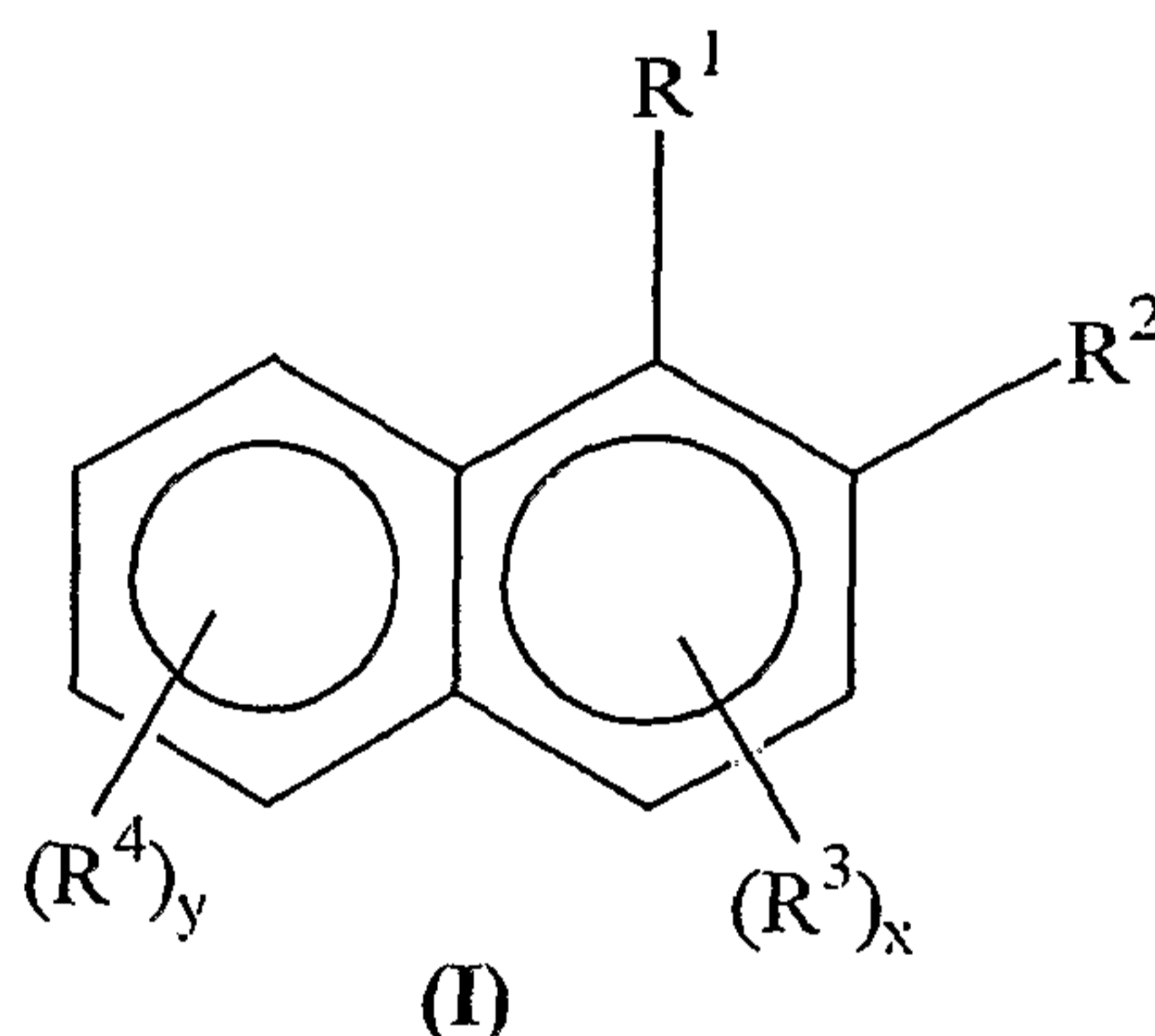
wherein R^1 and R^2 are H, methyl, ethyl, n-propyl, n-butyl, or t-butyl;
 R^3 and R^4 are an alkyl group having from about 6 to about 24 carbon atoms;
 x is from 0 to about 2; and
 y is from 0 to about 4;
with the proviso that at least one of R^1 and R^2 is other than H, and at least one of x and y is other than 0.

[0012] Preferably only one of R^1 and R^2 is alkyl and the other H, most preferably one of R^1 and R^2 is H and the other is methyl.

[0013] The compounds of formula (I) have unexpectedly superior thermal and oxidative properties, especially when compared to mono-substituted naphthalenes. The term mono-substituted naphthalenes, as used herein, generally refers to naphthalene having a single substitution, such as an alkyl group having from about 6 to about 24 carbon atoms.

[0014] Another aspect of the present invention is directed to a method for improving the oxidative stability of lubricants comprising adding to the lubricant a base oil comprising a compound of formula (I).

[0015] Hence the method is directed to a method for improving the oxidative stability of a lubricant having an RBOT of \leq about 200 minutes comprising adding to said lubricant a base oil comprising a compound of formula (I):



wherein R^1 and R^2 are H, methyl, ethyl, propyl, or butyl;

R^3 and R^4 are an alkyl group having from about 6 to about 24 carbon atoms;

x is from 0 to about 2; and

y is from 0 to about 4;

with the proviso that at least one of R^1 and R^2 is other than H, and at least one of x and y is other than 0;

and wherein the base oil has a RBOT value of greater than about 200 minutes.

DETAILED DESCRIPTION OF THE INVENTION

[0016] As used herein, "alkylated methylnaphthalene" refers to a naphthalene compound that has a methyl group at the one or two position of the naphthalene ring and at least one additional alkyl group containing about 6 carbon atoms to about 24 attached at another position of the ring. In addition, all values set forth herein include all combinations and sub-combinations of ranges and specific values given therein.

[0017] The starting materials for the production of compounds of formula (I) are substituted naphthalenes which may contain one or more short chain alkyl groups containing up to about eight carbon atoms, such as a methyl, ethyl, propyl, or butyl group. Preferably, the starting material comprises 1-methylnaphthalene, 2-methylnaphthalene or a mixture of the two in any proportion. For example, 1- and 2- methylnaphthalenes are present in coke liquids or in the heavy fraction (greater than 10 carbon atoms) of aromatic reformat streams or the heavy bottom stream from a toluene disproportionation process or the heavy fraction from a catalytic cracking process, such as light cycle oil from an FCC process. Feed streams with higher 2-methylnaphthalene content, such as those from the highly selective toluene disproportionation process, are preferable because the alkylated 2-methylnaphthalene products generally have better oxidative stability and the alkylation process tends to be more efficient when compared to feedstreams containing higher amounts of 1-methylnaphthalenes. Additionally, the starting material may comprise a mixture of methylnaphthalene and naphthalene.

[0018] The alkylating agents which may be used to alkylate the substituted naphthalenes include any aliphatic or aromatic organic compound having one or

more available alkylating aliphatic groups capable of alkylating the substituted naphthalene. The alkylatable group itself should have at least about 6 carbon atoms, preferably at least about 8, and still more preferably at least about 12 carbon atoms. For the production of functional fluids and additives, the alkyl groups on the naphthalene preferably have from about 12 to about 24 carbon atoms, with particular preference to about 14 to 18 carbon atoms. A preferred class of alkylating agents are the olefins with the requisite number of carbon atoms, for example, the dodecenes, tetradecenes, pentadecenes, hexadecenes, heptadecenes, octadecenes, nonadecenes, and their branched analogs.

[0019] In preferred embodiments, the alkylating agent will be an olefin which may include internal olefins (such as 2- or 3-tetradecene), alpha (or 1-) olefins, vinylidene olefins (such as 2-methyl-1-tetradecene or 2,3,3-trimethyl-1-butene, or 2,4,4-trimethyl-1-pentene, or 2,4,4-trimethyl-2-pentenes). The alpha olefins and linear internal olefins are most readily available.

[0020] Mixtures of olefins, for example, mixtures of C₁₂-C₂₀ or C₁₄-C₁₈ olefins, may also be used in the present invention. Branched alkylating agents, especially oligomerized olefins such as the trimers, tetramers, or pentamers of light olefins such as ethylene, propylene, and butylenes are also useful. Other useful alkylating agents which may be used, include alcohols such as hexadecanols, heptadecanols, octadecanols, nonadecanols, dodecanols and doundecanols. Alkyl halides such as hexadecyl chlorides, octadecyl chlorides, dodecanyl chlorides, and higher homologs may also be used in the present invention.

[0021] Previous prior art references relating to production of alkylaphthalenes emphasized making high amounts of mono-alkyl naphthalenes. In the present

invention, di-alkyl naphthalene (e.g. methyl at the 1 or 2 position and an alkyl group of about 6 carbon atoms attached at another position of the ring) may be consistently produced because one of the alkyl groups is a small alkyl substituent, such as methyl or ethyl. The di-alkyl product may be achieved by carefully selecting the starting material and by controlling the first alkyl group present in the naphthalene ring.

[0022] The alkylation reaction between the substituted naphthalene and the alkylating agent is carried out in the presence of an alkylation catalyst. Typically, the catalyst comprises a zeolite catalyst which contains a cation of certain specified radius. The molecular size of the alkylation products will require a relatively large pore size in the zeolite in order for the products to leave the zeolite, which will also tend to reduce diffusion limitations with the long chain alkylating agents. The large pore size zeolites are the most useful zeolite catalysts for this purpose although the less highly constrained intermediate pore size zeolites may also be used, as discussed below. Acidic clay materials such as Fitrol 20, 22, and 24 from Englehard Co. are also useful.

[0023] Large pore size zeolites include faujasite, the synthetic faujasites (zeolites X and Y), zeolite L, ZSM-4, ZSM-18, ZSM-20, mordenite and offretite. Such zeolites are characterized by the presence of a 12-membered oxygen ring system in the molecular structure and by the existence of pores with a minimum dimension of at least 7.4 Angstrom, as described by Frilette et al. in *J. Catalysis* 67, 218-222 (1981). See also, Chen et al., *Shape-Selective Catalysis in Industrial Applications, Chemical industries*, vol. 36, Marcel Dekker Inc., New York 1989, ISBN 0-8247-7856-1 and Hoelderich et al. *Angew. Chem. Int. Ed. Engl.*, 27, 226-246 (1988), pp.226-229. The large pore size zeolites may also be characterized by a "Constraint Index" (CI) of not more than 2, in most cases not more than 1. The method for determining CI is described in U.S. Pat. No.

4,016,218, together with values for typical zeolites. The significance of the Index is described in U.S. Pat. No. 4,861,932, to which reference is made for a description of the test procedure and its interpretation.

[0024] Zeolites whose structure is that of a ten membered oxygen ring, generally regarded as the intermediate pore size zeolites, may also be effective catalysts for this alkylation reaction if their structure is not too highly constrained. Zeolites such as ZSM-12 (CI 2) may be effective catalysts for the alkylation reaction. The zeolite identified as MCM-22 is also a useful catalyst for this reaction and is described in U.S. Pat. No. 4,954,325 incorporated herein by reference. In addition, MCM-56, described in U.S. Pat. No. 5,362,697, incorporated herein by reference, may also be used. Zeolites having a CI up to about 3 will generally be useful catalysts, although the activity may be found to be dependent on the choice of alkylating agent, especially its chain length, a factor which imposes diffusion limitations upon the choice of zeolite. Other useful catalysts include MCM-49, described in U.S. Pat. Nos. 5,236,575 and 5,371,310, incorporated herein by reference.

[0025] Another useful zeolite in accordance with the present invention includes ultrastable Y, usually referred to as USY. When this material contains hydrated cations, it catalyzes the alkylation in good yields with excellent selectivity. Zeolite USY is a material of commerce, available in large quantities as a catalyst for the cracking of petroleum. It is produced by the stabilization of zeolite Y by a procedure of repeated ammonium exchange and controlled steaming. Processes for the production of zeolite USY are described in U.S. Pat. Nos. 3,402,966 (McDaniel), 3,923,192 (Maher) and 3,449,070 (McDaniel); see also Wojciechowski, Catalytic Cracking, Catalysts, Chemistry and Kinetics, Chemical Industries, vol. 25, Marcel Dekker, New York, 1986, ISBN

0-8247-7503-8, to which reference is made for a description of zeolite USY, its preparation and properties.

[0026] The most preferred zeolites in accordance with the present invention include USY, MCM-22, MCM-49 and MCM-56.

[0027] Additionally, other catalysts that may be used in the present invention include a zeolite having both ammonium and protonic species associated with the exchangeable sites of the zeolite. Such a catalyst is disclosed in U.S. Pat. No. 5,457,254, Arditto et al., incorporated herein by reference. As also disclosed in U.S. Pat. No. 5,457,254, selected zeolite catalysts preferably contain a limited amount of one or more of the Rare Earths.

[0028] The catalyst of the present invention may be composited with a matrix material or binder which is resistant to the temperatures and other conditions employed in the alkylation process. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica or silica-alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gel including mixtures of silica and metal oxides. Use of an active material in conjunction with the zeolite may change the conversion and/or selectivity of the catalyst. Inactive materials suitably serve as diluents to control the amount of conversion so that alkylation products can be obtained economically and orderly without employing other means for controlling the rate of reaction. Binders which may be incorporated to improve the crush strength and other physical properties of the catalyst under commercial alkylation operating conditions include, but are not limited to, naturally occurring clays, e.g., bentonite and kaolin, as well as silica, alumina, zirconia and mixtures thereof.

[0029] The alpha value of the zeolite is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant = 0.016 sec⁻¹). The alpha test is described in U.S. Pat. No. 3,354,078 and in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test.

[0030] Generally, zeolites with high alpha values ranging from about 10 to about 1000 are preferred for use in the present invention. Most catalysts have alpha values greater than 30 and some zeolites, such as Y and USY have high initial alpha values up to about 1000. For purposes of the present invention, alpha values from about 10 and higher are effective in the alkylation process. MCM-22, MCM-49 and MCM-56 generally have stable and high alpha values from about 40 to about 500 and are especially suitable for fixed-bed continuous operations.

[0031] The stability of the alkylation catalyst of the invention may be increased by steaming. U.S. Pat. Nos. 4,663,492; 4,594,146; 4,522,929; and 4,429,176 are incorporated by reference herein, and describe conditions for the steam stabilization of zeolite catalysts which can be utilized to steam-stabilize the catalyst.

[0032] The alkylation process of this invention is conducted such that the organic reactants, e.g., the alkylatable methylnaphthalene compound and the alkylating agent, are brought into contact with the catalyst in a suitable reaction

zone such as, for example, in a flow reactor containing a fixed bed of the catalyst composition, under effective alkylation conditions. The preferred starting material, methylnaphthalene, will be used in describing the alkylation conditions.

[0033] Alkylation reaction conditions typically include a temperature of from about 100°C to about 400°C, preferably from about 150°C to about 250°C. Generally, reaction rates may be too slow below 100°C, and temperatures above 300°C may promote undesirable side reactions that may degrade product properties and yield.

[0034] Typical reaction pressures include a pressure from about 0.1 to about 100 atmospheres, preferably from about 1 to about 30 atmospheres. The required pressure may be maintained by inert gas pressurization, preferably with nitrogen.

[0035] Typical reaction times are from about 0.5 to about 100 hours, preferably from about 2 to about 30 hours. The reaction time is dependent on temperature and the amount of catalyst used in the process. Generally, higher reaction temperatures and a higher catalyst charge promotes faster reaction rates.

[0036] Typical alkylatable methylnaphthalene compound to alkylating agent mole ratio (MN:O) is from about 1:3 to about 10:1, preferably from about 1:2 to about 3:1.

[0037] Generally, the amount of catalyst charged is about 0.1 wt% to about 10 wt% in a slurry reactor. A low catalyst charge may cause longer reaction times and a high catalyst charge may be uneconomical to run, causing filter plugging during the catalyst removal step. Preferably, the catalyst charge is

about 0.5 wt% to about 5 wt%. The reaction may be carried out in a fixed-bed continuous operation where 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.

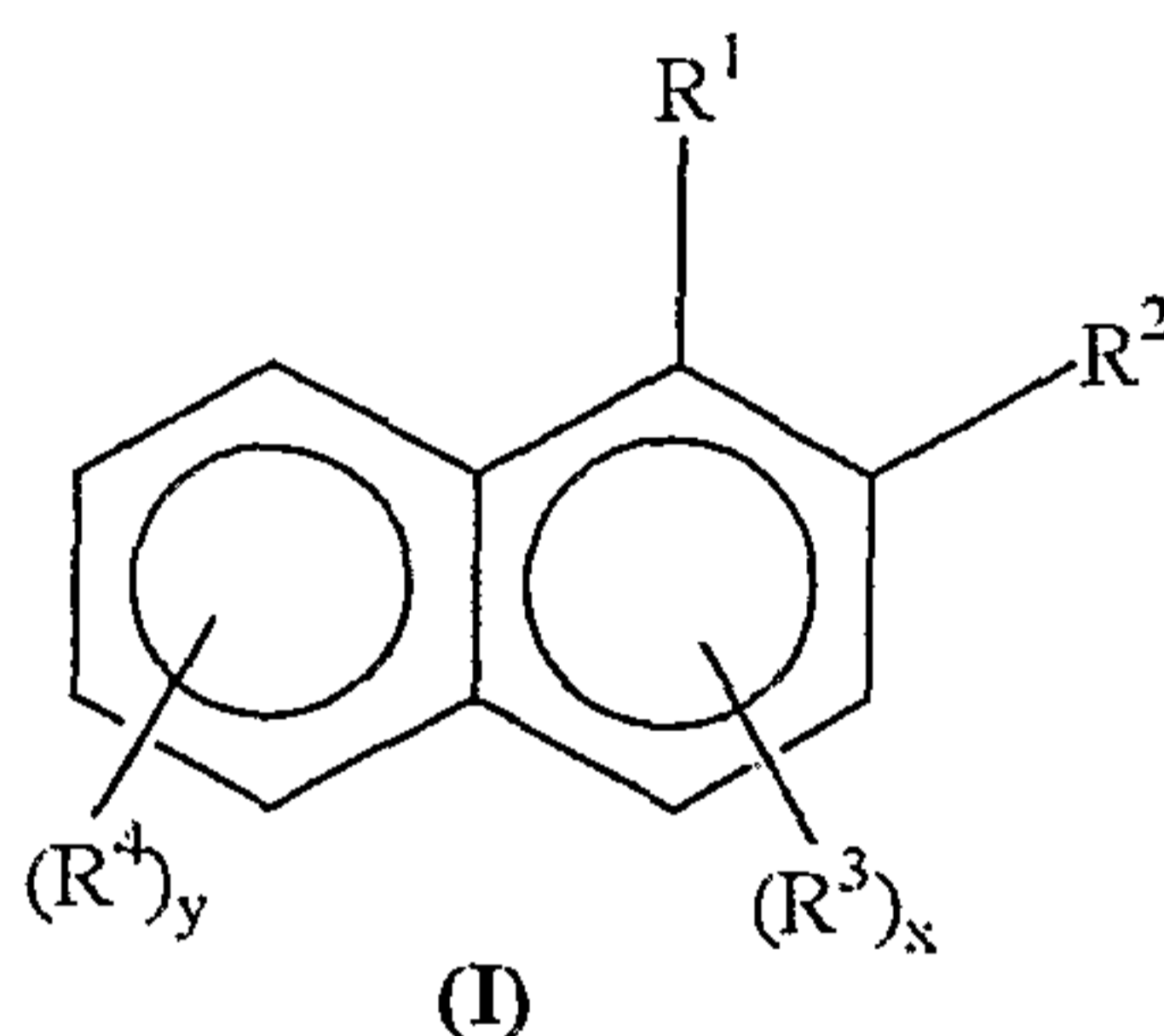
[0038] Preferred reaction conditions include a temperature within the approximate range of from about 150 to about 250°C, a pressure of from about 1 to about 30 atmospheres, a reaction time of from about 2 to about 30 hours, and an MN:O mole ratio of from about 1:2 to about 3:1, with a preferred catalyst 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.

[0039] 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.

[0040] In preparing compounds of formula (I), an amount of dimer of the alkylating olefin will be co-produced. The basestocks herein comprising formula (I) will typically contain < 1 wt% dimer whether used as a basestock or as a co-basestock.

[0041] The compounds of formula (I) are characterized by exceptional oxidative and thermal stability. They may be separated from the reaction mixture by stripping off unreacted alkylating agent and the formula (I) compound in the conventional manner. It has also been found that the stability of the alkylated product may be improved by filtration over activated charcoal and by alkali treatment to remove impurities, especially acidic by-products formed by oxidation during the course of the reaction. The alkali treatment is preferably carried out by filtration over a solid alkali material, preferably calcium carbonate (lime).

[0042] The synthetic lubricant base stocks of the present invention comprise



compounds represented by the following general formula (I):

wherein R¹ and R² are H, methyl, ethyl, propyl, or butyl;

R³ and R⁴ are an alkyl group having from about 6 to about 24 carbon atoms;

x is from 0 to about 2; and

y is from 0 to about 4;

with the proviso that at least one of R¹ and R² is other than H, and at least one of x and y is other than 0.

[0043] In preferred embodiments, either R¹ or R² is H and the other alkyl, most preferably either R¹ or R² is H and the other is methyl. Accordingly, 1- or 2-methylnaphthalenes or mixtures thereof are preferred starting materials. Generally, mixtures high in 2-methylnaphthalenes are more preferred because they may be more reactive than 1-methylnaphthalenes and the 2-

methylnaphthalene alkylation product has better stability than 1-methylnaphthalene alkylation products. As noted previously, the heavy bottom stream from highly shape-selective toluene disproportionation processes are typically high in 2-methylnaphthalenes and especially suitable for use in the present invention.

[0044] Also, in preferred embodiments, R^3 and R^4 comprise alkyl groups having from about 6 to about 24 carbon atoms, more preferably, from about 8 to about 18 carbon atoms. Exemplary R^3 and R^4 groups include hexyl, heptyl, octyl, nonyl, iso-octyl, 2-ethyl hexyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, each optionally having linear or branched alkyl groups.

[0045] The sum of x and y is preferably from about 1 to about 3. More preferably, the synthetic oils comprise di-alkyl naphthalenes wherein the sum of x and y is one, R^1 is H and R^2 is methyl. The synthetic oils may comprise higher-alkylated naphthalenes wherein the sum of x and y is greater than one, or from about 2 to about 3. Where mixtures of compounds of formula (I) are used, the ratio of di-alkyl naphthalenes to tri- or tetra-alkyl naphthalenes may be from about 3 to about 1, more preferably from about 25 to about 1. The amount of di-alkyl naphthalene product versus tri- or tetra-alkyl naphthalene product may be controlled by changing the methylnaphthalene to alkylating agent olefin ratio in the feed, catalyst type and/or reaction temperature. Usually, a lower methylnaphthalene to olefin ratio (higher olefin content) favors the formation of tri- or tetra-alkylated naphthalenes.

[0046] The compounds of formula (I) described herein exhibit excellent thermal and oxidative properties which make them particularly suitable for use in

lubricant base oils. Such properties have generally been superior and unexpected, particularly when compared to mono-substituted naphthalenes. The compounds of formula (I) may be characterized, for example, by oxidation stability, viscosity, and pour point. Generally speaking, the thermal and oxidative properties of the compounds of formula (I) may vary depending on the alkylating conditions including, for example, the starting material to alkylating agent ratio, the reaction temperature, and the particular alkylating agent used.

[0047] The compounds of formula (I) may be used to improve the oxidative stability of lubricants. For example, the oxidation stability of the compounds of formula (I) as measured under the Rotating Bomb Oxidation Test (RBOT) (ASTM D2272) is generally greater than about 200 minutes, more preferably greater than 500 minutes. In preferred embodiments, the RBOT values are from about 500 to 1500 minutes, more preferably between 700 and 1200 minutes. All values set forth herein include all combinations and subcombinations of ranges and specific values given therein.

[0048] In addition, the kinematic viscosity of the compounds of formula (I) at 100°C is from about 2 to about 30 cS, more preferably from about 3 to about 20 cS, with viscosity index (VI) values from about 50 to about 180, preferably greater than 60. The pour point of the compounds of formula (I) is from about 0 to about -60°C, more preferably from -10 to about -55°C. All values set forth herein include all combinations and sub-combinations of ranges and specific values given therein.

[0049] Typically, the base oils of the present invention which comprise basestocks of formula (I) comprise about 20 wt% of a compound of formula (I) or mixtures thereof and preferably greater than about 50 wt% of a compound of

formula (I) or mixtures thereof. Such amounts may depend on the particular application and/or the performance characteristics desired. The base oils of the present invention have RBOT of at least about 200.

[0050] The synthetic base oils comprising compounds of formula (I) may be used by themselves as the basestock for synthetic lubricant formulations. They can also be used as a co-base stock with other synthetic basestocks, such as polyalphaolefins (PAO), polyalkyleneglycol (PAG), polybutene (PIB), alkylbenzene (AB), or with conventional mineral oils, such as 100 to 800 SUS SN oils from catalytic or conventional dewaxed processes. The base oils comprising compounds of formula (I) may also be used with hydrocracked or hydroisomerized basestocks such as UCBO from Chevron, BP hydrocracked stocks, slack wax-isomerized basestocks or Fischer-Tropsh wax-isomerized basestocks (collectively, these fluids are referred to as Group II and Group III basestocks). The above basestocks typically have RBOT of \leq about 150.

[0051] Generally, when used as a co-basestock, the base oil of the present invention comprises from about 2 to about 60 wt% of the total lubricant basestock, and preferably greater than about 5 wt% of the total lubricant basestock. The use of the base oils of the present invention significantly improves the finished lubricant's thermal, oxidative, and hydrolytic stability as well as lubricant additive solvency, sludge dispersancy and antiwear or extreme-pressure metal surface protection.

[0052] As noted above and indicated in the following examples, compounds of formula (I) have superior oxidative stabilities and viscometrics when compared to mono-alkylated naphthalenes. Accordingly, the synthetic base oils

of the present invention may be substantially devoid of mono-alkylated naphthalenes and still provide excellent lubricating properties.

[0053] The base oils of the present invention may be incorporated with conventionally used additives for lubricating oils such as an antioxidant, detergent dispersant, viscosity index improver, pour point depressant, oiliness improver, anti-wear agent, extreme pressure agent, friction modifying additive, anti-corrosive agent, metal inactivating agent, anti-rust agent, seal compatibility improver, anti-foaming agent, emulsifier, demulsifier, bactericide, or colorant.

[0054] The base oils of the present invention may be used to lubricate surfaces of various structures and elements that require lubrication. As used herein, "surface" refers to the outer part of structures or particles. The compounds of formula (I) may be used in various functional fluid formulations such as crank case lubricant, two cycle engine oil, hydraulic lubricant, drilling lubricant, turbine oil, grease, gear oil, transmission oil, and paper machine oil.

[0055] The following examples are illustrative and not meant to be limitations.

EXAMPLES

[0055] The general procedure described herein was used to collect the following data and is specifically described for Example 2 of Table 1. In this experiment, 1-methylnaphthalene (1-MN), 142 gram (1 mole) and 12.5 gram USY catalyst were premixed in a 500 ml round bottom flask and the complete reaction system was purged with N₂ to eliminate air. The reaction flask was heated to 200°C under nitrogen atmosphere. 1-hexadecene, 112 gram (0.5 mole), was added slowly into this mixture in two hours. The reaction mixture

was reacted for three more hours and then cooled down to room temperature. Analysis of the reaction mixture by gas chromatography was used to determine the amounts of unreacted reactants and showed that most of the C₁₆ olefin was converted into product. The product, i.e. the lube product, was isolated by filtering off the solid catalyst and distilled at 120°C/<1 millitorr vacuum for more than one hour to remove any unreacted olefin and methylnaphthalene (MN).

[0056] The resulting product was analyzed and product properties are 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.

[0057] 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.

[0058] Other properties to be measured include Bromine No. (ASTM D1159), VI, and Pour Point (ASTM D97).

[0059] The following examples illustrate the excellent thermal and oxidative stabilities of the compounds of formula (I) as well as the effect of several variables on the properties and yield of the compounds, i.e., lube products.

[0060] The data in Table 1 demonstrates the effect of MN/olefin molar ratios on the lube product (a methylnaphthalene acts as the starting material and an olefin acts as the alkylating agent for purposes of the examples herein). Examples 1 to 3 show that increasing 1-MN/olefin molar ratios from 1/1 to 4/1 improves the oxidative stability of the lube product as measured by RBOT (the RBOT time increases from 145 minutes to 805 minutes). A similar trend was observed for 2-MN/olefin molar ratios (Examples 4 and 5). Varying the MN/olefin ratios do not appear to change product viscosities, VI, and pour points and conversion of olefins were very high (>90%) at all MN/olefin ratios.

Table 1. Effect of MN/Olefin Molar Ratio

Example No.	1	2	3	4	5
Feed, MN	1-MN	1-MN	1-MN	2-MN	2-MN
Olefin	C16	1-C16	C16	1-C16	1-C16
Mole Ratio MN/O	1/1	2/1	4/1	1.0/1	2.0/1
Catalyst Type	USY	USY	USY	USY	USY
Catalyst Wt%	5	5	5	5	5
Rxn Temp, °C	200	200	200	200	200
Rxn Time, Hrs.	18	4	4	9	18
% Total Conv.	94.5	71.3	58.0	95.3	77.9
% 1-C16 Conv.	94.2	95.9	98.5	95.7	97.7
Product Selectivity					
mono-C16-MN	95.6	94.1	99.6	96.1	99.7
di-C16-MN	4.4	2.8	0.4	3.9	0.3
others	0.0	3.1	0.0	0.0	0.0

Product Properties					
Kv @ 100°C, cS	5.7	5.6	5.8	5.5	5.3
Kv @40°C, cS	41.4	41.0	40.9	38.4	36.8
VI	67	62	76	67	64
Pour Point, °C	-47	-46	-46	-48	-49
Bromine No.	0.27	0.5	0.45	0.02	0.03
Oxidative Stability					
RBOT, min	145	703	805	239	744
B10 Test at 163°C/40 hrs					
% Kv Increase	21.8	6.5	0.0	12.0	10.2
TAN Incr., mg KOH	1.87	1.6	0.35	0.9	1.1
Sludge	nil	nil	trace	light	trace
wt% lead loss	19.5	7.2	2.6	10.1	8.6

[0061] The data in Table 2 demonstrates the effect of reaction temperature on lube yields and properties from 1-MN or 2-MN at a 2/1 MN/olefin mole ratio. Examples 6 to 8 show that increasing reaction temperature from 175 to 225°C increases 1-hexadecene conversion from 74% to 100%, but this has no effect on viscosities, VI and pour points. At lower reaction temperatures, such as 175°C and 200°C (Ex. 6 and 7), the lube products have longer RBOT time than the product produced at 225°C (Ex. 8, 168 minutes). Similar trends were observed for lube products from 2-MN (Ex. 9 to 12). For example, by running the

reaction at a lower reaction temperature, such as 150 and 175°C (Ex. 9 and 10), lube products with RBOT time of >1000 minutes were obtained.

Table 2. Effect of Reaction Temperature on Lube Yields and Properties from 1-MN and 2-MN

Example No.	6	7	8	9	10	11	12
Feed, MN	1-MN	1-MN	1-MN	2-MN	2-MN	2-MN	2-MN
Olefin	C16	1-C16	C16	C16	C16	1-C16	C16
Mole Ratio MN/O	2/1	2/1	2/1	2/1	2/1	2/1	2/1
Catalyst Type	USY	USY	USY	USY	USY	USY	USY
Catalyst Wt%	5	5	5	5	5	5	5
Rxn Temp, °C	175	200	225	150	175	200	225
Rxn Time, Hrs	8	4	3	72	8	4	2
% Total Conv.	49.2	71.3	79.8	63.9	67.3	70.8	69.7
% 1-C16 Conv.	73.8	95.9	99.9	75.8	92.6	98.7	94.3
Product Selectivity							
Mono-C16-MN	98.6	94.1	99.2	98.1	100.0	98.0	99.0
di-C16-MN	1.4	2.8	0.8	1.9	0.0	1.2	1.0
Others	0.0	3.1	0.0	0.0	0.0	0.8	0.0

Product Properties							
Kv @ 100°C, cS	5.5	5.6	5.6	5.3	5.3	5.3	5.3
Kv @ 40°C, cS	37.8	41.0	40.6	35.4	36.4	36.2	37.2
VI	72	62	62	73	68	64	59
Pour Point, °C	-43	-46	-46	-45	-49	-48	-49
Bro-mine No.	0.48	0.5	0.28	0.19	0.14	0	0.1
Oxidative Stability							
RBOT, min	737	703	168	1111	1280	847	600
B10 Test at 163°C/40 hrs							
% Kv Increase	0	6.5	13.8	7.2	6.5	9.2	9.9
TAN Incr., mg KOH	0.4	1.6	2.05	0.5	0.49	1.2	1.63
Sludge	trace	nil	trace	trace	trace	trace	trace
wt% lead loss	12.67	7.2	14.396	7.0	6.59	8.1	9.0

[0062] The data in Table 3 demonstrates the effect of different olefins, different MN sources and different catalysts on lube yields and properties.

[0063] Examples 13 to 15 showed that 1-tetradecene, 1-hexadecene and 1-octadecene may be used as the alkylating reagent. By changing the olefin feeds, lube products of 4.6 to 6.1 cS were obtained. All of the products possessed very long RBOT times (from 744 minutes to 1000 minutes).

[0064] Examples 16 to 18 illustrate that different sources of methyl-naphthalenes or a mixture of naphthalene and methyl-naphthalenes can be used to produce high quality lube products. Suresol-187 used in Ex. 16 and 17 is a commercial product available from Koch Chemical Co. and contains 52% 2-MN and 45% 1-MN. Example 18 used a feed containing equal weight of naphthalene, 1-MN and 2-MN. Again, the products of examples 16 to 18 were produced in high yields and had long RBOT time.

[0065] Example 19 and 20 demonstrate that using a MCM-22 catalyst, instead of a USY catalyst, produced lube products with excellent RBOT time.

Table 3. Effect of Different olefins, different MN sources and different catalysts on lube yields and properties.

Example No.	Different Olefins			Different MN Source		Different Catalyst		
	13	14	15	16	17	18	19	20
Feed, MN	2-MN	2-MN	2-MN	Suresol-187	Suresol-187	N, 1-2-MN	1-MN	2-MN
Olefin	C14	1-C16	C18	1-C16	1-C13	C16	1-C16	1-C16
Mole Ratio MN/O	2/1	2.0/1	2/1	2.0/1	2.0/1	2/1	2.0/1	2.0/1
Catalyst Type	USY	USY	USY	USY	USY	USY	MCM22/Al ₂ O ₃	MCM22/Al ₂ O ₃
Catalyst Wt%	5	5	5	5	5	5	5	5
Rxn Temp, °C	200	200	200	200	200	200	200	200
Rxn Time, Hrs	4	18	4	4	5	4	18	18

% Total Conv.	76.0	77.9	80.5	71.5	68.6	90.5	59.3	75.1
% 1-C16 Conv.	99.4	97.7	99.5	98.7	99.7	90.8	89.3	98.1
Product Selectivity								
Mono-C16-MN	99.2	99.7	98.4	96.8	99.1	92.0	88.4	81.4
di-C16-MN	0.8	0.3	1.6	1.8	0.9	8.0	11.4	18.5
Others	0.0	0.0	0.0	1.4	0.0	0.0	0.2	0.1
Product Properties								
Kv@100°C, cS	4.6	5.3	6.1	5.5	4.7	5.3	6.7	6.5
Kv@40°C, cS	30.8	36.8	43.3	38.1	32.0	35.5	53.0	51.1
VI	29	64	81	66	33	73	71	64
Pour Point, °C	-46	-49	-26	-47	-48	-48	-45	-47
Bromine No.	0.08	0.03	0.12	0	0	0.21	0.62	0
Oxidative Stability								
RBOT, min	1000	744	817	216	170	191	121	525
B10 Test at 163°C/40 hrs								
%Kv Increase	8.6	10.2	9.7	20.5	21.7	24.4	7.3	5.8
TAN Incr., mg KOH	0.77	1.1	0.74	2.6	1.7	1.26	0.94	0.9
Sludge	trace	trace	trace	light	trace	trace	nil	trace
wt% lead loss	8.056	8.6	8.904	16.5	15.8	13.911	8.4	3.7

[0066] Table 4 compares the lube properties made from 1-MN or 2-MN versus a commercial mono-alkylated naphthalene lube available from Mobil Chemical Co.

(produced according to the method disclosed in U.S. Pat. No. 5,034,563). The data demonstrates that MN-based lube products have better oxidative stability as measured by the RBOT times.

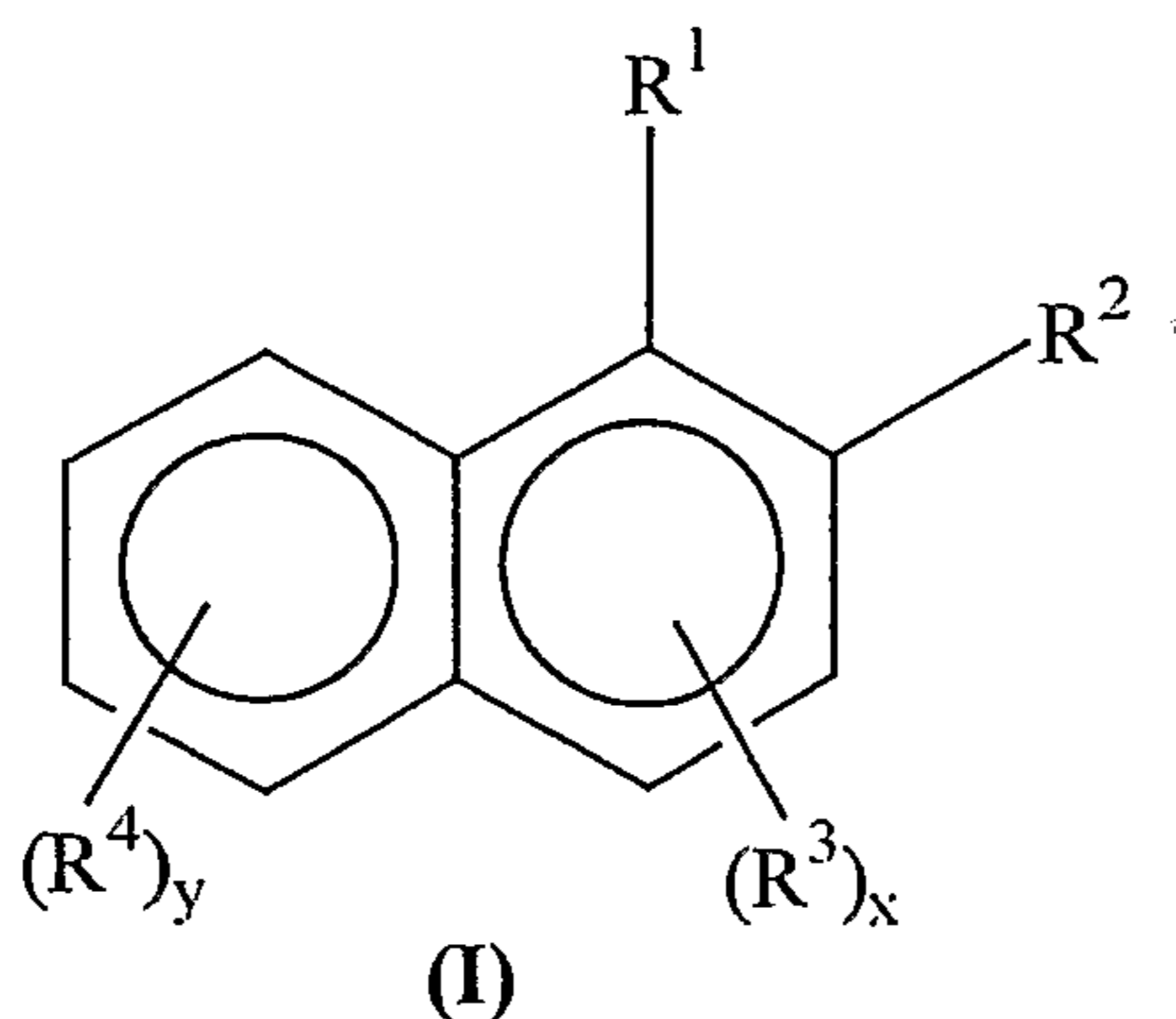
Table 4. Comparison of Lube properties Made from MN vs. from Naphthalene

Example No.	7	11	20	Alkyl Naphthalene From Mobil Chem
Feed, MN	1-MN	2-MN	2-MN	Naphthalene
Olefin	1-C16	1-C16	1-C16	1-C16
Product Properties				
Kv @100°C, cS	5.6	5.3	6.5	4.8
Kv @40°C, cS	41.0	36.2	51.1	27
VI	62	64	64	76
Pour Point, °C	-46	-48	-47	-43
Bromine No.	0.5	0	0	0.2
Oxidative Stability				
RBOT, min	703	847	525	150
Oxidative Stability				
% Kv Increase	6.5	9.2	5.8	7.6
TAN Incr., mg KOH	1.6	1.2	0.9	0.7
Sludge	nil	trace	trace	Trace
wt% lead loss	7.2	8.1	3.7	9.9

[0067] Although the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the scope and spirit of the present invention.

CLAIMS:

1. A method for improving the oxidative stability of a lubricant having an RBOT of \leq about 200 minutes comprising adding to said lubricant a base oil comprising a compound of formula (I):



wherein R^1 and R^2 are H, methyl, ethyl, propyl, or butyl;

R^3 and R^4 are an alkyl group having from about 6 to about 24 carbon atoms;

x is from 0 to about 2; and

y is from 0 to about 4;

with the proviso that at least one of R^1 and R^2 is other than H, and at least one of x and y is other than 0;

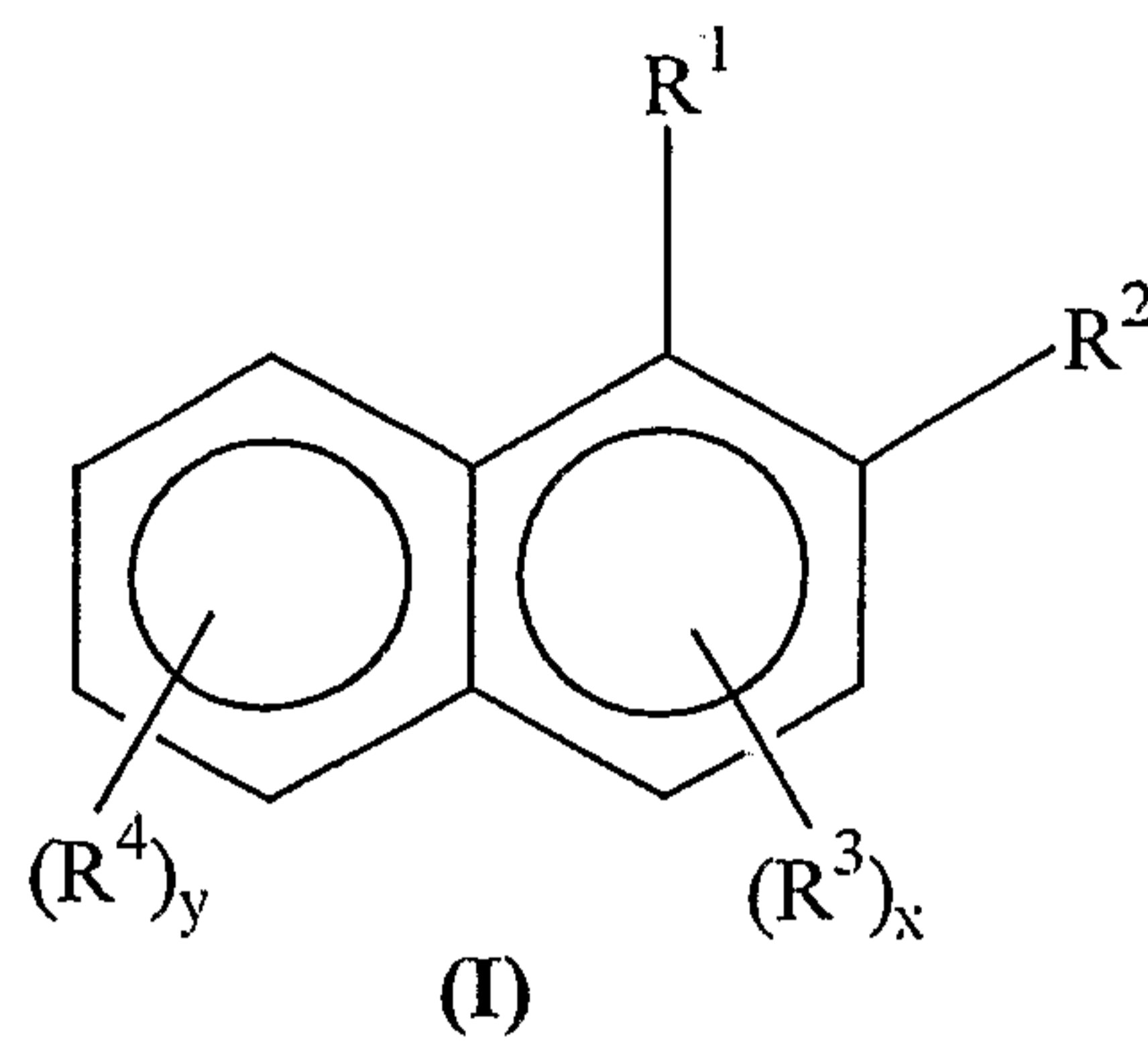
and wherein the base oil has a RBOT value of greater than about 200 minutes.

2. The method of claim 1, wherein said base oil comprises at least 20 wt% of a compound of formula (I) or mixtures thereof.

3. The method of claim 1, wherein said base oil comprises at least 50 wt% of a compound of formula (I) or mixtures thereof.

4. The method of claims 1 through 4, wherein said lubricant comprises at least 2 wt% of said base oil.
5. The method of claims 1 through 4, wherein R^1 is H and R^2 is methyl.
6. The method of claims 1 through 4, wherein R^2 is H and R^1 is methyl.
7. The method of claims 1 through 4, wherein the sum of x and y is one, R^1 is H and R^2 is methyl.
8. The method of claims 1 through 4, wherein the sum of x and y is one, R^1 is methyl and R^2 is H.
9. The method claims 1 through 4, wherein the sum of x and y is one.
10. The method of claims 1 through 4, wherein the sum of x and y is greater than 1.
11. The method of any of the preceding claims, wherein said base oil has an RBOT value of about 500 to about 1500 minutes.
12. A synthetic base oil comprising a mixture of monoalkylated and polyalkylated naphthalenes wherein the improvement comprises said synthetic base oil containing at least 20 wt% of an alkylated naphthalene selected from the group consisting of a compound or mixture of compounds of the following formula (I):

- 30 -



wherein R¹ and R² are H, methyl, ethyl, n-propyl, n-butyl, or t-butyl;
R³ and R⁴ are an alkyl group having from about 6 to about 24 carbon atoms;
x is from 0 to about 2; and
y is from 0 to about 4;

with the proviso that at least one of R¹ and R² is other than H, and at least one of x and y is other than 0.

13. The synthetic base oil of 12 wherein at least one of R¹ and R² is hydrogen.

14. The synthetic base oil of claim 13 wherein at least one of R¹ and R² is methyl.