

## PROCESS TO PREPARE A LUBRICATING BASE OIL AND ITS USE

The invention is directed to a process to prepare an iso-paraffinic base oil and use of said base oil products in hydraulic fluid applications and crankcase applications.

5 WO-A-0246333 describes a process to prepare two viscosity grades of base oil by solvent dewaxing a fraction having a T95% point above 621 °C and catalytically dewaxing a fraction having a T95% point of below 621 °C. The two fractions are Fischer-Tropsch  
10 derived fractions. Optionally the heavier or the lower boiling fraction may also be a slack wax, a distillate from crude oil, deasphalted residual stocks from crude oil.

NL-C-1015035 describes a process to prepare a base  
15 oil from a Fischer-Tropsch derived feed by performing a hydroisomerisation step. The effluent of the hydroisomerisation step is distilled and a residue boiling above 380 °C is obtained. This residue is subjected to a catalytic dewaxing treatment using a  
20 catalyst containing platinum and ferrierite.

US-A-6294077 describes a catalytic dewaxing treatment wherein a catalyst is used consisting of ZSM-5 and platinum.

US-A-6025305 discloses a process wherein a Fischer-  
25 Tropsch wax feed is first hydroisomerised. The effluent of the hydroisomerisation is then separated into fuels and lubricants. No pour point reducing treatment is disclosed in this publication.

US-A-2002/0146358 describes a process for  
30 hydroisomerisation of a Fischer-Tropsch derived wax feed. The effluent of the hydroisomerisation step is distilled

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and a bottoms fraction comprising compounds having 20 or more carbon atoms is obtained. This bottoms fraction may be subjected to a catalytic dewaxing treatment.

5 WO-A-0157166 describes the use of a highly paraffinic base oil as obtained from a Fischer-Tropsch wax in a motor engine lubricant formulation. The examples illustrate that such formulations will also consist of an ester, which according to the description of the patent are added to confer additional desired characteristics,  
10 such as additive solvency.

The problem with substantially iso-paraffinic base oils as prepared by the processes described above is that when such base oils are used in, for example, crankcase (gear oil) applications or as part of a hydraulic fluid  
15 wherein the oil contacts seals additional measures have to be taken in order to achieve sufficient swelling of the seals.

The object of the present invention is to provide a process to prepare base oils from a Fischer-Tropsch derived feed wherein the base oils have improved seal  
20 swelling properties.

This object is achieved by the following process. Process to prepare an iso-paraffinic base oil having an improved seal swelling properties by subjecting a mixture  
25 of (i) a petroleum derived feed having a pour point below -5 °C, an aromatic content of between 0 and 20 wt% and a naphthenic compound content of between 15 and 90 wt% and (ii) a Fischer-Tropsch derived feed to a catalytic pour point reducing treatment and wherein the content of the petroleum derived feed (i) in the mixture is between 5  
30 and 50 wt%.

Applicants found that by catalytically dewaxing a mixture as described above an iso-paraffinic base oil is obtained having improved seal swell properties.

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The petroleum-derived feed has a pour point below -5 °C, preferably below -10 °C and more preferably below -15 °C. The petroleum derived feed has an aromatic content of between 0 and 20 wt% and a naphthenic compound content of between 15 and 90 wt%. These contents can be measured by well-known techniques such as the technique described at Example 1 of this specification. The saturates content of the petroleum derived feed is preferably greater than 90 wt%, more preferably greater than 95 wt% and even more preferably greater than 98 wt% and most preferably higher than 99 wt%. The sulphur content is preferably less than 0.03 wt%, more preferably less than 0.01 wt% and even more preferably less than 0.001 wt%. An advantage of using such a typically dewaxed oil having such low contents of sulphur, nitrogen and high contents of saturates is that no additional hydrofinishing is required after performing the pour point reducing step of the process of the present invention. Advantageously the catalytic dewaxing will then not have to be performed at the higher pressure required for the subsequent hydrofinishing. In contrast the process of the present invention may then be performed at a more preferred lower hydrogen pressure range of between 15 and 70 bars.

The petroleum derived feed has preferably been subjected to a hydroprocessing step in order to reduce aromatic, sulphur and nitrogen content of such fractions and improve some of the desired properties such viscosity index. The hydroprocessing step may be a hydrotreating optionally followed by a hydrocracking step. The low pour point is preferably achieved by means of a solvent or more preferably a catalytic dewaxing step. Such processes are for example performed when preparing base oils from a petroleum derived vacuum distillate or de-asphalted oils.

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A very interesting petroleum derived feed are so-called API Group II or Group III base oils as for example prepared by hydroprocessing. Suitable hydroprocessing methods to prepare said base oils are for example described in WO-A-2004053029, WO-A-9801515, US-A-5976354 and WO-A-2004044097. Suitably the base oils are made from the bottoms fraction of a fuels hydrocracker. With a fuels hydrocracker in the context of the present invention is meant a hydrocracker process which main products are naphtha, kerosene and gas oil. The conversion, expressed in the weight percentage of the fraction in the feed to the hydrotreater-hydrocracker which boils above 370 °C which are converted to products boiling below 370 °C, in the hydrotreater-hydrocracker process is typically above 50 wt%. Examples of possible fuels hydrocracker processes, which may yield a bottoms fraction that can be dewaxed to yield the desired base oil, are described in the above referred to EP-A-699225, EP-A-649896, WO-A-9718278, EP-A-705321, EP-A-994173 and US-A-4851109.

Preferably the fuels hydrocracker is operated in two steps, consisting of a preliminary hydrotreating step followed by a hydrocracking step. In the hydrotreating step nitrogen and sulphur are removed and aromatics are saturated to naphthenes

Omitting such a hydrofinishing step is especially possible if the mineral derived dewaxed oils themselves are prepared by means of a process which does include a hydrofinishing step, preferably performed at a hydrogen pressure of above 100 bars. Examples of such hydrofinishing processes are for example those described below.

The oils are preferably made starting from a vacuum distillate or a de-asphalted vacuum residue of a mineral crude oil feedstock or from a waxy feed such as a slack

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wax, wherein the process includes a hydroprocessing step in which the sulphur and polar compounds are reduced to the preferred ranges. The viscosity index is preferably between 80-150, while good results have been achieved with oils having a viscosity index of between 80 and 120.

Preferably the T10wt% recovery point of this oil is between 200 and 450 °C, more preferably between 300 and 420 °C and the T90wt% recovery point is between 300 and 550 °C, more preferably between 400 and 550 °C. By using such a wide boiling oil it has been found possible to reduce the iso-paraffin content of the resultant base oils for both the lower viscosity grades, ranging from 2 cSt at 100 °C kinematic viscosity, to and including the higher viscosity grades having a kinematic viscosity at 100 °C of 15 cSt.

The dewaxed oil can be obtained as such by well known processes as for example described in Chapter 6 of Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker, Inc. New York, 1994, page 119-150. The preferred wide boiling oil can be prepared by mixing various viscosity grades of, preferably API Group II or Group III, base oils. Examples of processes which yield an oil which can be used in this process are described in EP-A-0909304, EP-A-1137741, EP-A-1392799, EP-A-1311651. Examples of suitable dewaxed oils are for example Shell's XHVI-4, XHVI-5.2 and XHVI-8 base oil products or ExxonMobil's Visom base oil grades and mixtures thereof. A possible commercial process which yields base oil for use in this invention is ExxonMobil's MSDW<sup>TM</sup>/MAXSAT<sup>TM</sup> type of process which is said to yield a base oil containing less than 1 wt% aromatics, < 1ppm sulphur, a Viscosity Index of greater than 120 and a pour point of less than -15 °C.

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A more preferred dewaxed oil, which meets the above description, are those obtained when the bottoms fraction of a fuels hydrocracker, as described above, is catalytically dewaxed followed by a hydrofinishing step. Examples of publications describing this route are WO-A-9802502, WO-A-0027950, WO-A-9500604, EP-A-0883664 and EP-A-0863963.

An additional advantage of adding a dewaxed oil as described above to the pour point reducing treatment of the process of the invention is that any undesired compounds in said oil, such as for example residual wax, polars, sulphur or nitrogen, can be further reduced in said treatment. A further advantage is that the boiling range properties, pour point and/or the volatility of the final base oil can be controlled in a simple manner by control of the dewaxing conditions and the optional further distillation of the product obtained in said dewaxing treatment. This is advantageous because it makes possible to use a wide variation of dewaxed oils in the process according to the invention. If for example such oils would have been blended after the dewaxing of a 100% Fischer-Tropsch derived feed and after a final distillation much stringent property specifications, like for example Noack volatility and viscosity, for the mineral derived blending component would have been required. Thus the process according the invention makes it possible to use a wide variation of dewaxed oils having the above properties and obtain a base oil having the desired paraffin content and other desired base oil properties like especially Noack volatility and pour point.

The Fischer-Tropsch derived feed preferably is a hydroisomerized Fischer-Tropsch wax. Such a feed may be obtained by well-known processes, for example the so-called commercial Sasol process, the Shell Middle

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Distillate Synthesis Process or by the ExxonMobil "AGC-21" process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-4943672, US-A-5059299, WO-A-9934917 and  
5 WO-A-9920720. The process will generally comprise a Fischer-Tropsch synthesis and a hydroisomerisation step as described in these publications. Such a process to prepare the hydroisomerised Fischer-Tropsch feed for use as feed in the present process will comprise the  
10 following steps:

- (a) hydrocracking/hydroisomerising a Fischer-Tropsch product,
- (b) separating by means of distillation the product of step (a) into one or more gas oil fractions and a higher  
15 boiling Fischer-Tropsch derived feed according to this invention.

Preferably the Fischer-Tropsch product used as feed in step (a) is a product wherein the weight ratio of compounds having at least 60 or more carbon atoms and  
20 compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms.

Applicants found that by performing the hydro-  
25 cracking/hydroisomerisation step with the relatively heavy feedstock a higher yield of gas oils as calculated on the feed to step (a) can be obtained. A further advantage is that both fuels, for example gas oil, and the Fischer-Tropsch derived feed are prepared in one  
30 hydrocracking/hydroisomerisation process step. In a preferred embodiment of the present invention a fraction boiling above the Fischer-Tropsch derived feed is isolated in step (b) and recycled to step (a).

A further advantage is that by performing step (a) on  
35 the relatively heavy feed a Fischer-Tropsch derived feed

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is prepared which already has a certain content of cyclo-paraffins.

The relatively heavy Fischer-Tropsch product used in step (a) has more preferably at least 50 wt%, and even  
5 more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product is more preferably at least 0.4 and even  
10 more preferably at least 0.50. Preferably the Fischer-Tropsch product comprises a  $C_{20}^+$  fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at  
15 least 0.955.

The initial boiling point of the Fischer-Tropsch product may range up to 400 °C, but is preferably below 200 °C. Preferably any compounds having 4 or less carbon atoms and any compounds having a boiling point in  
20 that range are separated from a Fischer-Tropsch synthesis product before the Fischer-Tropsch synthesis product is used in step (a). The Fischer-Tropsch product as described in detail above is a Fischer-Tropsch product, which has not been subjected to a hydroconversion step as  
25 defined according to the present invention. The content of non-branched compounds in the Fischer-Tropsch product will therefore be above 80 wt%. In addition to the Fischer-Tropsch product also other fractions may be additionally processed in step (a). Possible other  
30 fractions may suitably be the optional higher boiling fraction obtained in step (b) or part of said fraction and/or off-spec base oil fractions as obtained in the pour point reducing treatment of the process of the present invention.

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Such a Fischer-Tropsch product can be obtained by any process, which yields a relatively heavy Fischer-Tropsch product as described above. Not all Fischer-Tropsch processes yield such a heavy product. An example of a  
5 suitable Fischer-Tropsch process is described in WO-A-9934917 and in AU-A-698392. These processes may yields a Fischer-Tropsch product as described above.

The Fischer-Tropsch product will contain no or very little sulphur and nitrogen containing compounds. This is  
10 typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limits, which are currently 2 ppm for sulphur and 1 ppm for nitrogen respectively.

The Fischer-Tropsch product may optionally be subjected to a mild hydrotreatment step in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of the Fischer-Tropsch reaction. Such a hydrotreatment is described in  
15 EP-B-668342. The mildness of the hydrotreating step is preferably expressed in that the degree of conversion in this step is less than 20 wt% and more preferably less than 10 wt%. The conversion is here defined as the weight percentage of the feed boiling above 370 °C, which reacts  
20 to a fraction boiling below 370 °C. After such a mild hydrotreatment lower boiling compounds, having four or less carbon atoms and other compounds boiling in that range, will preferably be removed from the effluent before it is used in step (a).

The hydrocracking/hydroisomerisation reaction of step (a) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being  
25 suitable for this reaction of which some will be described in more detail below. The catalyst may in  
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principle be any catalyst known in the art to be suitable for isomerising paraffinic molecules. In general, suitable hydroconversion catalysts are those comprising a hydrogenation component supported on a refractory oxide carrier, such as amorphous silica-alumina, alumina, fluorided alumina, molecular sieves (zeolites) or mixtures of two or more of these. One type of preferred catalysts to be applied in the hydroconversion step in accordance with the present invention are hydroconversion catalysts comprising platinum and/or palladium as the hydrogenation component. A very much preferred hydroconversion catalyst comprises platinum and palladium supported on an amorphous silica-alumina (ASA) carrier. The platinum and/or palladium is suitably present in an amount of from 0.1 to 5.0% by weight, more suitably from 0.2 to 2.0% by weight, calculated as element and based on total weight of carrier. If both present, the weight ratio of platinum to palladium (calculated as element) may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5. Examples of suitable noble metal on ASA catalysts are, for instance, disclosed in WO-A-9410264 and EP-A-0582347. Other suitable noble metal-based catalysts, such as platinum on a fluorided alumina carrier, are disclosed in e.g. US-A-5059299 and WO-A-9220759. Preferably such catalysts do not comprise a molecular sieve, more preferably such catalysts do not comprise zeolite beta.

A second type of suitable hydroconversion catalysts are those comprising at least one Group VIB metal, preferably tungsten and/or molybdenum, and at least one non-noble Group VIII metal, preferably nickel and/or cobalt, as the hydrogenation component. Usually both metals are present as oxides, sulphides or a combination thereof. The Group VIB metal is suitably present in an amount of from 1 to 35% by weight, more suitably from 5

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to 30% by weight, calculated as element and based on total weight of catalyst. The non-noble Group VIII metal is suitably present in an amount of from 1 to 25 %wt, preferably 2 to 15 %wt, calculated as element and based on total weight of carrier. A hydroconversion catalyst of this type which has been found particularly suitable is a catalyst comprising nickel and tungsten supported on fluorided alumina.

A preferred catalyst which can be used in a non-sulphided form comprises a non-noble Group VIII metal, e.g., iron, nickel, in conjunction with a Group IB metal, e.g., copper, supported on an acidic support. The catalyst has a surface area in the range of 200-500 m<sup>2</sup>/g, preferably 0.35 to 0.80 ml/g, as determined by water adsorption, and a bulk density of about 0.5-1.0 g/ml. The catalyst support is preferably an amorphous silica-alumina where the alumina is present in amounts of less than about 30 wt%, preferably 5-30 wt%, more preferably 10-20 wt%. Also, the support may contain small amounts, e.g., 20-30 wt%, of a binder, e.g., alumina, silica, Group IVA metal oxides, and various types of clays, magnesia, etc., preferably alumina.

The preparation of amorphous silica-alumina microspheres has been described in Ryland, Lloyd B., Tamele, M.W., and Wilson, J.N., Cracking Catalysts, Catalysis: volume VII, Ed. Paul H. Emmett, Reinhold Publishing Corporation, New York, 1960, pp. 5-9.

The catalyst is prepared by co-impregnating the metals from solutions onto the support, drying at 100-150 °C, and calcining in air at 200-550 °C. The Group VIII metal is present in amounts of about 15 wt% or less, preferably 1-12 wt%, while the Group IB metal is usually present in lesser amounts, e.g., 1:2 to about 1:20 weight ratio respecting the Group VIII metal.

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A typical catalyst is shown below:

|   |                                                      |                           |
|---|------------------------------------------------------|---------------------------|
|   | Ni, wt%                                              | 2.5-3.5                   |
|   | Cu, wt%                                              | 0.25-0.35                 |
|   | Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> wt% | 65-75                     |
| 5 | Al <sub>2</sub> O <sub>3</sub> (binder) wt%          | 25-30                     |
|   | Surface Area                                         | 290-325 m <sup>2</sup> /g |
|   | Pore Volume (Hg)                                     | 0.35-0.45 ml/g            |
|   | Bulk Density                                         | 0.58-0.68 g/ml            |

Another class of suitable hydroconversion catalysts are those based on zeolitic materials, suitably comprising at least one Group VIII metal component, preferably Pt and/or Pd, as the hydrogenation component. Suitable zeolitic materials, then, include Zeolite Y, Ultra Stable Y, ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-48, ZSM-35, SSZ-32, ferrierite, zeolite beta, mordenite and silica-aluminophosphates, such as SAPO-11 and SAPO-31 or combinations of catalysts comprising said molecular sieves. Examples of suitable hydroisomerisation catalysts and processes are, for instance, described in WO-A-9201657, WO-A-0107538 or US-A-20040065581.

A process wherein step (b) can be omitted is for example described in US-A-20040065581 and EP-A-1029029. These publication describe the conversion of a narrow boiling Fischer-Tropsch derived wax to a base oil by contacting the feed with a platinum/zeolite beta followed by directly contacting the effluent with a platinum/ZSM-48 or platinum/ZSM-23 dewaxing catalyst. In such a line-up the petroleum derived feed may be advantageously added prior to contacting with the platinum/ZSM-48 or platinum/ZSM-23 catalyst according to the present invention.

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In step (a) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt%, more preferably not more than 70 wt%. The feed as used above in the definition is the total hydrocarbon feed fed to step (a), thus also any optional recycle of the higher boiling fraction as obtained in step (b).

In step (b) the product of step (a) is separated into one or more gas oil fractions and a Fischer-Tropsch derived feed having preferably a T10 wt% boiling point of between 200 and 450 °C. If a higher boiling fraction is separated from the Fischer Tropsch feed the T90 wt% of said feed is preferably between 300 °C, and preferably between 430 and 550 °C. The separation is preferably performed by means of a first distillation at about atmospheric conditions, preferably at a pressure of between 1.2-2 bara, wherein the gas oil product and lower boiling fractions, such as naphtha and kerosine fractions, are separated from the higher boiling fraction

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of the product of step (a). The higher boiling fraction, of which suitably at least 95 wt% boils above 370 °C, may be further separated in a vacuum distillation step wherein a higher boiling fraction is separated. The vacuum distillation is suitably performed at a pressure of between 0.001 and 0.05 bara.

The vacuum distillation of step (b) is preferably operated such that the desired Fischer Tropsch derived feed is obtained boiling in the specified range and having a kinematic viscosity, which relates to the base oil end product(s) specification. The kinematic viscosity at 100 °C of the Fischer Tropsch derived feed is preferably between 3 and 10 cSt.

The mixture of petroleum derived and Fischer-Tropsch derived feeds will suitably have a viscosity corresponding to the desired viscosity of the base oil product. Preferably the kinematic viscosity at 100 °C of the mixture is between 3 and 10 cSt. Suitable distillate fractions have a T10wt% boiling point of between 200 and 450 °C, preferably between 300 and 420 °C and a T90wt% boiling point of between 300 and 550 °C, preferably between 400 and 550 °C. The fraction of petroleum derived feed in the mixture is preferably higher than 5 wt%, more preferably higher than 10 wt% and preferably lower than 50 wt% and more preferably below 30 wt% and even more preferably below 25 wt%. The actual content of petroleum-derived feed in the mixture will of course depend on the paraffin content of said feed. The mixture will preferably contain less than 50 ppm sulphur and/or less than 10 ppm nitrogen.

In a preferred embodiment the Fischer-Tropsch derived feed is partly dewaxed to a pour point close to the pour point of the petroleum derived feed before both feeds are mixed to be further dewaxed to the target pour point. The advantage of this embodiment is that conversion of the

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petroleum feed to distillate or lighter products is thus minimised. With close to the pour point is here meant that the difference between the pour point of the Fischer-Tropsch derived feed and the pour point of the petroleum derived feed is less than 40 °C, preferably less than 20 °C. The pour point is the pour point of the entire feeds to step (b). The reduction of the pour point of the Fischer-Tropsch derived feed is suitably performed by the catalytic dewaxing process here described. More preferably the pre-dewaxing is performed in the top beds of a catalytic dewaxing reactor and the petroleum derived feed is added at an intermediate stage such that the combined feed is dewaxed to its target pour point in the lower beds, i.e. the more downstream beds, of the dewaxing reactor. The volume ratio of dewaxing catalyst in the upper catalyst beds and the lower catalyst bed 1:9 and 9:1, and more preferably between 3:1 and 5:1.

With the catalytic pour point reducing treatment is understood every process wherein the pour point of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

The catalytic dewaxing or pour point reducing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the mixture is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the distillate base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are

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mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminaphosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in  
5 US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of  
10 possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

15 The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The  
20 binder is preferably a porous binder material, for example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-  
25 alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a low acidity refractory oxide binder material which is essentially free of alumina is used. Examples of these binder materials are silica, zirconia, titanium dioxide,  
30 germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and  
35 a low acidity refractory oxide binder material which is

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essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or WO-A-2000029511. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22 as for example described in WO-A-200029511 and EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil. By varying the temperature between 315 and 375 °C at a pressure of between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having different pour point specifications varying from suitably lower than -60 to -10 °C.

Optionally a noble metal guard bed may be positioned just upstream the dewaxing step, for example as a separate catalyst bed in the dewaxing reactor. Such a guard bed is advantageous to remove any remaining sulphur and especially nitrogen compounds present in the feed to the dewaxing process of the present invention. Such a

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guard bed is suitably used when a bottoms fraction of a fuels hydrocracker process is used as the petroleum derived feed. An example of such a process is described in WO-A-9802503, which reference is hereby incorporated by reference.

After performing the pour point reducing treatment lower boiling compounds formed during said treatment are suitably removed, preferably by means of distillation, optionally in combination with an initial flashing step.

The effluent of the pour point reducing treatment may suitably be subjected to a hydrogenation treatment. Hydrogenation may be performed on the entire effluent or on specific base oil grades after the above described fractionation. This may be required in order to reduce the content of aromatic compounds in the reduced pour point product to preferably values of below 1 wt%. Such a hydrogenation is also referred to as a hydrofinishing step. This step is suitably carried out at a temperature between 180 and 380 °C, a total pressure of between 10 to 250 bar and preferably above 100 bar and more preferably between 120 and 250 bar. The WHSV (Weight hourly space velocity) ranges from 0.3 to 2 kg of oil per litre of catalyst per hour (kg/l.h). Preferably a hydrogenation is performed in the same reactor as the catalytic dewaxing reactor. In such a reactor the beds of dewaxing catalyst and hydrogenation catalyst will be placed in a stacked bed on top of each other.

The hydrogenation catalyst is suitably 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 are low acidity amorphous refractory oxides. Examples of suitable amorphous refractory oxides include inorganic oxides,

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such as alumina, silica, titania, zirconia, boria, silica-alumina, fluorided alumina, fluorided silica-alumina and mixtures of two or more of these.

Examples of suitable hydrogenation catalysts are  
5 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  
10 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  
15 amorphous silica-alumina. Examples of suitable silica-  
alumina carriers are disclosed in WO-A-9410263. A  
preferred catalyst comprises an alloy of palladium and  
platinum preferably supported on an amorphous silica-  
alumina carrier of which the commercially available  
20 catalyst C-624 of Criterion Catalyst Company  
(Houston, TX) is an example.

After performing the catalytic pour point reducing  
treatment or after the optional hydrofinishing step  
hydrogen is suitably separated from the dewaxed/  
25 hydrofinished effluent, contacted with a means to remove  
hydrogen sulphide and recycled to said catalytic pour  
point reducing treatment. Such means could be amine  
washing of the hydrogen recycle stream. If the content of  
hydrogen sulphide is expected to be low, for example  
30 below 100 ppm or even below 20 ppm, in the recycle stream  
contacting said stream with a suitable adsorbent will be  
preferred. Examples of suitable heterogeneous adsorbents  
are comprise at least one metal or oxide of the metal,  
the metal(s) being selected from Fe, Ni, Co, Ag, Sn Re,  
35 Mo, Cu, Pt, Pd and Zn. In a preferred embodiment, the

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metal is at least one of Fe, Ni, Co, Cu, and Zn. In a more preferred embodiment the adsorbent is zinc oxide. The adsorbent may be supported on an inorganic support material in order to, for example, increase surface area, pore volume, and pore diameter. Suitable support materials contain at least one inorganic refractory support materials including, but not necessarily limited to, alumina, silica, zirconia, carbon, silicon carbide, kieselguhr, amorphous and crystalline silica-aluminas, silica-magnesias, aluminophosphates, boria, titania, and zinc oxide. Preferred support materials include alumina, zirconia, and silica. The metal(s) or metal oxide(s) may be loaded onto these supports by conventional techniques known in the art. Non-limiting examples of suitable supported metal and metal oxide based regenerable sulfur adsorbents include, but are not necessarily limited to: Co/Al<sub>2</sub>O<sub>3</sub>; Co/SiO<sub>2</sub>; Co/TiO<sub>2</sub>; Co/ZrO<sub>2</sub>; Ni/Al<sub>2</sub>O<sub>3</sub>; Ni/SiO<sub>2</sub>; Ni/ZrO<sub>2</sub>; Cu/Al<sub>2</sub>O<sub>3</sub>; Cu/SiO<sub>2</sub>; Cu/ZrO<sub>2</sub>; Fe/Al<sub>2</sub>O<sub>3</sub>; Fe/SiO<sub>2</sub>; Fe/ZrO<sub>2</sub>; Co/Cu/Al<sub>2</sub>O<sub>3</sub>; Co/Cu/SiO<sub>2</sub>; Ni/Cu/SiO<sub>2</sub>; Ni/Cu/ZrO<sub>2</sub>; Co/Pt/Al<sub>2</sub>O<sub>3</sub>; Co/Pd/SiO<sub>2</sub>; Co/Sn/Al<sub>2</sub>O<sub>3</sub>; Ni/Sn/SiO<sub>2</sub>; Zn/Al<sub>2</sub>O<sub>3</sub>, ZnO/SiO<sub>2</sub>, Co/ZnO; Mo/ZnO; Ni/ZnO; Co/Mo/ZnO; Ni/Mo/ZnO; Pt/ZnO; Pd/ZnO; Pt/Pd/ZnO. The adsorbent may also be employed as a bulk metal oxide or as a bulk metal, including but not necessarily limited to, a finely divided skeleton metal, including Raney metals, ponderous metals, Rieke metals, and metal sponges. The temperature and pressure conditions during said contacting are preferably within the ranges specified for the catalytic pour point reduction.

From the effluent of the pour point reducing treatment and the optional hydrogenation treatment one or more base oil grades may be isolated by means of fractionation. Base oil products having kinematic viscosity at 100 °C of between 2 and 10 cSt, having a

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volatility of between 8 and 11% (according to CEC L40 T87) and a pour point of between -20 and -60 °C (according to ASTM D 97) may advantageously be obtained.

5 The content of paraffins in the base oils as prepared is preferably between 75 and 95 wt% and more preferably less than 90 wt% and more preferably higher than 80 wt%.

The above-described base oil can suitably find use as base oil for an Automatic Transmission Fluids (ATF), motor engine oils, electrical oils or  
10 transformer oils and refrigerator oils. lubricant formulations such as motor engine oils of the 0W-x and 5W-x specification according to the SAE J-300 viscosity classification, wherein x is 20, 30, 40, 50 or 60 may be advantageously made using this base oil.

15 It has been found that lubricant formulations can be prepared with the base oils obtainable by the process of the current invention without the need to add high contents of additional ester or aromatic co-base oils. Preferably less than 15 wt% and more preferably less than  
20 10 wt% of such ester or aromatic co-base oil is present in such formulations.

The Fischer-Tropsch process is sometimes performed at a remote location far away from the end-users of the base oils. It has also been found that for certain  
25 applications the end-users do not necessarily require base oils having the high paraffin contents as prepared by the prior art processes which operate on 100% Fischer-Tropsch derived feed. For these applications blending with mineral derived base oils containing less paraffins  
30 will have to take place such to reduce the paraffin content. It is however not always the case that suitable mineral blending components are found near the end users. As explained above such blending components need to have the right volatility and viscosity to obtain the desired  
35 blend. The present invention solves this problem, wherein

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at the remote location the desired lower paraffin base oils are prepared having the specified volatility and viscosity and in addition pour point and viscosity index from a petroleum derived feed which does not have to meet all the stringent quality properties. Thus a process is obtained wherein for example the petroleum derived feed is obtained from one location and the base oils obtained by the present process are marketed in many different locations. In a preferred embodiment the petroleum derived feed is shipped to the remote location from another location and part of the base oils as made by the present process are shipped to said other location making use of the same vessel. This is advantageous because efficient use of shipping capacity between the two locations is thus achieved.

The base oil as obtained according to the above process has improved seal swell capabilities as compared to base oils which are made exclusively from a Fischer-Tropsch derived feed. This makes the base oil particularly applicable for use in automotive transmission oils. Automotive transmission gear oils are well known applications and are for example described in Lubricants and related products, Dieter Klamann, Verlag Chemie, Basel, 1984 ISBN 3-527-26022-6, Chapter 11.6, pages 279-286. Preferred gear oil applications are passenger car transmission applications, and light and heavy duty diesel transmission applications. Automotive transmission applications of both the manual and automatic change variety as well as continuously variable transmissions of the belt and toroidal type are preferred transmission oil applications. Another preferred use of the base oil as obtained by the present process are as part of a hydraulic fluid composition. Hydraulic fluids are well known applications and are for example described in Lubricants and related products, Dieter Klamann,

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Verlag Chemie, Basel, 1984 ISBN 3-527-26022-6,  
Chapter 11.9, pages 307-330. A preferred use of the base  
oil is in hydraulic oils requiring a high viscosity index  
as described in Lubricants and related products, Dieter  
5 Klamann, Verlag Chemie, Basel, 1984 ISBN 3-527-26022-6,  
Chapter 11.9.5, page 320. The content of the improved  
base oil in these applications and the optional additives  
to be used in such compositions are easily derivable for  
the skilled person based on his or hers knowledge and on  
10 general knowledge as for example disclosed the general  
reference book referred to in this paragraph.

Example 1

12.7 weight parts of a wide boiling dewaxed and  
hydrofinished oil having the properties as listed in  
15 Table 3 was mixed with 87.3 weight parts of a Shell  
MDS waxy Raffinate having the properties listed in  
Table 1. The wide boiling dewaxed and hydrofinished  
oil was prepared by catalytic dewaxing of a bottoms  
fraction of a fuels hydrocracker followed by a  
20 hydrofinising step on the dewaxed effluent. The  
hydrocracker in turn was fed by a vacuum distillate  
of a mineral crude feed.

This blend of API Group II base oils was mixed  
with a Shell MDS waxy Raffinate (No. 1) having the  
25 properties listed in Table 1.

Table 1

| Feed                                | Wide boiling<br>Mineral<br>dewaxed and<br>hydrofinished<br>Oil | Shell MDS<br>Waxy<br>Raffinate<br>1 |
|-------------------------------------|----------------------------------------------------------------|-------------------------------------|
| Density (D20/4)                     | 0.847                                                          | 0.784                               |
| Pour point (°C)                     | -24                                                            | 45                                  |
| Nitrogen (ppmw)                     | < 1                                                            | < 1                                 |
| Sulphur (ppmw)                      | 8                                                              | < 2                                 |
| Kinematic<br>viscosity at<br>100 °C | 4.679                                                          | 5.098                               |
| Initial boiling<br>point (IBP) °C   | 137                                                            | 362                                 |
| IBP-390 °C<br>(wt%)                 | 20.6                                                           | 2.3                                 |
| 390-520 °C<br>(wt%)                 | 67.9                                                           | 88.4                                |
| 520 °C - FBP<br>(wt%)               | 11.5                                                           | 9.3                                 |
| Final boiling<br>point (FBP) °C     | 600                                                            | 573                                 |
| Wax<br>content (wt%)                | No wax                                                         | 27.1(*)                             |

(\*) as measured after solvent dewaxing at -27 °C.

The above blend was contacted with a dewaxing catalyst consisting of 0.7 wt% platinum, 25 wt% ZSM-12 and a silica binder. The dewaxing conditions were 40 bar hydrogen, WHSV = 1 kg/l.h, and a hydrogen gas rate of 700 Nl/kg feed. The experiment was carried out at two different reaction temperatures, namely 317 °C.

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From the effluent of the dewaxing step a base oil boiling between 400 and 470 °C was isolated from lower and higher boiling products. The yield of this fraction was 40 wt% on the blended feed. The pour point was  
5 -30 °C, the Kinematic viscosity at 100 °C was 4,059 cSt and the Viscosity Index was 129. The composition of this fraction was analysed using the following technique.

The cyclo-paraffin (naphthenic compounds) content in this mixture of cyclo-, normal and iso-paraffins is  
10 measured by the following method. Any other method resulting in the same results may also be used. The base oil sample is first separated into a polar (aromatic) phase and a non-polar (saturates) phase by making use of a quantitative high performance liquid chromatography  
15 (HPLC) method IP368/01, wherein as mobile phase pentane is used instead of hexane as the method states. The saturates and aromatic fractions are then analyzed using a Finnigan MAT90 mass spectrometer equipped with a Field desorption/Field Ionisation (FD/FI) interface, wherein FI  
20 (a "soft" ionisation technique) is used for the quantitative determination of hydrocarbon types in terms of carbon number and hydrogen deficiency of this particular base oil fraction. The instrument conditions to achieve such a soft ionization technique are a source  
25 temperature of 30 °C, an extraction voltage of 5kV, an emitter current of 5mA and a probe temperature ramp of 40 °C to 400 °C (20 °C/min)

The type classification of compounds in mass spectrometry is determined by the characteristic ions  
30 formed and is normally classified by "z number". This is given by the general formula for all hydrocarbon species:  $C_nH_{2n+z}$ . Because the saturates phase is analysed separately from the aromatic phase it is possible to determine the content of the different (cyclo)-paraffins

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having the same stoichiometry. The results of the mass spectrometer are processed using commercial software (poly 32; available from Sierra Analytics LLC, 3453 Dragoo Park Drive, Modesto, Calif. GA95350 USA) to  
5 determine the relative proportions of each hydrocarbon type and the average molecular weight and polydispersity of the saturates and aromatics fractions.

For the base oil fraction boiling between 400 and 470 °C as obtained above the composition was determined  
10 using the above technique. The base oil consisted of 83 wt% paraffins, 16 wt% naphthenic compounds and 1 wt% polar compounds.

#### Example 2

30 ml of the base oil as obtained in Example 1 and an  
15 2 mm thickness size elastomer strip (nitrile rubber NBR) submersed in said oil was kept for 168 hours at 100 °C. After 168 hours the average volume and hardness was measured and compared to its initial values. See Table 2 for results.

#### 20 Comparative Example A

Example 2 was repeated except that instead of the base oil of Example 1 a base oil was used which was exclusively obtained from a hydroisomerised and catalytically dewaxed Fischer-Tropsch wax. The pour  
25 point, viscosity and viscosity index of this oil was as the oil of Example 1. The base oil consisted of 92 wt% of paraffins. See Table 2 for results.

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Table 2

|                  |                                 | Example 2 | Comparative A |
|------------------|---------------------------------|-----------|---------------|
| Average volume   | Initial<br>(g/cm <sup>3</sup> ) | 0.8274    | 0.8122        |
|                  | Final<br>(g/cm <sup>3</sup> )   | 0.8534    | 0.8343        |
| Change           | %                               | 3.1       | 2.7           |
| Average hardness | Initial*                        | 84        | 83            |
|                  | Final                           | 81        | 81            |
| Change           | %                               | -3.6      | -2.0          |

(\*) as measured by BS903:Part A16:1987/ISO 1817-1985

The results in Table 2 show that the base oil of Example 1 has improved seal swell capabilities.

#### Example 3

5 A partly dewaxed Fischer-Tropsch derived feed was prepared by contacting a Waxy Raffinate feed (No. 2) having the properties as listed in Table 3 with the dewaxing catalyst used in Example 1 at 'first' dewaxing conditions. The 'first' dewaxing conditions were 40 bar hydrogen, 306 °C reactor temperature, WHSV = 1.67 kg/l.h, 10 and a hydrogen gas rate of 750 Nl/kg feed. The effluent was analysed as reported in Table 3.

88.5 weight parts of the partly dewaxed Fischer-Tropsch feed was blended with 11.5 weight parts of a wide boiling dewaxed and hydrofinished oil having the 15 properties as listed in Table 3.

The difference in pour point of the partly dewaxed Fischer-Tropsch feed and the Wide boiling Mineral dewaxed and hydrofinished Oil-2 was +6 °C.

Table 3

| Feed                                    | Waxy<br>Raffinate<br>2 | Wide boiling<br>Mineral<br>dewaxed and<br>hydrofinished<br>Oil-2 | Partly dewaxed<br>Fischer-<br>Tropsch feed |
|-----------------------------------------|------------------------|------------------------------------------------------------------|--------------------------------------------|
| Density<br>(D20/4)                      | 0.784                  | 0.863                                                            | 0.814                                      |
| Pour point<br>(°C)                      | +42                    | -15                                                              | -9                                         |
| Nitrogen<br>(ppmw)                      | <1                     | <1                                                               | <1                                         |
| Sulphur<br>(ppmw)                       | <2                     | 33                                                               | <2                                         |
| Kinematic<br>viscosity<br>at 100 °C     | 5.12                   | 6.99                                                             | 4.6                                        |
| Initial<br>boiling<br>point (IBP)<br>°C | 356                    | 341                                                              | 203                                        |
| IBP-390 °C<br>(wt%)                     | 6                      | 8.8                                                              | 11.3                                       |
| 390-520 °C<br>(wt%)                     | 82                     | 85.2                                                             | 78.3                                       |
| 520 °C -<br>FBP (wt%)                   | 12                     | 6                                                                | 10.4                                       |
| Final<br>boiling<br>point (FBP)<br>°C   | 565                    | 559                                                              | 565                                        |
| Wax<br>content (wt%)                    | 18.2(*)                | No wax                                                           | Not analysed                               |

(\*) as measured after solvent dewaxing at -27 °C.

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5 The blended feed as prepared above was contacted with the dewaxing catalyst used in Example 1. The 'second' dewaxing conditions were 40 bar hydrogen, 315 °C reactor temperature, WHSV = 2.83 kg/l.h, and a hydrogen gas rate of 500 Nl/kg feed.

10 From the effluent of the second dewaxing step, the 400 and 470 °C fraction was obtained with a yield of 42 wt% as calculated on the original Shell MDS waxy Raffinate and on the Wide boiling Mineral dewaxed and hydrofinished Oil-2 of Table 3.

The pour point of fraction boiling above 50 °C was -30 °C, the cloud point was -24 °C, the Kinematic viscosity at 100 °C was 4.103 cSt.

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C L A I M S

1. Process to prepare an iso-paraffinic base oil having an improved seal swelling properties by subjecting a mixture of (i) a petroleum derived feed having a pour point below  $-5^{\circ}\text{C}$ , an aromatic content of between 0 and 20 wt% and a naphthenic compound content of between 15 and 90 wt% and (ii) a Fischer-Tropsch derived feed to a catalytic pour point reducing treatment and wherein the content of the petroleum derived feed (i) in the mixture is between 5 and 50 wt%.
2. Process according to claim 1, wherein the content of sulphur in the mixed feed to the pour point reducing treatment is below 50 ppm and the content of nitrogen in the mixed feed to the pour point reducing treatment is below 10 ppm.
3. Process according to any one of claims 1-2, wherein the petroleum derived feed has a saturates content of greater than 98 wt% a viscosity index of between 80 and 150 and a sulphur content of below 0.001 wt%.
4. Process according to any one of claims 1-3, wherein the petroleum derived feed has been obtained in a process involving a hydrofinishing step performed at a hydrogen pressure of greater than 100 bars.
5. Process according to any one of claims 1-4, wherein the base oil is hydrogenated after performing the pour point reducing treatment such that the content of aromatics is below 1 wt%.
6. Process according to any one of claims 1-5, wherein the catalytic pour point reducing treatment is a catalytic dewaxing process performed in the presence of a catalyst comprising a Group VIII metal and an

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intermediate pore size zeolite having pore diameter between 0.35 and 0.8 nm, and a binder.

5 7. Process according to any one of claims 1-6, wherein the difference in pour point of the Fischer-Tropsch derived feed and the petroleum derived feed is less than 40 °C.

8. Process according to claim 7, wherein the difference in pour point of the Fischer-Tropsch derived feed and the petroleum derived feed is less than 20 °C.

10 9. Process according to any one of claims 1-8, wherein after performing the catalytic pour point reducing treatment hydrogen is separated from the dewaxed effluent, contacted with a heterogeneous adsorbent selective for removing hydrogen sulphide and recycled to  
15 said catalytic pour point reducing treatment.

10. Process according to claim 9, wherein the heterogeneous adsorbent is zinc oxide.

11. Process according to any one of claims 1-10, wherein the Fischer-Tropsch feed is obtained by  
20 hydroisomerisation of a Fischer-Tropsch product.

12. Process according to claim 11, wherein the hydroisomerised Fischer-Tropsch feed is obtained by means of the following steps:

25 (a) hydrocracking/hydroisomerising a Fischer-Tropsch product,

(b) separating by means of distillation the product of step (a) into one or more gas oil fractions and a higher boiling Fischer-Tropsch derived feed.

13. Process according to claim 12, wherein the Fischer-Tropsch product used as feed in step (a) is a product  
30 wherein the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.4 and wherein at least 30 wt% of compounds in the  
35 Fischer-Tropsch product have at least 30 carbon atoms.

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14. Use of the base oil as obtained by the process according any one of claims 1-13 in a gear oil application.

5 15. Use of the base oil as obtained by the process according any one of claims 1-13 in a hydraulic oil application.