Disclosed is a lubricant base stock, exhibiting a combination of high flash point, low evaporation loss, high viscosity and unexpectedly exceptionally low pour point and high viscosity index value. Said lubricant base stock comprises at least one ester between 2-propylheptanoic acid and at least one 2,2-substituted 1,3-propanediol or at least one dimer, trimer or polymer thereof and/or at least one alkoxyalted species of a said 2,2-substituted 1,3-propanediol or a said dimer, trimer or polymer thereof.
LOW POUR POINT LUBRICANT BASE STOCK

[0001] The present invention refers to an automotive, an aeronautic, a marine or a stationary engine or turbine lubricant base stock comprising at least one ester between 2-propylyheptanoic acid and at least one 2,2-substituted 1,3,5-pentanediol and/or at least one dimer, trimer or polymer thereof and/or at least one alkoxylated species of a said 2,2-substituted 1,3,5-pentanediol or a said dimer, trimer or polymer thereof. In a further aspect the present invention refers to the use of said lubricant base stock in production of lubricants.

[0002] Qualifying for a specific application, a lubricant, comprising a lubricant base stock formulated with appropriate performance additives, must comprehensively comply with the requirements of a specific application and it is typically not enough to comply with one specific parameter, such as viscosity, only, but compliance is required for the whole set of application properties, often comprising specific demands for parameters such as viscosity, viscosity stability, flash point, pour point, volatility etc.

[0003] Lubricant base stocks are classified according to API (American Petroleum Institute, API Publication 1509) into five categories according to their chemical composition: Groups I to III consisting of different grades of mineral oil base stocks, Group IV being defined for Poly(α-olefins) and Group V being reserved for all other base stocks, including ester base stocks. It is known in the art that base stocks of different groups contribute to certain typical lubricant performance, such as low temperature properties, oxidation stability and/or compatibility properties. It is also known in the art, when formulating a final lubricant product for a specific application, that two or more base stocks of one or multiple groups can be combined. Synthetic esters are known to be combined with base stocks from other groups, such as poly (α-olefin) of API Group IV as disclosed in U.S. Pat. No. 5,151,205 or with mineral oils, API Groups 1 to 3 as disclosed in U.S. Pat. No. 5,665,683.

[0004] A lubricant is typically formulated by combining a lubricant base stock, or a mixture of lubricant base stocks, of suitable inherent properties with additives and other optional formulation aids. Esters of diols, triols, tetrols and polyols are frequently used lubricant base stocks in a number of high-performance lubricant applications. Said esters are obtained from an alcohol, having two or more hydroxyl groups, which alcohol is esterified with a carboxylic acid or acid mixture. During the esterification process the hydroxyl groups of said alcohol are converted partially or fully into ester groups, by means of having an acid component attached to them.

[0005] Formulation of a lubricant meeting specific end-properties typically involves the step of selecting a base-stock inherently exhibiting properties being close to the ones required. It is known in the art, that the final fine-tuning of the desired properties can be made by means of blending the base-stock with other components, capable of modifying the properties in accordance to the specification and other demands. Blending is, however, not always preferred, as this introduces complexity to the system, at least in the form of an increased number of components included in the lubricant.

[0006] It is, furthermore, known in the art that certain ester properties can be strongly influenced by selecting mixtures of starting materials instead of single reactants. The ester product may, for instance, be composed of a mixture of said alcohols esterified with a carboxylic acid or a said alcohol can be esterified with a mixture of carboxylic acids in order to obtain for instance improved compatibility and cold-flow properties. In even more general terms this may apply when combining a mixture of said alcohols with a mixture of carboxylic acids in order to obtain a statistical mixture of ester end-products. Esters based on said mixtures of raw materials are not, however, desired in all cases. They induce a degree of composition uncertainty to the system, and one or more of the statistically formed ester compounds may contribute to undesired and/or adverse performance. There are thus needs and demands for a range of different, essentially single reactants esters showing advantageous inherent properties.

[0007] Pour point is a lubricant property, which characterises the cold flow properties of a lubricant. Pour point is reported as the reading of the lowest temperature where a test lubricant shows a defined degree of fluidity. A more detailed description is given in the standard ASTM D5950. Low pour point is desired in lubricants aimed for use at low temperature conditions, occurring for instance at the startup of engines in cold climate and/or winter conditions. Examples of applications requiring good cold properties include, but are not limited to, automotive and aviation lubricants, lubricants for automotive, stationary and 2-stroke engines, hydraulic fluids, refrigeration lubricants, dielectric fluids and greases.

[0008] Esters of branched carboxylic acids are known to contribute to reduced pour point, as disclosed in for instance U.S. Pat. No. 4,514,314. So far, however, reported and used branched carboxylic acids are either neo- or iso-branched. 2-ethylhexanoic acid is the only used 2-branched carboxylic acid having more than four carbons and in the literature disclosed carboxylic acids having 10 or more carbon atoms are either linear acids, iso-acids or neo-acids.

[0009] It has now quite surprisingly been found that introduction of 2-propylyheptanoic acid as the acid component in an ester, intended as a lubricant base stock, significantly reduces the pour point of the ester. The, according to the present invention, obtained combination of high flash point, low evaporation loss, high viscosity and the unexpected and exceptionally low pour point and the high viscosity index value imply new technological opportunities in adjusting the properties of presently known lubricants. Neither 2-branched carboxylic acids, besides the in the art well known 2-ethylhexanoic acid, as starting material, nor any correlation between the molecular weight of the ester and the pour point of the lubricant, has so far been reported for ester lubricants and/or lubricant base stocks.

[0010] The present invention accordingly refers to an automotive, an aeronautic, a marine or a stationary engine or turbine lubricant base stock comprising at least one ester between 2-propylyheptanoic acid and at least one 2,2-substituted 1,3,5-pentanediol and/or at least one dimer, trimer or polymer thereof and/or at least one alkoxylated species of a said 2,2-substituted 1,3,5-pentanediol or a said dimer, trimer or polymer thereof.

[0011] Said 2,2-substituted 1,3,5-pentanediol is in preferred embodiments of the present invention a 2,2-dialkyl-1,3,5-pentanediol, a 2-alkyl-2-hydroxyalkyl-1,3,5-pentanediol or a 2,2-dihydroxy-alkyl-1,3,5-pentanediol, wherein said alkyl preferably is a C1-C8 alkyl. The most preferred embodiments of said 2,2-substituted 1,3,5-pentanediol and said dimer, trimer and polymer thereof include neopentyl glycol, 2-butyl-2-ethyl-1,3-propanediol, trimethyleneethane, trimethylenebutane, trimethylene propane, pentaerythritol, di-trimethylene and di-pentaerythritol. Said alkoxylated species are preferably selected from the group consisting of ethoxylated and/or pro-
oxylated trimethylolcethane, trimethylolpropane, trimethylolbutane, pentaerythritol, di-trimethylolpropane and di-pentaerythritiol.

[0012] Said ester is especially preferred embodiments of the present invention a triester or tetraster of a said 2-alkyl-2-hydroxyalkyl-1,3-propanediol or a said 2,2-dihydroxyalkyl-1,3-propanediol or a said dimer, trimer of polymer thereof, such as an esterification product, between 2-propylheptanoic acid and pentaerythritol, trimethylolpropane or di-trimethylolpropane, having a triester or tetraster content of at least 95%, such as at least 97%, by weight.

[0013] In a further aspect, the present invention relates to the use of a lubricant base stock as disclosed above in production of a lubricant for internal combustion engines and turbine engines, such as automotive engines, aeronautic engines, marine engines and stationary engines. Said engines can suitably be exemplified by for instance Otto, diesel, wankel and jet engines, including 2-stroke engines. The herein most preferred lubricant base stock comprises a triester of trimethylolpropane or a tetraster of pentaerythritol and/or di-trimethylolpropane.

[0014] Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilise the present invention to its fullest extent. The following preferred embodiments are, therefore, to be construed as merely illustrative and not limiting of the remainder of the disclosure in any way whatsoever. In the following Examples 1 and 2 refer to preparation of esters oils according to embodiments of the present invention and Example 3 to a comparative ester oil outside the scope of said invention. Example 4 and 5 and Table 1 present evaluations of prepared esters.

EXAMPLE 1

[0015] 120.9 g of pentaerythritol, 733.8 g of 2-propylheptanoic acid, 2.5 g of p-toluenesulphonic acid as catalyst and 43.0 g of n-octane as azetric solvent were charged in a reaction vessel equipped with mechanical agitator, nitrogen purge, heating device, condensers and a Dean-Stark water trap. The reaction mixture was rapidly heated to 170°C. and heating was subsequently continued at a gradient of 20°C./min until an esterification temperature of 235°C. was reached. The esterification was now allowed to continue until GC analysis evidenced less than 1% triester (ester having one unreacted hydroxyl group) in the reaction mixture. 15.6 g of active carbon was then added for control of discoloration and re-heated to 100°C. for dehydration. The resulting reaction product was finally filtered yielding pale yellow ester product having following properties.

[0016] Colour: 144 APHA
[0017] Acid value: 0.04 mg KOH/g
[0018] Hydroxyl value: 0.23 mg KOH/g
[0019] Pentaerythritol tetraster content: 97% by weight.

EXAMPLE 2

[0020] Example 1 was repeated with the difference that pentaerythritol was replaced by the same amount of trimethylolpropane and that 561.5 g of 2-propylheptanoic acid was charged instead of 733.8 g, yielding pale yellow ester product having following properties.

[0021] Colour: 44 APHA
[0022] Acid value: 0.02 mg KOH/g
[0023] Hydroxyl value: 0.52 mg KOH/g
[0024] Trimethylolpropane triester content: 97% by weight.

EXAMPLE 3 (COMPARATIVE)

[0025] Example 1 was repeated with the difference that 2-propylheptanoic acid was replaced by 613.4 g of 2-ethylhexanoic acid, yielding pale yellow ester product having following properties.

[0026] Colour: 5 APHA
[0027] Acid value: 0.03 mg KOH/g
[0028] Hydroxyl value: 0.52 mg KOH/g
[0029] Pentaerythritol tetraster content: 98.7% by weight.

EXAMPLE 4

[0030] The in Examples 1,2 and 3 (comparative) obtained ester products (lubricant base stocks) were evaluated with regard to properties important in lubricants. The ester products according to embodiments of the present invention exhibited substantially improved properties. The result is given in Table 1 below.

EXAMPLE 5

[0031] The ester products obtained in Example 1 and Example 3 (comparative) were over night placed in a freezer at –18-20°C. The product of Example 1 was after said time a clear high viscous liquid, while the product of Example 3 was an opaque waxy solid.

<table>
<thead>
<tr>
<th>Property</th>
<th>Viscosity at 40°C, cSt</th>
<th>Viscosity at 100°C, cSt</th>
<th>Viscosity index value ASTM D 2270</th>
<th>Pour point °C</th>
<th>Flash point closed cup °C</th>
<th>NOACK evaporation %/w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 1</td>
<td>57.2</td>
<td>7.83</td>
<td>110</td>
<td>–56</td>
<td>270</td>
<td>1.7</td>
</tr>
<tr>
<td>Ex. 2</td>
<td>34.4</td>
<td>5.44</td>
<td>89</td>
<td>–52</td>
<td>244</td>
<td>5.0</td>
</tr>
<tr>
<td>Ex. 3</td>
<td>46.2</td>
<td>6.39</td>
<td>82</td>
<td>–6</td>
<td>178</td>
<td>3.4</td>
</tr>
</tbody>
</table>

1-14. (canceled)

15. A method of lubricating an internal combustion engine or a turbine engine comprising contacting an engine with a lubricant comprising at least one ester selected from the group consisting of a triester obtained by esterifying 2-propylheptanoic acid with at least one 2-alkyl-2-hydroxyalkyl-
1,3-propanediol and a tetraester obtained by esterifying 2-propylheptanoic acid with at least one 2,2-dihydroxyalkyl-1,3-propanediol.

16. The method of claim 15, wherein the ester is a triester obtained by esterifying 2-propylheptanoic acid with at least one 2-alkyl-2-hydroxyalkyl-1,3-propanediol.

17. The method of claim 15, wherein the ester is a tetraester obtained by esterifying 2-propylheptanoic acid with at least one 2,2-dihydroxyalkyl-1,3-propanediol.

18. The method of claim 15, where the alkyl is a C₁-C₈ alkyl.

19. The method of claim 16, where the alkyl is a C₁-C₈ alkyl.

20. The method of claim 17, where the alkyl is a C₁-C₈ alkyl.

21. The method of claim 15, wherein the 2-alkyl-2-hydroxyalkyl-1,3-propanediol is trimethylolethane, trimethylolbutane, or trimethylolpropane.

22. The method of claim 15, wherein the 2,2-dihydroxyalkyl-1,3-propanediol is pentaerythritol.

23. The method of claim 15, wherein the engine is an automotive engine, an aeronautic engine, a marine engine or a stationary engine.

24. The method of claim 15, wherein the engine is an Otto, a diesel, a wankel or a jet engine.

25. The method of claim 15, wherein the engine is a 2-stroke engine.

* * * * *