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A METHOD FOR REDUCING DEPOSIT FORMATION IN LUBRICANT COMPOSITIONS

FIELD OF THE INVENTION

[001] The present invention relates to a method for reducing deposit formation in lubricant compositions. More particularly, the present invention relates to a synergistic combination of antioxidants that when added to lubricants reduce deposit formation in the lubricant.

BACKGROUND OF THE INVENTION

[002] Modern lubricating compositions contain a major amount of an oil of lubricating viscosity and a minor amount of a plethora of performance enhancing additives such as antioxidants, extreme pressure agents, pour point depressants, viscosity modifiers, and metal passivators to mention just a few.

[003] Notwithstanding the development of numerous lubricating compositions to meet specific equipment needs, current trends in equipment design require lubricants to function at higher temperatures and for longer periods of time. Higher temperatures can lead to increased oxidation of the lubricating composition, thus stimulating the search for increasingly improved antioxidants.

[004] In Patent Publication U. S. 2003/0096713 A1, there is disclosed a lubricating composition with improved oxidation resistance. The lubricant contains at least 2 wt% of one or more antioxidants and a dispersant or detergent. The antioxidants are selected from the group consisting of amine antioxidants, dithiophosphoric esters, phenol antioxidants, dithiocarbonates, aromatic phosphites, and sulfurized fatty oils and olefins.

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[005] In Patent Publication U. S. 2003/0171227 A1 there is disclosed stabilizing compositions for lubricants that contain at least one diphenylamine and a neutral organophosphate or phosphite. Blends of the aminic antioxidant with certain phenolic antioxidants also are disclosed. The stabilizing compositions are prepared by heating the antioxidants and phosphite for 0.2 to 6 hours at 40°C to 150°C.

[006] U. S. Patent 6,172,014 B1 discloses a method for reducing compressor gas leakage by using a lubricant having at least one phosphite antioxidant and at least one second antioxidant. The second antioxidant is selected from the group consisting of amine compounds, phenolic compounds and mixtures thereof.

[007] Although one might believe that improving the oxidation stability of a lubricating composition should also result in reducing deposit formation, experience has shown such is not always the case. Thus, there remains a need for lubricant additives that will reduce deposit formation in lubricating compositions.

SUMMARY OF THE INVENTION

[008] Very simply, the present invention is based, in part, on the surprising and unexpected discovery that reduced deposit formation in Group II, III and IV lubricating base oils can be achieved through the use of synergistic mixtures of diphenylamines or phenyl- α -naphthylamines with triaryl phosphites.

[009] Thus, in one aspect of the invention, a method is provided for reducing deposit formation in lubricant base oils selected from the group consisting of Group II, III, IV and mixtures thereof by adding to the base oils an effective amount of a mixture of diphenylamines or phenyl- α -naphthylamines with triaryl phosphites.

[010] In another aspect, there is provided a lubricating composition comprising a major amount of an oil of lubricating viscosity selected from the group consisting

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of Group II, III, IV and mixtures thereof and a minor but effective amount of a mixture of diphenylamines or phenyl- α -naphthylamines with triaryl phosphites.

[011] The lubricating base oil suitable in the practice of the invention is any natural or synthetic oil selected from the group consisting of Groups II, III, IV and mixtures thereof. Particularly preferred are Group III base oils and especially GTL Group III base oils.

DETAILED DESCRIPTION OF THE INVENTION

[012] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds, and/or elements as feedstocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons, for example waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feedstocks. GTL base stock(s) include oils boiling in the lube oil boiling range separated/fractionated from GTL materials such as by, for example, distillation or thermal diffusion, and subsequently subjected to well-known catalytic or solvent dewaxing processes to produce lube oils of reduced/low pour point; wax isomerates, comprising, for example, hydroisomerized or isodewaxed synthesized hydrocarbons; hydroisomerized or isodewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates); preferably hydroisomerized or isodewaxed F-T hydrocarbons or hydroisomerized or isodewaxed F-T waxes, hydroisomerized or isodewaxed synthesized waxes, or mixtures thereof.

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[013] GTL base stock(s) derived from GTL materials, especially, hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax derived base stock(s) are characterized typically as having kinematic viscosities at 100°C of from about 2 mm²/s to about 50 mm²/s, preferably from about 3 mm²/s to about 50 mm²/s, more preferably from about 3.5 mm²/s to about 30 mm²/s, as exemplified by a GTL base stock derived by the isodewaxing of F-T wax, which has a kinematic viscosity of about 4 mm²/s at 100°C and a viscosity index of about 130 or greater. Reference herein to Kinematic viscosity refers to a measurement made by ASTM method D445.

[014] GTL base stocks and base oils derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s), such as wax hydroisomerates/isodewaxates, which are base stock components of this invention are further characterized typically as having pour points of about -5°C or lower, preferably about -10°C or lower, more preferably about -15°C or lower, still more preferably about -20°C or lower, and under some conditions may have advantageous pour points of about -25°C or lower, with useful pour points of about -30°C to about -40°C or lower. If necessary, a separate dewaxing step may be practiced to achieve the desired pour point. References herein to pour point refer to measurement made by ASTM D97 and similar automated versions.

[015] The GTL base stock(s) derived from GTL materials, especially hydroisomerized/isodewaxed F-T material derived base stock(s), and other hydroisomerized/isodewaxed wax-derived base stock(s) which are base stock components of this invention are also characterized typically as having viscosity indices of 80 or greater, preferably 100 or greater, and more preferably 120 or greater. Additionally, in certain particular instances, viscosity index of these base stocks may be preferably 130 or greater, more preferably 135 or greater, and even

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more preferably 140 or greater. For example, GTL base stock(s) that derive from GTL materials preferably F-T materials especially F-T wax generally have a viscosity index of 130 or greater. References herein to viscosity index refer to ASTM method D2270.

[016] In addition, the GTL base stock(s) are typically highly paraffinic (>90% saturates), and may contain mixtures of monocycloparaffins and multicycloparaffins in combination with non-cyclic isoparaffins. The ratio of the naphthenic (i.e., cycloparaffin) content in such combinations varies with the catalyst and temperature used. Further, GTL base stocks and base oils typically have very low sulfur and nitrogen content, generally containing less than about 10 ppm, and more typically less than about 5 ppm of each of these elements. The sulfur and nitrogen content of GTL base stock and base oil obtained by the hydroisomerization/isodewaxing of F-T material, especially F-T wax is essentially nil.

[017] In a preferred embodiment, the GTL base stock(s) comprises paraffinic materials that consist predominantly of non-cyclic isoparaffins and only minor amounts of cycloparaffins. These GTL base stock(s) typically comprise paraffinic materials that consist of greater than 60 wt% non-cyclic isoparaffins, preferably greater than 80 wt% non-cyclic isoparaffins, more preferably greater than 85 wt% non-cyclic isoparaffins, and most preferably greater than 90 wt% non-cyclic isoparaffins.

[018] Useful compositions of GTL base stock(s), hydroisomerized or isodewaxed F-T material derived base stock(s), and wax-derived hydroisomerized/isodewaxed base stock(s), such as wax isomerates/isodewaxes, are recited in U.S. Patents 6,080,301; 6,090,989, and 6,165,949 for example.

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[019] Isomerate/isodewaxate base stock(s) derived from waxy feeds which are also suitable for use in this invention, are paraffinic fluids of lubricating viscosity derived from hydroisomerized or isodewaxed waxy feedstocks of mineral oil, non-mineral oil, non-petroleum, or natural source origin, e.g., feedstocks such as one or more of gas oils, slack wax, waxy fuels hydrocracker bottoms, hydrocarbon raffinates, natural waxes, hydrocrackates, thermal crackates, foots oil, wax from coal liquefaction or from shale oil, or other suitable mineral oil, non-mineral oil, non-petroleum, or natural source derived waxy materials, linear or branched hydrocarbyl compounds with carbon number of about 20 or greater, preferably about 30 or greater, and mixtures of such isomerate/isodewaxate base stocks and base oils.

[020] As used herein, the following terms have the indicated meanings:

- (a) "wax" - hydrocarbonaceous material having a high pour point, typically existing as a solid at room temperature, at about 15°C to 25°C, and consisting predominantly of paraffinic materials;
- (b) "paraffinic" material: any saturated hydrocarbons, such as alkanes. Paraffinic materials may include linear alkanes, branched alkanes (iso-paraffins), cycloalkanes (cycloparaffins; mono-ring and/or multi-ring), and branched cycloalkanes;
- (c) "hydroprocessing": a refining process in which a feedstock is heated with hydrogen at high temperature and under pressure, commonly in the presence of a catalyst, to remove and/or convert less desirable components and to produce an improved product;
- (d) "hydrotreating": a catalytic hydrogenation process that converts sulfur- and/or nitrogen-containing hydrocarbons into hydrocarbon products with reduced sulfur and/or nitrogen content, and which generates hydrogen sulfide and/or ammonia (respectively) as byproducts; similarly, oxygen containing hydrocarbons can also be reduced to hydrocarbons and water;

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- (e) "hydrodewaxing" (or catalytic dewaxing): a catalytic process in which normal paraffins (wax) and/or waxy hydrocarbons are converted by cracking/fragmentation into lower molecular weight species, and by rearrangement/isomerization into more branched iso-paraffins;
- (f) "hydroisomerization" (or isomeriation or isodewaxing): a catalytic process in which normal paraffins (wax) and/or slightly branched iso-paraffins are converted by rearrangement/isomerization into more branched iso-paraffins;
- (g) "hydrocracking": a catalytic process in which hydrogenation accompanies the cracking/fragmentation of hydrocarbons, e.g., converting heavier hydrocarbons into lighter hydrocarbons, or converting aromatics and/or cycloparaffins (naphthenes) into non-cyclic branched paraffins.

[021] As previously indicated, isomerase/isodewaxate base stock(s) suitable for use as the necessary components in the present invention, can be derived from waxy feeds such as slack wax(es).

[022] Slack wax is the wax recovered from petroleum oils by solvent or autorefrigerative dewaxing. Solvent dewaxing employs chilled solvent such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/MIBK, mixtures of MEK and toluene, while autorefrigerative dewaxing employs pressurized, liquefied low boiling hydrocarbons such as propane or butane.

[023] Slack waxes, being secured from petroleum oils, may contain sulfur and nitrogen containing compounds. Such heteroatom compounds must be removed by hydrotreating (and not hydrocracking), as for example by hydrodesulfurization

(HDS) and hydrodenitrogenation (HDN) so as to avoid subsequent poisoning/deactivation of the hydroisomerization catalyst.

[024] In a preferred embodiment, the GTL material, from which the GTL base stock(s) is/are derived is a F-T material (i.e., hydrocarbons, waxy hydrocarbons, wax). A slurry F-T synthesis process may be beneficially used for synthesizing the feed from CO and hydrogen and particularly one employing a F-T catalyst comprising a catalytic cobalt component to provide a high alpha for producing the more desirable higher molecular weight paraffins. This process is also well known to those skilled in the art.

[025] In a F-T synthesis process, a synthesis gas comprising a mixture of H₂ and CO is catalytically converted into hydrocarbons and preferably liquid hydrocarbons. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but which is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. As is well known, F-T synthesis processes include processes in which the catalyst is in the form of a fixed bed, a fluidized bed or as a slurry of catalyst particles in a hydrocarbon slurry liquid. The stoichiometric mole ratio for a F-T synthesis reaction is 2.0, but there are many reasons for using other than a stoichiometric ratio as those skilled in the art know. In a cobalt slurry hydrocarbon synthesis process the feed mole ratio of the H₂ to CO is typically about 2.1/1. The synthesis gas comprising a mixture of H₂ and CO is bubbled up into the bottom of the slurry and reacts in the presence of the particulate F-T synthesis catalyst in the slurry liquid at conditions effective to form hydrocarbons, a portion of which are liquid at the reaction conditions and which comprise the hydrocarbon slurry liquid. The synthesized hydrocarbon liquid is separated from the catalyst particles as filtrate by means such as filtration, although other separation means such as centrifugation can be used. Some of the synthesized hydrocarbons pass out the top of the hydrocarbon synthesis reactor as

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vapor, along with unreacted synthesis gas and other gaseous reaction products. Some of these overhead hydrocarbon vapors are typically condensed to liquid and combined with the hydrocarbon liquid filtrate. Thus, the initial boiling point of the filtrate may vary depending on whether or not some of the condensed hydrocarbon vapors have been combined with it. Slurry hydrocarbon synthesis process conditions vary somewhat depending on the catalyst and desired products. Typical conditions effective to form hydrocarbons comprising mostly C_{5+} paraffins, (e.g., C_{5+} - C_{200}) and preferably C_{10+} paraffins, in a slurry hydrocarbon synthesis process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from about 320-850°F, 80-600 psi and 100-40,000 V/hr/V, expressed as standard volumes of the gaseous CO and H_2 mixture (0°C, 1 atm) per hour per volume of catalyst, respectively. It is preferred that the hydrocarbon synthesis reaction be conducted under conditions in which limited or no water gas shift reaction occurs and more preferably with no water gas shift reaction occurring during the hydrocarbon synthesis. It is also preferred to conduct the reaction under conditions to achieve an alpha of at least 0.85, preferably at least 0.9 and more preferably at least 0.92, so as to synthesize more of the more desirable higher molecular weight hydrocarbons. This has been achieved in a slurry process using a catalyst containing a catalytic cobalt component. Those skilled in the art know that by alpha is meant the Schultz-Flory kinetic alpha. While suitable F-T reaction types of catalyst comprise, for example, one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re, it is preferred that the catalyst comprise a cobalt catalytic component. In one embodiment the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts comprise titania, particularly. Useful catalysts and their preparation are known and

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illustrative, but nonlimiting examples may be found, for example, in U.S. Patents 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674.

[026] As set forth above, the waxy feed from which the base stock(s) is/are derived is wax or waxy feed from mineral oil, non-mineral oil, non-petroleum, or other natural source, especially slack wax, or GTL material, preferably F-T material, referred to as F-T wax. F-T wax preferably has an initial boiling point in the range of from 650-750°F and preferably continuously boils up to an end point of at least 1050°F. A narrower cut waxy feed may also be used during the hydroisomerization. A portion of the n-paraffin waxy feed is converted to lower boiling isoparaffinic material. Hence, there must be sufficient heavy n-paraffin material to yield an isoparaffin containing isomerate boiling in the lube oil range. If catalytic dewaxing is also practiced after isomerization/isodewaxing, some of the isomerate/isodewaxate will also be hydrocracked to lower boiling material during the conventional catalytic dewaxing. Hence, it is preferred that the end boiling point of the waxy feed be above 1050°F (1050°F+).

[027] The waxy feed preferably comprises the entire 650-750°F+ fraction formed by the hydrocarbon synthesis process, with the initial cut point between 650°F and 750°F being determined by the practitioner and the end point, preferably above 1050°F, determined by the catalyst and process variables employed by the practitioner for the synthesis. Waxy feeds may be processed as the entire fraction or as subsets of the entire fraction prepared by distillation or other separation techniques. The waxy feed also typically comprises more than 90%, generally more than 95% and preferably more than 98 wt% paraffinic hydrocarbons, most of which are normal paraffins. It has negligible amounts of sulfur and nitrogen compounds (e.g., less than 1 wppm of each), with less than 2,000 wppm, preferably less than 1,000 wppm and more preferably less than 500 wppm of oxygen, in the form of oxygenates. Waxy feeds having these properties and useful in the process

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of the invention have been made using a slurry F-T process with a catalyst having a catalytic cobalt component, as previously indicated.

[028] The process of making the lubricant oil base stocks from waxy stocks, e.g., slack wax or F-T wax, may be characterized as a hydrodewaxing process. If slack waxes are used as the feed, they may need to be subjected to a preliminary hydrotreating step under conditions already well known to those skilled in the art to reduce (to levels that would effectively avoid catalyst poisoning or deactivation) or to remove sulfur- and nitrogen-containing compounds which would otherwise deactivate the hydroisomerization/ hydrodewaxing catalyst used in subsequent steps. If F-T waxes are used, such preliminary treatment is not required because, as indicated above, such waxes have only trace amounts (less than about 10 ppm, or more typically less than about 5 ppm to nil) of sulfur or nitrogen compound content. However, some hydrodewaxing catalyst fed F-T waxes may benefit from removal of oxygenates while others may benefit from oxygenates treatment. The hydrodewaxing process may be conducted over a combination of catalysts, or over a single catalyst. Conversion temperatures range from about 150°C to about 500°C at pressures ranging from about 500 to 20,000 kPa. This process may be operated in the presence of hydrogen, and hydrogen partial pressures range from about 600 to 6000 kPa. The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) typically range from about 10 to 3500 n.l.l.⁻¹ (56 to 19,660 SCF/bbl) and the space velocity of the feedstock typically ranges from about 0.1 to 20 LHSV, preferably 0.1 to 10 LHSV.

[029] Following any needed hydridenitrogenation or hydrodesulfurization, the hydroprocessing used for the production of base stocks from such waxy feeds may use an amorphous hydrocracking/hydroisomerization catalyst, such as a lube hydrocracking (LHDC) catalysts, for example catalysts containing Co, Mo, Ni, W,

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Mo, etc., on oxide supports, e.g., alumina, silica, silica/alumina, or a crystalline hydrocracking/hydroisomerization catalyst, preferably a zeolitic catalyst.

[030] Other isomerization catalysts and processes for hydrocracking/hydroisomerized/isodewaxing GTL materials and/or waxy materials to base stock or base oil are described, for example, in U.S. Patents 2,817,693; 4,900,407; 4,937,399; 4,975,177; 4,921,594; 5,059,299; 5,200,382; 5,516,740; 5,182,248; 5,290,426; 5,580,442; 5,976,351; 5,935,417; 5,885,438; 5,965,475; 6,190,532; 6,375,830; 6,332,974; 6,103,099; 6,025,305; 6,080,301; 6,096,940; 6,620,312; 6,676,827; 6,383,366; 6,475,960; 5,059,299; 5,977,425; 5,935,416; 4,923,588; 5,158,671; and 4,897,178; EP 0324528 (B1), EP 0532116 (B1), EP 0532118 (B1), EP 0537815 (B1), EP 0583836 (B2), EP 0666894 (B2), EP 0668342 (B1), EP 0776959 (A3), WO 97/031693 (A1), WO 02/064710 (A2), WO 02/064711 (A1), WO 02/070627 (A2), WO 02/070629 (A1), WO 03/033320 (A1) as well as in British Patents 1,429,494; 1,350,257; 1,440,230; 1,390,359; WO 99/45085 and WO 99/20720. Particularly favorable processes are described in European Patent Applications 464546 and 464547. Processes using F-T wax feeds are described in U.S. Patents 4,594,172; 4,943,672; 6,046,940; 6,475,960; 6,103,099; 6,332,974; and 6,375,830.

[031] Hydrocarbon conversion catalysts useful in the conversion of the n-paraffin waxy feedstocks disclosed herein to form the isoparaffinic hydrocarbon base oil are zeolite catalysts, such as ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-12, ZSM-38, ZSM-48, offretite, ferrierite, zeolite beta, zeolite theta, zeolite alpha, as disclosed in USP 4,906,350. These catalysts are used in combination with Group VIII metals, in particular palladium or platinum. The Group VIII metals may be incorporated into the zeolite catalysts by conventional techniques, such as ion exchange.

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[032] In one embodiment, conversion of the waxy feedstock may be conducted over a combination of Pt/zeolite beta and Pt/ZSM-23 catalysts in the presence of hydrogen. In another embodiment, the process of producing the lubricant oil base stocks comprises hydroisomerization and dewaxing over a single catalyst, such as Pt/ZSM-35. In yet another embodiment, the way feed can be fed over Group VIII metal loaded ZSM-48, preferably Group VIII noble metal loaded ZSM-48, more preferably Pt/ZSM-48 in either one stage or two stages. In any case, useful hydrocarbon base oil products may be obtained. Catalyst ZSM-48 is described in USP 5,075,269, the disclosure of which is incorporated herein by reference in its entirety. The use of the Group VIII metal loaded ZSM-48 family of catalysts in the isodewaxing of the waxy feedstock eliminates the need for any subsequent, separate dewaxing step, and is preferred.

[033] A dewaxing step, when needed, may be accomplished using either well known solvent or catalytic dewaxing processes and either the entire hydroisomerate or the 650-750°F+ fraction may be dewaxed, depending on the intended use of the 650-750°F- material present, if it has not been separated from the higher boiling material prior to the dewaxing. In solvent dewaxing, the hydroisomerate may be contacted with chilled solvents such as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK/MIBK, or mixtures of MEK/toluene and the like, and further chilled to precipitate out the higher pour point material as a waxy solid which is then separated from the solvent-containing lube oil fraction which is the raffinate. The raffinate is typically further chilled in scraped surface chillers to remove more wax solids. Low molecular weight hydrocarbons, such as propane, are also used for dewaxing, in which the hydroisomerate is mixed with liquid propane, a least a portion of which is flashed off to chill down the hydroisomerate to precipitate out the wax. The wax is separated from the raffinate by filtration, membrane separation or centrifugation. The solvent is then stripped out of the raffinate, which is then fractionated to

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produce the preferred base stocks useful in the present invention. Also well known is catalytic dewaxing, in which the hydroisomerate is reacted with hydrogen in the presence of a suitable dewaxing catalyst at conditions effective to lower the pour point of the hydroisomerate. Catalytic dewaxing also converts a portion of the hydroisomerate to lower boiling materials, in the boiling range, for example, 650-750°F-, which are separated from the heavier 650-750°F+ base stock fraction and the base stock fraction fractionated into two or more base stocks. Separation of the lower boiling material may be accomplished either prior to or during fraction of the 650-750°F+ material into the desired base stocks.

[034] Any dewaxing catalyst which will reduce the pour point of the hydroisomerate and preferably those which provide a large yield of lube oil base stock from the hydroisomerate may be used. These include shape selective molecular sieves which, when combined with at least one catalytic metal component, have been demonstrated as useful for dewaxing petroleum oil fractions and include, for example, ferrierite, mordenite, ZSM-5, ZSM-11, ZSM-23, ZSM-35, ZSM-22 also known as theta one or TON, and the silicoaluminophosphates known as SAPO's. A dewaxing catalyst which has been found to be unexpectedly particularly effective comprises a noble metal, preferably Pt, composited with H-mordenite. The dewaxing may be accomplished with the catalyst in a fixed, fluid or slurry bed. Typical dewaxing conditions include a temperature in the range of from about 400-600°F, a pressure of 500-900 psig, H₂ treat rate of 1500-3500 SCF/B for flow-through reactors and LHSV of 0.1-10, preferably 0.2-2.0. The dewaxing is typically conducted to convert no more than 40 wt% and preferably no more than 30 wt% of the hydroisomerate having an initial boiling point in the range of 650-750°F to material boiling below its initial boiling point.

[035] GTL base stock(s), isomerized or isodewaxed wax-derived base stock(s), have a beneficial kinematic viscosity advantage over conventional Group II and

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Group III base stocks and base oils, and so may be very advantageously used with the instant invention. Such GTL base stocks and base oils can have significantly higher kinematic viscosities, up to about 20-50 mm²/s at 100°C, whereas by comparison commercial Group II base oils can have kinematic viscosities, up to about 15 mm²/s at 100°C, and commercial Group III base oils can have kinematic viscosities, up to about 10 mm²/s at 100°C. The higher kinematic viscosity range of GTL base stocks and base oils, compared to the more limited kinematic viscosity range of Group II and Group III base stocks and base oils, in combination with the instant invention can provide additional beneficial advantages in formulating lubricant compositions.

[036] In the present invention the one or more isomerase/isodewaxate base stock(s), the GTL base stock(s), or mixtures thereof, preferably GTL base stock(s) can constitute all or part of the base oil.

[037] The preferred base stock(s) derived from GTL materials and/or from waxy feeds is/are characterized as having predominantly paraffinic compositions and are further characterized as having high saturates levels, low-to-nil sulfur, low-to-nil nitrogen, low-to-nil aromatics, and are essentially water-white in color.

[038] The one or more isomerase/isodewaxate base stock(s), GTL base stock(s), or mixtures thereof, preferably GTL base stock(s) can constitute from 5 to 100%, preferably 40 to 100%, more preferably 70 to 100% by weight of the total of the base oil, the amount employed being left to the practitioner in response to the requirements of the finished lubricant.

[039] In addition to the one or more hydroisomerized/isodewaxate base stock(s), GTL base stock(s), or mixtures thereof, preferably GTL base stock(s) which is/are an essential, necessary component to achieve the unexpected improvement in both

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the initial and long term metal corrosion resistance, the base oil can contain natural oils as well as other synthetic oils and non-conventional oils and mixtures thereof.

[040] Natural oil, other synthetic oils, and unconventional oils and mixtures thereof can be used unrefined, refined, or rerefined (the latter is also known as reclaimed or reprocessed oil). Unrefined oils are those obtained directly from a natural, synthetic or unconventional source and used without further purification. These include for example shale oil obtained directly from retorting operations, oils derived from coal, petroleum oil obtained directly from primary distillation, and ester oil obtained directly from an esterification process. Refined oils are similar to the oils discussed for unrefined oils except refined oils are subjected to one or more purification or transformation steps to improve at least one lubricating oil property. One skilled in the art is familiar with many purification or transformation processes. These processes include, for example, solvent extraction, secondary distillation, acid extraction, base extraction, filtration, percolation, hydrogenation, hydrorefining, and hydrofinishing. Rerefined oils are obtained by processes analogous to refined oils, but use an oil that has been previously used.

[041] Groups I, II, III, IV and V are broad categories of base oil stocks developed and defined by the American Petroleum Institute (API Publication 1509; [www. API . org](http://www.API.org)) to create guidelines for lubricant base oils. Group I base stocks generally have a viscosity index of between about 80 to 120 and contain greater than about 0.03% sulfur and less than about 90% saturates. Group II base stocks generally have a viscosity index of between about 80 to 120, and contain less than or equal to about 0.03% sulfur and greater than or equal to about 90% saturates. Group III stock generally has a viscosity index greater than about 120 and contains less than or equal to about 0.03% sulfur and greater than about 90% saturates. Group IV includes polyalphaolefins (PAO). Group V base stocks include base

stocks not included in Groups I-IV. Table A summarizes properties of each of these five groups.

TABLE A: Base Stock Properties

	Saturates	Sulfur	Viscosity Index
Group I	< 90% and/or	> 0.03% and	≥ 80 and < 120
Group II	$\geq 90\%$ and	$\leq 0.03\%$ and	≥ 80 and < 120
Group III	$\geq 90\%$ and	$\leq 0.03\%$ and	≥ 120
Group IV	Polyalphaolefins (PAO)		
Group V	All other base oil stocks not included in Groups I, II, III, or IV		

[042] Natural oils include animal oils, vegetable oils (castor oil and lard oil, for example), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful in the present invention. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrotreated, or solvent extracted.

[043] Synthetic oils include hydrocarbon oils as well as non hydrocarbon oils. Synthetic oils can be derived from processes such as chemical combination (for example, polymerization, oligomerization, condensation, alkylation, acylation, etc.), where materials consisting of smaller, simpler molecular species are built up (i.e., synthesized) into materials consisting of larger, more complex molecular species. Synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers, for example). Polyalphaolefin (PAO) oil base stock is a commonly used synthetic

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hydrocarbon oil. By way of example, PAO's derived from C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof may be utilized. See U.S. Patents 4,956,122; 4,827,064; and 4,827,073.

[044] The number average molecular weights of the PAO's, which are known materials and generally available on a major commercial scale from suppliers such as ExxonMobil Chemical Company, Chevron, BP-Amoco, and others, typically vary from about 250 to about 3000, or higher, and PAO's may be made in viscosities up to about 100 mm²/s (100°C), or higher. In addition, higher viscosity PAO's are commercially available, and may be made in viscosities up to about 3000 mm²/s (100°C), or higher. The PAO's are typically comprised of relatively low molecular weight hydrogenated polymers or oligomers of alphaolefins which include, but are not limited to, about C₂ to about C₃₂ alphaolefins with about C₈ to about C₁₆ alphaolefins, such as 1-octene, 1-decene, 1-dodecene and the like, being preferred. The preferred polyalphaolefins are poly-1-octene, poly-1-decene and poly-1-dodecene and mixtures thereof and mixed olefin-derived polyolefins. However, the dimers of higher olefins in the range of about C₁₄ to C₁₈ may be used to provide low viscosity base stocks of acceptably low volatility. Depending on the viscosity grade and the starting oligomer, the PAO's may be predominantly trimers and tetramers of the starting olefins, with minor amounts of the higher oligomers, having a viscosity range of about 1.5 to 12 mm²/s.

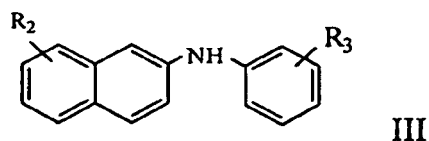
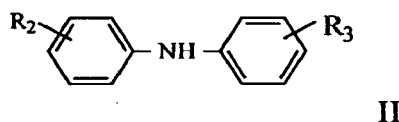
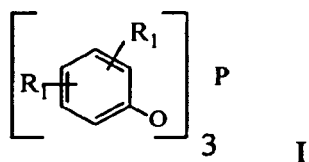
[045] PAO fluids may be conveniently made by the polymerization of an alphaolefin in the presence of a polymerization catalyst such as the Friedel-Crafts catalysts including, for example, aluminum trichloride, boron trifluoride or complexes of boron trifluoride with water, alcohols such as ethanol, propanol or butanol, carboxylic acids or esters such as ethyl acetate or ethyl propionate. For example the methods disclosed by USP 4,149,178 or USP 3,382,291 may be conveniently used herein. Other descriptions of PAO synthesis are found in the

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following U.S. Patents 3,742,082; 3,769,363; 3,876,720; 4,239,930; 4,367,352; 4,413,156; 4,434,408; 4,910,355; 4,956,122; and 5,068,487. The dimers of the C₁₄ to C₁₈ olefins are described in USP 4,218,330.

[046] Other useful synthetic lubricating base stock oils such as silicon-based oil or esters of phosphorus containing acids may also be utilized. For examples of other synthetic lubricating base stocks are the seminal work "Synthetic Lubricants", Gunderson and Hart, Reinhold Publ. Corp., NY 1962.

[047] In the practice of the invention, the deposit reducing additive comprises a mixture of triaryl phosphites represented by Formula I with diphenylamines or phenyl- α -naphthylamines represented by Formula II and III respectively.



wherein R₁ is H or a hydrocarbyl group having from 1 to about 8 carbon atoms and R₂ is H or a hydrocarbyl group of from 1 to about 12 carbon atoms and R₃ is a hydrocarbyl group of from 1 to 12 carbon atoms or NHR₄ where R₄ is a hydrocarbyl group of from 1 to about 12 carbon atoms. Preferably R₁ is tert-butyl, R₂ is H and R₃ is octyl

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[048] In the practice of the invention, the weight ratio of the diphenylamine or phenyl- α -naphthylamine to alkylated triaryl phosphite used will generally be in the range of from about 5:1 to about 1: 5 and preferably about 2: 1 to about 1: 2.

[049] Typically, the deposit reducing additive will be added to the lubricating base oil in the range of from about 0.1 wt% to about 2.0 wt%, and preferably from about 0.4 wt% to about 1.0 wt%, based on the total weight of the composition.

[050] A lubricating oil composition of the invention comprises the major amount of an oil of lubricating viscosity selected from the group consisting of Group II, III, IV and mixtures thereof and a minor amount of the deposit-reducing additive mixture of the invention.

[051] The lubricating composition may be formulated with one or more additional additives such as pour point depressants, rust inhibitors, metal passivators, VI improvers, extreme pressure additives, demulsifiers, dispersants, solubilizers, antifoamants and dyes.

EXAMPLES

[052] In the formulations presented in Tables 2 and 3, Irganox L06 is octylphenyl- α -naphthylamine sold by Ciba-Geigy and Irgafos 168 is alkylated triaryl phosphite also sold by Ciba-Geigy.

[053] The formulated oils were subjected to the performance tests listed in the Tables along with the results of those tests. In the Tables, RPVOT refers to the Rotary Pressure Vessel Oxidation Test (ASTM D2272). The Hot Tube Test is a test designed to simulate actual engine conditions. A rating of 10 in the test indicates heavy deposits, while a rating of 0 indicates no discernable deposit.

EXAMPLE 1 AND COMPARATIVE EXAMPLES 1 TO 4

[054] A series of oils was prepared having the composition and properties shown in Table 2:

Table 2

Component, wt%	Comparative 1	Example 1	Comparative 2	Comparative 3	Comparative 4
Irganox 106	0.3	0.3	0.6		0.3
Irgafos 168	0.3	0.3		0.6	
Rust inhibitor	0.1	0.1	0.1	0.1	0.1
Triphenyl phosphate					0.3
Metal deactivator	0.01	0.01	0.01	0.01	0.01
Defoamant	0.1	0.1	0.1	0.1	0.1
Group I oil	99.19				
Group II oil (1)		99.19	99.19	99.19	99.19
Properties					
Hot tube test, 250°C	7/6	2/2	9/10	10/10	
Hot tube test, 270°C	9	9	9.5	9	9
RPVOT, mins	586	2520	2067	221	1280

(1) = JURONG 150

[055] This data illustrates the synergistic and deposit reducing effect of the additive mixture of the invention. The data also illustrates that the oxidation stability of an oil is not indicative of its deposit forming tendency. Note that Comparative Oil 2 had a relatively high oxidation stability test result but also had a very high deposit test result.

EXAMPLES 2 TO 5 AND COMPARATIVE EXAMPLES 5 TO 8

[056] Another series of oils was prepared. Their compositions and properties are given in Table 3.

Table 3

Component, wt%	Example 2	Example 3	Example 4	Comparative 5	Comparative 6	Comparative 7	Comparative 8
Irganox 106	0.3	0.3	0.3	0.3	0.3	0.6	
Irgafos 168	0.3	0.3	0.3				0.6
Rust inhibitor	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Triphenylphosphate				0.3	0.3		
Metal deactivator	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Defoamant	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Group III (2)	99.19						
Group III (GTL)		99.19			99.19	99.19	99.19
Group III (3)			99.19	99.19			
Properties							
Hot tube test, 250°C	2.5	2	-	-	-	-	-
Hot tube test, 270°C	6.5	4	9	9	3/3	3	4
RBOT, mins	2870	2506	2067	1672	2792	2830	548

(2) = VISOM

(3) = YUBASE

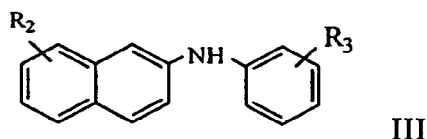
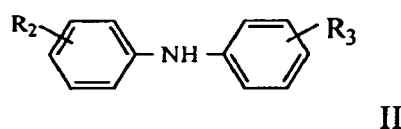
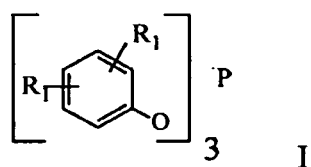
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[057] As can be seen, the additive mixture of the invention has a beneficial effect on the deposit forming tendencies of the Group III and IV lubricant compositions. The data also shows that the mixture of additives of the invention results in significantly less deposits formed when used in a GTL base oil as compared to other Group III base oils.

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CLAIMS:

1. A method for reducing deposit formation in a lubricating base oil selected from the group consisting of Group II, III, IV oils and mixtures thereof comprising adding to the oil an effective amount of a mixture of triaryl phosphites represented by Formula I with diphenylamines or phenyl- α -naphthylamines represented by Formula II and III respectively,



wherein R_1 is H or a hydrocarbyl group having from 1 to about 8 carbon atoms and R_2 is H or a hydrocarbyl group of from 1 to about 12 carbon atoms and R_3 is a hydrocarbyl group of from 1 to 12 carbon atoms or NHR_4 where R_4 is a hydrocarbyl group of from 1 to about 12 carbon atoms.

2. The method of Claim 1 wherein the weight ratio of diphenylamine or phenyl- α -naphthylamine to the triaryl phosphite in the mixture is in the range of from about 5:1 to about 1:5.

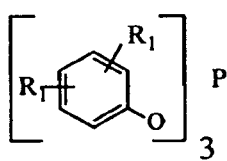
3. The method of Claim 2 wherein the amount of the mixture added to the base oil is in the range of about 0.1 wt% to about 2 wt% based on the total weight of the composition.

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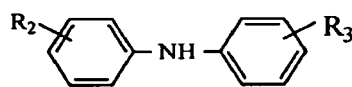
4. The method of Claim 3 wherein R_1 is tert-butyl, R_2 is H and R_3 is octyl.
5. The method of Claim 4 wherein the oil is a Group III oil.
6. The method of Claim 5 wherein the Group III oil is a GTL oil.
7. A lubricating composition having reduced deposit forming tendency as evidenced by the Hot Tube Test, comprising:

a major amount of an oil of lubricating viscosity selected from the group consisting of Group II, III, IV oils and mixtures thereof; and

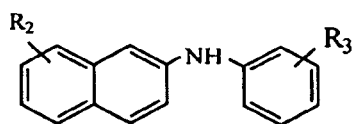
a minor amount of a mixture of triaryl phosphites represented by Formula I with diphenylamines or phenyl- α -naphthylamines represented by Formula II and III respectively.



I



II



III

wherein R_1 is H or a hydrocarbyl group having from 1 to about 8 carbon atoms and R_2 is H or a hydrocarbyl group of from 1 to about 12 carbon atoms and R_3 is a

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hydrocarbonyl group of from 1 to 12 carbon atoms or NHR_4 where R_4 is a hydrocarbonyl group of from 1 to about 12 carbon atoms.

8. The composition of Claim 7 wherein the weight ratio of diphenylamine or phenyl- α -naphthylamine to triaryl phosphite in the mixture is in the range of from about 5:1 to about 1:5.

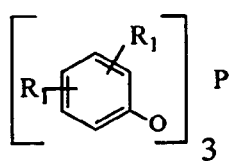
9. The composition of Claim 8 wherein the amount of the mixture is in the range of from about 0.1 wt% to about 2 wt%, based on the total weight of the composition.

10. The composition of Claim 9 wherein R_1 is tert-butyl, R_2 is H and R_3 is octyl.

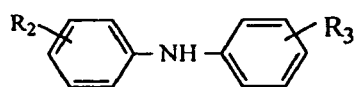
11. The composition of Claim 10 wherein the base oil is a Group III base oil.

12. The composition of Claim 11 wherein the Group III base oil is a GTL oil.

13. A method for reducing deposit formation in a lubricating base oil selected from the group consisting of Group II, III, IV oils and mixtures thereof comprising adding to the oil an effective amount of a mixture of triaryl phosphites represented by Formula I with diphenylamines or phenyl- α -naphthylamines represented by Formula II and III respectively,

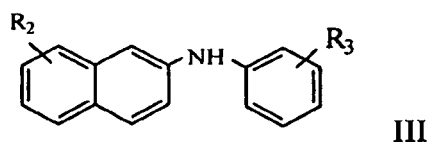


I



II

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wherein R_1 is H or a hydrocarbyl group having from 1 to about 8 carbon atoms and R_2 is H or a hydrocarbyl group of from 1 to about 12 carbon atoms and R_3 is a hydrocarbyl group of from 1 to 12 carbon atoms or NHR_4 where R_4 is a hydrocarbyl group of from 1 to about 12 carbon atoms and wherein the weight ratio of diphenylamines or phenyl- α -naphthylamines to triaryl phosphites is in the range of about 5:1 to about 1:5.