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(54) **Lubricating oil composition**

(57) The invention relates to a base oil blend comprising (A) bright stock oil, (B) de-asphalted cylinder oil (DACO) and, optionally, (C) one or more medium to high viscosity distillate base oils, wherein said de-asphalted cylinder oil is present in an amount in the range of from

5 to 40 wt. %, based on the total amount of said base oil blend; a process to prepare said base oil blend; and a lubricating oil composition comprising said base oil blend.

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**Description**

**[0001]** The present invention relates to a base oil blend, a process to prepare a base oil blend and a lubricating oil composition comprising said base oil blend.

**[0002]** GB-A-1496045 describes a process to prepare high viscosity base oils wherein a vacuum residue of a crude petroleum source is first subjected to a propane de-asphalting step to obtain a de-asphalted oil (DAO). The DAO is further subjected to a furfural extraction process in order to extract de-asphalted cylinder oil (DACO) therefrom as the polycyclic compounds therein are undesirable because of their low viscosity index and oxidative stability. The bright stock waxy raffinate obtained after furfural extraction is then subjected to a solvent de-waxing step and hydrofinishing in order to produce bright stock oil.

**[0003]** US-A-4592832 discloses a process to prepare a bright stock oil having a kinematic viscosity at 100 °C of 37 MM<sup>2</sup>/sec and a viscosity index of 95 as prepared from a light Arabian Vacuum Resid. The light Arabian Vacuum Resid is subjected to a propane de-asphalting step to prepare a DAO. The DAO is subjected to a N-methylpyrrolidone (NMP) solvent extraction step followed by de-waxing to obtain the bright stock oil.

**[0004]** Bright stock oil is commonly used as a base oil in lubricating oil compositions, in particular in lubricating oil compositions for marine and stationary low-speed crosshead diesel engines burning residual fuels with sulphur contents of up to 4.0 wt. % and for trunk piston, medium-speed diesel engines operating on residual fuel in industrial and marine applications.

**[0005]** It will be appreciated in the art that the term "marine" does not restrict such engines to those used in water-borne vessels. That is to say, in addition said term also includes engines used for power generation applications. These highly rated, fuel efficient, slow-speed marine and stationary diesel engines operate at high pressures, high temperatures and long strokes.

**[0006]** However, as bright stock oil availability is becoming increasingly constrained within the market place, it is highly desirable to find alternative base oils for use in lubricating oil compositions for such applications.

**[0007]** It has now been surprisingly found in the present invention that particular base oil blends comprising bright stock oil and de-asphalted cylinder oil (DACO) not only have no adverse effect on the lubricating properties of lubricating oil compositions, but also have advantageous viscometric properties in cylinder oil lubricants for use in cross-head engines and trunk piston engines.

**[0008]** Accordingly, in the present invention there is provided a base oil blend comprising (A) bright stock oil, (B) de-asphalted cylinder oil (DACO) and, optionally, (C) one or more medium to high viscosity distillate base oils, wherein said de-asphalted cylinder oil is present in an amount in the range of from 5 to 40 wt. %, based on the total amount of said base oil blend.

**[0009]** In another embodiment of the present invention there is provided a process to prepare said base oil blend comprising:

- (i) de-asphalting a mineral-derived vacuum residue to obtain a de-asphalted oil (DAO), solvent-extracting a de-asphalted cylinder oil (DACO) from the de-asphalted oil to produce a bright stock waxy raffinate; and de-waxing the bright stock waxy raffinate to produce a bright stock oil; and
- (ii) blending the bright stock oil with some or all of the de-asphalted cylinder oil.

**[0010]** Furthermore, the present invention also provides a lubricating oil composition comprising said base oil blend and one or more additives selected from dispersants, detergents, antiwear agents, friction reducing agents, viscosity thickeners, metal passivators, acid sequestering agents, pour point depressants, corrosion inhibitors, defoaming agents, seal fix or seal compatibility agents and antioxidants.

**[0011]** The present invention further provides for the use of said lubricating oil composition as a cylinder oil lubricant for cross-head engines or a trunk piston engine oil. Additionally, the lubricating oil composition of the present invention may be used in medium-speed industrial or marine propulsion and auxiliary engines burning residual fuel oils.

**[0012]** It has been surprisingly found in the present invention that high viscosity and medium viscosity index base oil blends are possible if a bright stock oil is blended with a de-asphalted cylinder oil.

**[0013]** The base oil blend of the present invention preferably comprises an amount in the range of from 5 to 30 wt. %, more preferably in the range of from 5 to 21 wt. % of de-asphalted cylinder oil, based on the total amount of said base oil blend.

**[0014]** The base oil blend of the present invention preferably has a kinematic viscosity at 100 °C of at least 10 mm<sup>2</sup>/s, more preferably at least 13 mm<sup>2</sup>/s. Preferably, the kinematic viscosity at 100 °C of said base oil blend is no more than 16 mm<sup>2</sup>/s. In a preferred embodiment of the present invention, said base oil blend has a kinematic viscosity at 100 °C in the range of from 10 mm<sup>2</sup>/s to 16 mm<sup>2</sup>/s, more preferably in the range of from 13 mm<sup>2</sup>/s to 16 mm<sup>2</sup>/s.

**[0015]** The viscosity index of the base oil blend of the present invention is preferably at least 71, more preferably in the range of from 80 to 120 and most preferably in the range of from 83 to 100.

**[0016]** The de-asphalted oil (DAO) used in the process of the present invention is defined as the product of a de-asphalting process step wherein asphalt is removed from a reduced crude petroleum feed or from the residue, bottom fraction, of a vacuum distillation of a crude petroleum feed (hereinafter referred to as "mineral-derived vacuum residues").

**[0017]** The de-asphalting process utilises a light hydrocarbon liquid solvent, for example propane, for asphalt compounds.

**[0018]** De-asphalting processes are well known and for example, are described in "Lubricant base oil and wax processing", Avilino Sequeira, Jr., Marcel Dekker, Inc, New York, 1994, ISBN 0-8247-9256-4, pages 53-80.

**[0019]** In step (i) of the process of the present invention, the de-asphalted oil undergoes solvent extraction, wherein aromatic extract known as de-asphalted cylinder oil (DACO) is removed therefrom. The de-asphalted solvent-extracted oil is known as bright stock waxy raffinate.

**[0020]** Examples of solvent extraction process that may be conveniently used include furfural or NMP solvent extraction processes or other solvent extraction processes, for example, as described in Chapter 5 of "Lubricant base oil and wax processing", Avilino Sequeira, Jr., Marcel Dekker, Inc, New York, 1994, ISBN 0-8247-9256-4.

**[0021]** In step (i) of the process of the present invention, the bright stock waxy raffinate subsequently undergoes a de-waxing process.

**[0022]** The de-waxing process is for example a solvent dewaxing process. The de-waxed product is known as bright stock oil and preferably has a pour point of below  $-5^{\circ}\text{C}$ .

**[0023]** Said bright stock oil may be optionally hydro-finished prior to blending with a de-asphalted cylinder oil in step (ii) of the process of the present invention.

**[0024]** Hydrofinishing is typically carried out, for example, if the bright stock oil contains olefins or when the bright stock oil is sensitive to oxygenation.

**[0025]** Hydrofinishing may be conveniently carried out at a temperature between  $180$  and  $380^{\circ}\text{C}$ , a total pressure of between  $10$  to  $250$  bar, preferably above  $100$  bar and more preferably between  $120$  and  $250$  bar. The WHSV (Weight hourly space velocity) may range from  $0.3$  to  $2$  kg of oil per litre of catalyst per hour (kg/l.h).

**[0026]** The hydrogenation catalyst for hydrofinishing may suitably be a supported catalyst comprising a dispersed Group VIII metal. Possible Group VIII metals are cobalt, nickel, palladium and platinum. Cobalt and nickel containing catalysts may also comprise a Group VIB metal, suitably molybdenum and tungsten. Suitable carrier or support materials include low acidity amorphous refractory oxides. Examples of suitable amorphous refractory oxides include inorganic oxides, such as alumina, silica, titania, zirconia, boron, silica-alumina, fluorided alumina, fluorided silica-alumina and mixtures of two or more of these.

**[0027]** Examples of suitable hydrogenation catalysts for hydrofinishing are nickel-molybdenum containing catalyst such as KF-847 and KF-8010 (AKZO Nobel) M-8-24 and M-8-25 (BASF), and C-424, DN-190, HDS-3 and HDS-4 (Criterion); nickel-tungsten containing catalysts such as NI-4342 and NI-4352 (Engelhard) and C-454 (Criterion); cobalt-molybdenum containing catalysts such as KF-330 (AKZO-Nobel), HDS-22 (Criterion) and HPC-601 (Engelhard). Preferably, platinum-containing and more preferably platinum- and palladium-containing catalysts are used. Preferred supports for these palladium and/or platinum containing catalysts are amorphous silica-alumina. Examples of suitable silica-alumina carriers are disclosed in WO-A-94/10263. A preferred catalyst comprises an alloy of palladium and platinum preferably supported on an amorphous silica-alumina carrier of which the commercially available catalyst C-624 of Criterion Catalyst Company (Houston, TX) is an example.

**[0028]** Preferably, the kinematic viscosity at  $100^{\circ}\text{C}$  of the bright stock oil is in the range of from  $29$  to  $35$   $\text{mm}^2/\text{s}$ .

**[0029]** The viscosity index of the bright stock oil is preferably in the range of from  $92$  to  $98$ .

**[0030]** The de-asphalted cylinder oil preferably has a negative viscosity index or a viscosity index in the range of from  $-45$  to  $80$ .

**[0031]** The kinematic viscosity at  $100^{\circ}\text{C}$  of the de-asphalted cylinder oil is preferably at least  $40$   $\text{mm}^2/\text{s}$ , more preferably at least  $48$   $\text{mm}^2/\text{s}$ .

**[0032]** The pour point of the de-asphalted cylinder oil is preferably below  $50^{\circ}\text{C}$ , more preferably below  $27^{\circ}\text{C}$  and most preferably below  $21^{\circ}\text{C}$ .

**[0033]** The de-asphalted cylinder oil may be prepared by de-asphalting a mineral-derived vacuum residue to obtain a de-asphalted oil, solvent-extracting the de-asphalted oil and obtaining the de-asphalted cylinder oil (DACO) extract.

**[0034]** The de-asphalted cylinder oil (DACO) extract may be subjected to a solvent de-waxing step prior to being used in the present invention. Preferably, the de-asphalted cylinder oil extract is used as obtained in the solvent extraction process step without subjecting said de-asphalted cylinder oil to a de-waxing step.

**[0035]** In one embodiment of the present invention, the de-asphalted cylinder oil used in step (ii) of the process of the present invention may be conveniently obtained from a separate process or process run to that in which the bright stock oil is prepared. This embodiment has particular utility in situations wherein the base oil blend is to be prepared in a separate location or at a different time from that in which the bright stock oil and/or de-asphalted cylinder oil are prepared.

**[0036]** However, in another embodiment of the present invention, the de-asphalted cylinder oil extracted in step (i) of the process of the present invention may be subsequently blended in step (ii) with the bright stock oil prepared in step

(i) in an integrated process. That is to say, in said embodiment of the present invention, the preparation, isolation and subsequent blending of bright stock oil and de-asphalted cylinder oil are integral parts of the same process.

**[0037]** In a preferred embodiment of the process of the present invention, in an optional additional step (iii), which may take place before or after step (ii), one or more medium to high viscosity distillate base oils may be blended with the bright stock oil and/or de-asphalted cylinder oil.

**[0038]** It will be appreciated that in the present invention, there is no limitation on the order in which said process blending steps (ii) and (iii) may occur. That is to say, (a) said optional step (iii) may take place after blending together of the bright stock oil and de-asphalted cylinder oil in step (ii), (b) said optional step (iii) may take place by blending the one or more medium to high viscosity distillate base oils with the bright stock oil prior to blending with the de-asphalted cylinder oil in step (ii), (c) said optional step (iii) may take place by blending the one or more medium to high viscosity distillate base oils with the de-asphalted cylinder oil prior to blending with the bright stock oil in step (ii) or, alternatively, (d) the bright stock oil, de-asphalted cylinder oil and one or more medium to high viscosity distillate base oils may be conveniently blended together simultaneously in step (ii).

**[0039]** The one or more medium to high viscosity distillate base oils which may be optionally present in the base oil blend of the present invention may be conveniently prepared by vacuum distillation, solvent extraction, de-waxing, and hydrogenation and/or hydroisomerisation.

**[0040]** Said one or more medium to high viscosity distillate base oils may conveniently be base oils having a kinematic viscosity at 100 °C in the range of from 5 to 13 mm<sup>2</sup>/s and a viscosity index in the range of from 80 to 120, preferably in the range of from 94 to 120.

**[0041]** Particularly preferred medium to high viscosity distillate base oils that may be used include Group I and Group II base oils.

**[0042]** By "Group I" base oils and "Group II" base oils, in the present invention are meant base oils according to the definitions of American Petroleum Institute (API) categories I and II. Such API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

**[0043]** Group I base oils contain less than 90 % saturates (according to ASTM D2007) and/or greater than 0.03 % sulphur (according to ASTM D2622, D4294, D4927 or D3120) and have a viscosity index of greater than or equal to 80 and less than 120 (according to ASTM D2270).

**[0044]** Group II base oils contain greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur and have a viscosity index of greater than or equal to 80 and less than 120, according to the aforementioned ASTM methods.

**[0045]** The base oil blend of the present invention preferably comprises an amount in the range of from 40 to 80 wt. % of said one or more medium to high viscosity distillate base oils, based on the total amount of said base oil blend.

**[0046]** In the process of the present invention, the bright stock oil (A), de-asphalted cylinder oil (B) and, optionally, one or more medium to high viscosity distillate base oils (C) may be conveniently blended together in a blending unit under elevated temperatures of not exceeding 80 °C.

**[0047]** One embodiment of the process of the present invention will now be described by way of example with reference to the Figure 1, which is a functional block diagram of said process.

**[0048]** By way of example, de-asphalting utilising propane is described.

**[0049]** A feedstock 1 of a mineral-derived vacuum residue and propane 2 enter a de-asphalting unit 3, wherein asphalt 4 is removed therefrom.

**[0050]** The resulting de-asphalted oil (DAO) 5 is fed to a solvent extraction unit 6 wherein said material undergoes solvent extraction, for example with furfural or NMP, in order to extract de-asphalted cylinder oil (DACO) 7 therefrom.

**[0051]** The resulting bright stock waxy raffinate 8 is then passed to a de-waxing unit 9 wherein said material undergoes de-waxing utilising, for example, methyl ethyl ketone (MEK) and/or toluene to remove bright stock slack wax 10 therefrom.

**[0052]** The resulting bright stock oil 11 may undergo optional hydrofinishing (not shown in Figure 1) prior to being fed to blending unit 12.

**[0053]** The bright stock oil 11 is blended with de-asphalted cylinder oil 7 from the solvent extraction unit 6 in blending unit 12 in order to produce the base oil blend 13 as described herein.

**[0054]** The amount of de-asphalted cylinder oil (DACO) 7 required in the base oil blend 13 will depend on the desired resultant properties thereof. Any non-used de-asphalted cylinder oil (DACO) 7 may be conveniently discharged from the process as a separate product via a separate line (not shown in Figure 1).

**[0055]** The base oil blend of the present invention may conveniently find application in lubricating oil compositions, in particular in cylinder oil lubricants for cross-head engines or trunk piston engine oils.

**[0056]** Cylinder oil lubricants are preferably used on a once-through basis by means of injection devices that apply the cylinder oil lubricant to lubricators positioned around the cylinder liner of a slow speed diesel engine.

**[0057]** Diesel engines may generally be classified as slow-speed, medium-speed or high-speed engines, with the slow-speed variety being used for the largest, deep draft vessels and in industrial applications.

**[0058]** Slow-speed diesel engines are typically direct coupled, direct reversing, two-stroke cycle engines operating in

the range of about 57 to 250 rpm and usually run on residual fuels. These engines are of crosshead construction with a diaphragm and stuffing boxes separating the power cylinders from the crankcase to prevent combustion products from entering the crankcase and mixing with the crankcase oil.

**[0059]** Medium-speed engines typically operate in the range of 250 to about 1100 rpm and may operate on the four-stroke or two-stroke cycle. These engines are trunk piston design, and many also operate on residual fuel containing in excess of 2.5 wt. % of sulphur. They may also operate on distillate fuel containing little or no residua. On deep-sea vessels these engines may be used for propulsion, ancillary applications or both.

**[0060]** Slow speed and medium speed marine diesel engines are also extensively used in power plant operations. The present invention is also applicable to such applications.

**[0061]** Each type of diesel engine employs lubricating oils to lubricate piston rings, cylinder liners, bearings for crank shafts and connecting rods, valve train mechanisms including cams and valve lifters, among other moving members. The lubricant prevents component wear, removes heat, neutralizes and disperses combustion products, prevents rust and corrosion, and prevents sludge formation or deposits.

**[0062]** In low-speed marine crosshead diesel engines, the cylinders and crankcase are lubricated separately, with cylinder lubrication being provided on a once-through basis by means of injection devices that apply cylinder oil to lubricators positioned around the cylinder liner. This is known as an "all-loss" lubrication system. The cylinder oil is typically formulated to provide for good oxidation and thermal stability, water demulsability, corrosion protection and good antifoam performance. Alkaline detergent additives are also present to neutralize acids formed during the combustion process. Dispersant, antioxidant, antifoam, antiwear and extreme pressure (EP) performance may also be provided by the use of suitable additives.

**[0063]** The lubricating oil composition according to the present invention comprises a base oil blend as hereinbefore described, which base oil blend comprises

(A) bright stock oil, (B) de-asphalted cylinder oil and, optionally, (C) one or more medium to high viscosity distillate base oils, and one or more additives selected from dispersants, detergents, antiwear agents, friction reducing agents, viscosity thickeners, metal passivators, acid sequestering agents, pour point depressants, corrosion inhibitors, defoaming agents, seal fix or seal compatibility agents and antioxidants.

**[0064]** In a preferred embodiment, the base oil blend as hereinbefore described is present in said lubricating oil composition in an amount in the range of from 72 to 90 wt. %, more preferably in an amount in the range of from 74 to 87 wt. %, based on the total amount of said lubricating oil composition.

**[0065]** Preferably all of the afore-mentioned listed additives are present in the lubricating oil composition of the present invention. Examples of such additives are for example described in US-B-6596673, which publication is hereby incorporated by reference.

**[0066]** Detergents that may be conveniently used in the lubricating oil composition of the present invention, include one or more detergents selected from phenate detergents, salicylate detergents and sulphonate detergents.

**[0067]** Alkali metal and alkaline earth metal salicylate, phenate and sulphonate detergents are preferred in the lubricating oil compositions of the present invention. Calcium and magnesium salicylates, phenates and sulphonates are particularly preferred detergents therein.

**[0068]** Detergents used in the lubricating oil composition of the present invention, may each, independently, have a TBN (total base number) value in the range of from 30 to 350 mg KOH/g, preferably about 70 mg KOH/g, as measured by ISO 3771 and are preferably present in a total amount in the range of from 0.5 to 18 wt. %, based on the total weight of said lubricating oil composition.

**[0069]** Antioxidants which may be conveniently used in the lubricating oil composition of the present invention, include one or more antioxidants selected from the group of aminic antioxidants and/or phenolic antioxidants.

**[0070]** Said antioxidants may be generally present in a total amount in the range of from 0 to 2 wt. %, based on the total weight of said lubricating oil composition.

**[0071]** Examples of aminic antioxidants which may be conveniently used include alkylated diphenylamines, phenyl- $\alpha$ -naphthylamines, phenyl- $\beta$ -naphthylamines and alkylated  $\alpha$ -naphthylamines.

**[0072]** Preferred aminic antioxidants include dialkyldiphenylamines such as p,p'-dioctyl-diphenylamine, p,p'-di- $\alpha$ -methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butylidiphenylamine and mono-octyldiphenylamine, bis(dialkylphenyl)amines such as di-(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octylphenyl-1-naphthylamine and n-t-dodecylphenyl-1-naphthylamine, 1-naphthylamine, aryl-naphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine and 3,7-dioctylphenothiazine.

**[0073]** Preferred aminic antioxidants include those available under the following trade designations:

"Sonoflex OD-3" (ex. Seiko Kagaku Co.), "Irganox L-57" (ex. Ciba Specialty Chemicals Co.) and phenothiazine (ex. Hodogaya Kagaku Co.).

**[0074]** Examples of phenolic antioxidants which may be conveniently used include C7-C9 branched alkyl esters of 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctylacetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, n-butyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,6-d-t-butyl- $\alpha$ -dimethylamino-p-cresol, 2,2'-methylene-bis(4-alkyl-6-t-butylphenol) such as 2,2'-methylenebis(4-methyl-6-t-butylphenol, and 2,2'-methylenebis(4-ethyl-6-t-butylphenol), bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethyleneglycol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycolbis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate], 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 2,2'-thiobis(4,6-di-t-butylresorcinol), polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, bis-[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)methyl-4-(2",4"-di-t-butyl-3"-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol, and p-t-butylphenol - formaldehyde condensates and p-t-butylphenol - acetaldehyde condensates.

**[0075]** Preferred phenolic antioxidants include those available under the following trade designations:

"Irganox L-135" (ex. Ciba Specialty Chemicals Co.), "Anteeji DBH" (ex. Kawaguchi Kagaku Co.), "Yoshinox SS" (ex. Yoshitomi Seiyaku Co.), "Antage W-400" (ex. Kawaguchi Kagaku Co.), "Antage W-500" (ex. Kawaguchi Kagaku Co.), "Antage W-300" (ex. Kawaguchi Kagaku Co.), "Ionox 220AH" (ex. Shell Japan Co.), bisphenol A, produced by the Shell Japan Co., "Irganox L109" (ex. Ciba Specialty Chemicals Co.), "Tominox 917" (ex. Yoshitomi Seiyaku Co.), "Irganox L115" (ex. Ciba Specialty Chemicals Co.), "Sumilizer GA80" (ex. Sumitomo Kagaku), "Antage RC" (ex. Kawaguchi Kagaku Co.), "Irganox L101" (ex. Ciba Specialty Chemicals Co.), "Yoshinox 930" (ex. Yoshitomi Seiyaku Co.), "Ionox 330" (ex. Shell Japan Co.).

**[0076]** In a preferred embodiment, the lubricating oil composition of the present invention may comprise one or more zinc dithiophosphates as antiwear additives, the or each zinc dithiophosphate being selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates. Zinc dialkyl dithiophosphates are particularly preferred.

**[0077]** Examples of suitable zinc dithiophosphates which are commercially available include those available ex. Lubrizol Corporation under the trade designations "Lz 1097" and "Lz 1395", those available ex. Chevron Oronite under the trade designations "OLOA 26,7" and "OLOA 269R", and that available ex. Ethyl under the trade designation "HITEC 7197"; zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 677A", "Lz 1095" and "Lz 1371", that available ex. Chevron Oronite under the trade designation "OLOA 262" and that available ex. Ethyl under the trade designation "HITEC 7169"; and zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 1370" and "Lz 1373" and that available ex. Chevron Oronite under the trade designation "OLOA 260".

**[0078]** The lubricating oil composition according to the present invention may generally comprise in the range of from 0.1 to 1.5 wt. % of zinc dithiophosphate, preferably in the range of from 0.4 to 0.9 wt. % and most preferably in the range of from 0.45 to 0.8 wt. %, based on total weight of the lubricating oil composition.

**[0079]** Further antiwear additives that may be conveniently used include molybdenum-containing compounds and boron-containing compounds.

**[0080]** Examples of such molybdenum-containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example as described in WO-A-98/26030, sulphides of molybdenum and molybdenum dithiophosphate.

**[0081]** Said molybdenum-containing antiwear additives may be conveniently added to the lubricating oil composition of the present invention in an amount in the range of from 0.1 to 3.0 wt. %, based on the total weight of lubricating oil composition.

**[0082]** Boron-containing compounds that may be conveniently used include borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

**[0083]** Said boron-containing anti-wear additives may be conveniently added to the lubricating oil composition of the

present invention in an amount in the range of from 0.1 to 3.0 wt. %, based on the total weight of lubricating oil composition.

[0084] The lubricating oil compositions of the present invention may additionally contain one or more dispersants which may be preferably admixed in an amount in the range of from 5 to 15 wt. %, based on the total weight of the lubricating oil composition.

[0085] Examples of dispersants which may be used include the polyalkenyl succinimides and polyalkenyl succinic acid esters disclosed in Japanese Patent Nos. 1367796, 1667140, 1302811 and 1743435. Preferred dispersants include borated succinimides.

[0086] Preferred friction reducing agents that may be conveniently used include fatty acid amides, more preferably unsaturated fatty acid amides.

[0087] The total amount of friction reducing agents that may be added to the lubricating oil composition of the present invention is conveniently in the range of from 0.05 to 1.2 wt. %, based on the total weight of the lubricating oil composition.

[0088] Polymethacrylates such as those as disclosed in Japanese Patent Nos. 1195542 and 1264056 may be conveniently employed in the lubricating oil compositions of the present invention as effective pour point depressants.

[0089] Furthermore, compounds such as alkenyl succinic acid or ester moieties thereof, benzotriazole-based compounds and thiodiazole-based compounds may be conveniently used in the lubricating oil composition of the present invention as corrosion inhibitors.

[0090] Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating oil composition of the present invention as defoaming agents.

[0091] Compounds which may be conveniently used in the lubricating oil composition of the present invention as seal fix or seal compatibility agents include, for example, commercially available aromatic esters.

[0092] The lubricating oil compositions of the present invention may be conveniently prepared by admixing the base oil blend and the one or more additives selected from dispersants, detergents, antiwear agents, friction reducing agents, viscosity thickeners, metal passivators, acid sequestering agents, pour point depressants, corrosion inhibitors, defoaming agents, seal fix or seal compatibility agents and antioxidants.

[0093] In another embodiment of the present invention, there is provided a method of lubricating a marine or stationary low-speed crosshead diesel engine or a trunk piston medium speed diesel engine comprising applying a lubricating oil composition as hereinbefore described thereto.

[0094] The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the invention in any way.

#### Examples

[0095] Oil blends A-F were made using base oils listed in Table 1. Two different de-asphalted cylinder oils are listed in Table 1.

[0096] The de-asphalted cylinder oils (DACO) were prepared by furfuryl extraction of de-asphalted oil (DAO).

[0097] The bright stock oil was prepared by dewaxing waxy raffinate from a furfuryl extraction unit.

[0098] The High Viscosity Oil 1 (Medium VI) and Medium Viscosity Oil 3 were prepared by furfuryl extraction, dewaxing and hydrotreatment of distillate streams from Vacuum Distillation.

[0099] The High Viscosity Oil 2 (High VI) and Medium Viscosity Oil 4 were prepared by hydroisomerisation using catalytic isomerisation, dewaxing, and hydrogenation processes to lower the sulphur and nitrogen contents, increase the amount of saturated components to greater than 90 wt. %, and decrease the pour point of the saturated components to less than -12 °C.

TABLE 1

	DACO 1*	DACO 2**	Bright Stock Oil	High Viscosity Oil 1	High Viscosity Oil 2***	Medium Viscosity Oil 3	Medium Viscosity Oil 4***
Kinematic Viscosity at 100°C (mm <sup>2</sup> /sec)	48.7	57.2	31	11.5	10.9	8.47	5.59
Viscosity Index	-25	9	97	98	107	102	120
Total Sulphur (wt. %)	3.27	4.00	1.37	0.88	<0.001	1.00	<0.001

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(continued)

	DACO 1*	DACO 2**	Bright Stock Oil	High Viscosity Oil 1	High Viscosity Oil 2***	Medium Viscosity Oil 3	Medium Viscosity Oil 4***
5	Total Nitrogen (wt. %)	0.15	0.20	0.014	0.004	<0.001	<0.001
10	Total Aromatics and Polars (wt. %)	88	90	59	37	1.0	37
15	Total Saturates (wt. %)	12	10	41	63	99	63
20	Pour Point (°C)	48	15	-6	-6	-15	-6
	* De-asphalted cylinder oil from Asia Pacific. ** De-asphalted cylinder oil from Europe. *** API Group II Base oil.						

[0100] The base oil blends shown in Table 2 target a kinematic viscosity at 100 °C of 14.4 mm<sup>2</sup>/s.

[0101] The base oil blends range in viscosity index from 84 to 100.

[0102] Increasing the amount of DACO has the effect of lowering the VI. A greater amount of DACO may be blended with medium viscosity oil. For example, blending the High Viscosity Oil 2 (high VI) with DACO raises the VI to 100.

[0103] Blend A is comparative in nature whilst blends B to F are according to the present invention.

TABLE 2

	Base Oil Blends					
	A	B	C	D	E	F
De-asphalted cylinder oil 1* (DACO) (wt. %)	0	8	0	34	10	39
De-asphalted cylinder oil 2** (DACO) (wt. %)	0	0	19	0	0	0
Bright Stock Oil (wt. %)	24	15	21.5	5	17	17.5
High Viscosity Oil 1 (wt. %)	76	77	0	0	0	0
High Viscosity Oil 2 (wt. %)	0	0	0	0	73	0
Medium Viscosity Oil 3 (wt. %)	0	0	59.5	61	0	0
Medium Viscosity Oil 4 (wt. %)	0	0	0	0	0	43.5
<b>Total Base Oil Blend (wt. %)</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>
<b>Kinematic Viscosity at 100 °C (mm<sup>2</sup>/sec)</b>	<b>14.4</b>	<b>14.4</b>	<b>14.4</b>	<b>14.4</b>	<b>14.4</b>	<b>14.4</b>
<b>Viscosity Index</b>	<b>97</b>	<b>94</b>	<b>91</b>	<b>86</b>	<b>100</b>	<b>94</b>
* De-asphalted cylinder oil from Asia Pacific. ** De-asphalted cylinder oil from Europe.						

[0104] Lubricating oil compositions were made by blending the base oil blends A-C with a 26.4 wt. % of a conventional fully formulated 70 mg KOH/g TBN detergent cylinder oil additive package containing highly overbased calcium phenate and sulphonate detergents, succinimide dispersant and zinc alkyl dithiophosphate in diluent oil (approximately 44 % of the total additive package). The resulting lubricating oil compositions are denoted in Table 3 as A'-C', respectively.

[0105] Oxidation stability tendency was tested by using differential scanning calorimetry (DSC) at 210°C at 10 bar oxygen at continuous flow. Longer induction times inferred greater oxidation stability.

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**[0106]** Tendency towards formation of deposits and viscosity increase was tested by using the Wolf Strip test apparatus (DIN 51392 method). Test conditions were 12 hour duration at 280 °C.

**[0107]** Determination of oil detergency at high temperatures was done using Komatsu hot tube testing. Measurements were made at temperatures of 310 °C, 320 °C and 330 °C. Tube inspection ratings range from 1 to 10 (clean).

**[0108]** High temperature deposit forming tendency was tested by using a Micro Coker test. Test duration was 90 minutes. The temperature is recorded when deposits are observed to form.

**[0109]** The blends A'-C' showed good to excellent test results compared with commercial products X and Y.

**[0110]** As shown in Table 3, blends B' and C' (which contained DACO) showed comparable DSC and Wolf Strip data to blend A' (which did not contain DACO).

**[0111]** It is apparent that blend A' showed better DSC results, Komatsu hot tube test and Micro Coker test results, as compared to the commercial products X and Y.

TABLE 3

Test Results	Lubricating Oil Compositions				
	A'	B'	C'	X*	Y**
<b>Differential Scanning Calorimetry (DSC) (Induction time in minutes)</b>	40	46	58	21	28
<b>Wolf Strip Test (Deposits in grams)</b>	0.020	na	0.030	na	0.025
<b>Wolf Strip Test Viscosity Increase @ 100 °C</b>	38	na	48	na	45
<b>Komatsu Hot Tube Test at 310 °C (Rating)</b>	9.0	na	na	7.0	8.7
<b>Komatsu Hot Tube Test at 320 °C (Rating)</b>	8.0	na	na	6.6	6.6
<b>Komatsu Hot Tube Test at 330 °C (Rating)</b>	7.0	na	na	Fail	Fail
<b>Micro Coker Test (°C)</b>	270	na	na	264	237
* Fully formulated marine oil available from BP under the trade designation "Energol CLO 50M". ** Fully formulated marine oil available from Texaco under the trade designation "Taro Special HT 70". na = not tested.					

### Claims

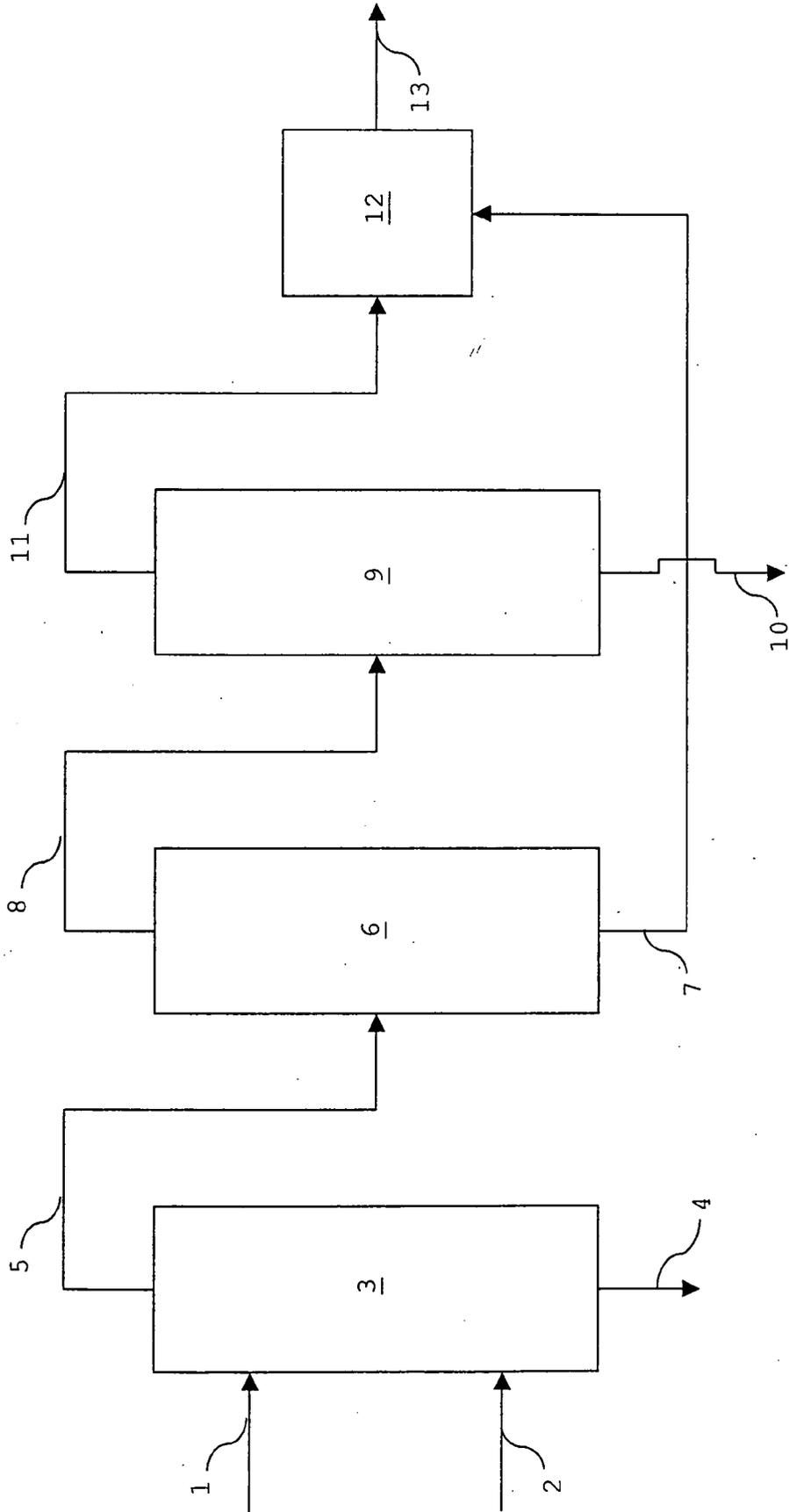
1. A base oil blend comprising (A) bright stock oil, (B) de-asphalted cylinder oil (DACO) and, optionally, (C) one or more medium to high viscosity distillate base oils, wherein said de-asphalted cylinder oil is present in an amount in the range of from 5 to 40 wt. %, based on the total amount of said base oil blend.
2. Base oil blend according to Claim 1, wherein the base oil blend has a kinematic viscosity at 100 °C of at least 10 mm<sup>2</sup>/s and/or a viscosity index of at least 71.
3. Base oil blend according to Claim 1 or 2, wherein the base oil blend has a kinematic viscosity at 100 °C in the range of from 10 mm<sup>2</sup>/s to 16 mm<sup>2</sup>/s.
4. Base oil blend according to any one of Claims 1 to 3, wherein the de-asphalted cylinder oil has one or more of the following characteristics, a viscosity index in the range of from -45 to 80, a kinematic viscosity at 100 °C of at least 40 mm<sup>2</sup>/s and/or a pour point of below 50 °C.
5. Base oil blend according to any one of Claims 1 to 4, wherein the bright stock oil has one or more of the following characteristics, a viscosity index in the range of from 92 to 98, a kinematic viscosity at 100 °C in the range of from 29 to 35 mm<sup>2</sup>/s and/or a pour point of below -5 °C.
6. Base oil blend according to any one of Claims 1 to 5, wherein the one or more medium to high viscosity distillate base oils have a viscosity index in the range of from 80 to 120 and/or a kinematic viscosity at 100 °C in the range of from 5 to 13 mm<sup>2</sup>/s.
7. Process to prepare a base oil blend according to any one of Claims 1 to 6 comprising:

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(i) de-asphalting a mineral-derived vacuum residue to obtain a de-asphalted oil (DAO), solvent-extracting a de-asphalted cylinder oil (DACO) from the de-asphalted oil to produce a bright stock waxy raffinate; and de-waxing the bright stock waxy raffinate to produce a bright stock oil; and  
(ii) blending the bright stock oil with some or all of the de-asphalted cylinder oil.

- 5
8. Process according to Claim 7, wherein in an additional step (iii), which may take place before or after step (ii), one or more medium to high viscosity distillate base oils are blended with the bright stock oil and/or de-asphalted cylinder oil.
- 10
9. Process according to Claim 7 or 8, wherein the bright stock oil is hydro-finished prior to blending with de-asphalted cylinder oil in step (ii).
- 15
10. Lubricating oil composition comprising base oil blend according to any one of Claims 1 to 6 and one or more additives selected from dispersants, detergents, antiwear agents, friction reducing agents, viscosity thickeners, metal passivators, acid sequestering agents, pour point depressants, corrosion inhibitors, defoaming agents, seal fix or seal compatibility agents and antioxidants.
- 20
11. Lubricating oil composition according to Claim 10, wherein base oil blend is present therein in an amount in the range of from 72 to 90 wt. %, based on the total amount of said lubricating oil composition.
- 25
12. Use of a lubricating oil composition according to Claim 10 or 11 as a cylinder oil lubricant for cross-head engines or as a trunk piston engine oil.
- 30
- 35
- 40
- 45
- 50
- 55

FIGURE 1





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 9 December 2005	Examiner Bertrand, S
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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