

## **LUBE BASESTOCK WITH IMPROVED LOW TEMPERATURE PROPERTIES**

### **FIELD OF THE INVENTION**

[0001] This invention relates to base stocks and base oils with improved low temperature properties and formulated lubricant compositions or functional fluids created by blending at least one such lube basestock with at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors.

### **BACKGROUND OF THE INVENTION**

[0002] Historically, lubricating oil products for use in many applications have used additives to impart specific properties to the finished oils to augment the properties of the basestocks used to prepare the finished products. With the advent of more demanding test requirements, the performance requirements for the basestocks themselves have increased. The American Petroleum Institute (API) definition of a Group II basestock is one that has a saturates content of at least 90%, a sulfur content of 0.03 wt.% or less and a viscosity index (VI) between 80 and 120. Similarly, the API definition of a Group III basestock is one that has a saturates content of at least 90%, a sulfur content of 0.03 wt% or less, and a viscosity index of 120 or greater. Currently, there is a trend in the lube oil market to use increasing amounts of Group II and III basestocks to replace the traditionally used Group I basestocks in order to meet the demand for higher quality finished lubricants and meet more stringent requirements for improved oxidative stability, reduced deposits, reduced evaporative emissions, superior low temperature performance, controlled wear performance, improved fuel economy, and compatibility with aftertreatment devices.

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[0003] While Group II and Group III basestocks provide some of the attributes desired, further improvements in many properties, particularly low temperature quality, as well as combinations of properties, such as superior low temperature fluidity at low product volatility, continue to challenge the industry. Benefits in basestock low temperature performance would be beneficial for a wide range of formulated lubricants and would be particularly advantageous for passenger vehicle crankcase oils, automatic transmission fluids, automotive gear oils, hydraulic fluids, and commercial vehicle crankcase oils.

[0004] Low temperature quality for basestocks and base oils have historically been controlled using bulk property measurements such as pour point measured on the basestock, base oils, or formulated oil composition. However, small amounts of residual wax may not impact this bulk property measurement and thus, small amounts of residual wax may go undetected through this analysis. This small amount of residual wax, however, does negatively impact performance and can lead to issues such as crankcase oil gelling and loss of fluidity. Operating an engine in this scenario can lead to engine damage. Hence, the Mini-Rotary Viscometer (MRV) test was established to protect engines under cold weather conditions. The MRV test temperature is set by the Society of Automotive Engineers (SAE) J-300 Viscosity Classification system for each multigrade engine oil grade.

[0005] To improve the low temperature performance as measured by the MRV or other tests sensitive to very small amounts of residual wax, refineries utilizing solvent dewaxing can dewax to lower pour points. While this can be somewhat effective, it may not be as effective as needed. Catalytic dewaxing, a relatively newer processing approach, is often more effective

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than solvent dewaxing, especially for the light and medium neutral stocks. However, many existing refineries in operation today utilize solvent dewaxing only and do not have a reactor available for catalytic dewaxing which often requires significant quantities of hydrogen provided at high pressure.

[0006] As the demand for quality formulated lubricant oils continues to increase, the search for better basestocks produced from new and different processes, catalysts, and catalyst systems that exhibit improved quality and performance at high activity and yield is a continuous, ongoing exercise. Therefore, there is a need in the lube oil market to provide lube basestocks, that when formulated into a finished oil, can help to meet the demand for improved low temperature properties.

#### **SUMMARY OF THE INVENTION**

[0007] This invention relates to basestocks with superior low temperature properties and formulated lubricant compositions or functional fluids created by blending at least one such lube basestock with at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors.

[0008] In particular the invention relates to a dewaxed lube basestock having a Free Carbon Index of less than 4.3 and an Epsilon Carbon mole% of less than 14%. In other embodiments it relates to dewaxed lube basestocks having a Free Carbon Index of less than 4.3 and an Epsilon Carbon mole% of less than 14% or a dewaxed lube basestock having a Free Carbon Index of less than 4.3 and an Epsilon Carbon mole% of less than 14%, or a dewaxed lube basestock wherein the Pour Point is between -6 °C and -30 °C.

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[0009] In other embodiments the lube basestock is prepared by a process comprising

- a. solvent dewaxing a lube oil boiling range feedstream in a solvent dewaxing stage operated under effective solvent dewaxing conditions thereby producing at least a partially dewaxed fraction; and
- b. contacting said partially dewaxed fraction with a hydrodewaxing catalyst in the presence of a hydrogen-containing treat gas in a reaction stage operated under effective hydrodewaxing conditions thereby producing a reaction product comprising at least a gaseous product and liquid product, wherein said liquid product comprises a dewaxed lube basestock. In other embodiments said hydrodewaxing catalyst is selected from ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, Beta, SSZ-31, SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, fluorided alumina, silica-alumina, fluorided silica alumina, synthetic Ferrierites, Mordenite, Offretite, Erionite, Chabazite, and mixtures thereof under effective catalytic dewaxing conditions.

[0010] In yet other embodiments said hydrodewaxing catalyst comprises a zeolite selected from ZSM-48, ZSM-22 and ZSM-23. In yet other embodiments said hydrodewaxing catalyst further comprises at least one metal hydrogenation component, which is selected from Group VI metals, Group VIII metals, or mixtures thereof and contains at least one Group VIII noble metal.

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[0011] Other embodiments of the invention relate to a formulated oil comprising:

- a. a major amount of at least one dewaxed lube basestock according to the embodiments described above and ,
- b. at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors.

[0012] Other embodiments include an engine oil according to the above embodiments wherein said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 30,000 cP, or has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP, or has a Mini Rotary Viscometer viscosity from about 12,000 cP to about 20,000 cP.

[0013] In yet other embodiments the invention relates to an engine oil comprising:

- a) at least 60 % by weight of the total composition of a dewaxed lube basestock having a Free Carbon Index of from 3.0 to 4.3 and an Epsilon Carbon mole% from 10.0% to 14.0% and wherein the kinematic viscosity at 100°C is between 3 cSt and 7 cSt, the Viscosity Index is between 95 and 150, and the Pour Point is between -6 °C and -30 °C
  - b) at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors, and
- wherein the said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP.

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[0014] In yet other embodiments the invention relates to an engine oil comprising:

- a) at least 60% by weight of the total composition of a dewaxed lube basestock having a Free Carbon Index of from 3.0 to 4.3 and an Epsilon Carbon mole% from 10.0% to 14.0% and wherein the kinematic viscosity at 100°C is between 3 cSt and 7 cSt, the Viscosity Index is between 95 and 150, and the Pour Point is less than -6 °C and wherein said dewaxed lube basestock is prepared by a process comprising
    - (i) solvent dewaxing a lube oil boiling range feedstream in a solvent dewaxing stage operated under effective solvent dewaxing conditions thereby producing at least a partially dewaxed fraction; and
    - (ii) contacting said partially dewaxed fraction with a hydrodewaxing catalyst in the presence of a hydrogen-containing treat gas in a reaction stage operated under effective hydrodewaxing conditions thereby producing a reaction product comprising at least a gaseous product and liquid product, wherein said liquid product comprises a dewaxed lube basestock.
  - b) at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors, and
- wherein the said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP.

[0015] In yet other embodiments the invention relates to an engine oil comprising:

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- a) at least 60% by weight of the total composition of a dewaxed lube basestock having a Free Carbon Index of from 3.0 to 4.3 and an Epsilon Carbon mole% from 10.0% to 14.0% and wherein the kinematic viscosity at 100°C is between 3 cSt and 7 cSt, the Viscosity Index is between 95 and 150, and the Pour Point is less than -6°C and wherein said dewaxed lube basestock is prepared by a process comprising
- (i) solvent dewaxing a lube oil boiling range feedstream in a solvent dewaxing stage operated under effective solvent dewaxing conditions thereby producing at least a partially dewaxed fraction; and
  - (ii) contacting said partially dewaxed fraction with a hydrodewaxing catalyst in the presence of a hydrogen-containing treat gas in a reaction stage operated under effective hydrodewaxing conditions thereby producing a reaction product comprising at least a gaseous product and liquid product, wherein said liquid product comprises a dewaxed lube basestock.
- b) at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors, and wherein the said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP.

**[0016]** In yet other embodiments the invention relates to a method of formulating an engine oil comprising blending a dewaxed lube basestock as characterized in the previously described embodiments with at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction

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modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors.

#### **DETAILED DESCRIPTION OF THE INVENTION**

[0017] This invention relates to basestocks and base oils with superior low temperature properties and formulated lubricant compositions or functional fluids created by blending at least one such lube basestock with at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors.

[0018] It should be noted that the terms "feedstock" and "feedstream" can be used interchangeably herein.

[0019] Tests used in describing lubricant compositions of this invention are:

- (a) MRV viscosity measured by Mini-Rotary Viscometer Test (ASTM D4684);
- (b) CCS viscosity measured by Cold Cranking Simulator Test (ASTM D5293);
- (c) Noack volatility (or evaporative loss) correlated from Simulated Distillation by Gas Chromatography using ASTM D2887 or measured directly by ASTM D5800;
- (d) Viscosity index (VI) measured by ASTM D2270;
- (e) Kinematic viscosity measured by ASTM D445
- (f) Pour point (ISL) as measured by ASTM D5950.

[0020] Lube basestocks in the present invention can also be described as those lube basestocks having a Free Carbon Index (FCI) of less than 4.3, preferably less than 4.1 or from 3.0 to 4.3, preferably from 3.0 to 4.1, and an Epsilon Carbon content (mole%) of less than 14%, preferably less than 13.3. The FCI can be measured by the method described in, for example, United States Patent Number 6,676,827. The FCI is further explained as follows. The basestock is analyzed by  $^{13}\text{C}$  NMR using a 400 MHz spectrometer. At this magnetic field strength, all normal paraffins with carbon numbers greater than  $\text{C}_9$  have only five non-equivalent NMR absorptions corresponding to the terminal methyl carbons (alpha), as well as methylenes from the second, third and fourth positions from the molecular ends (beta, gamma, and delta respectively), and the other carbon atoms along the backbone which have a common chemical shift (epsilon). For normal paraffins, the intensities of the alpha, beta, gamma and delta are equal and the intensity of the epsilon depends on the length of the molecule. Similarly, the side branches on the backbone of an iso-paraffin have distinctive chemical shifts; the presence of a side chain causes a measurable shift at the tertiary carbon (branch point) on the backbone to which it is anchored. Further, it also perturbs the chemical sites within three carbons from this branch point imparting unique chemical shifts (alpha, beta, and gamma).

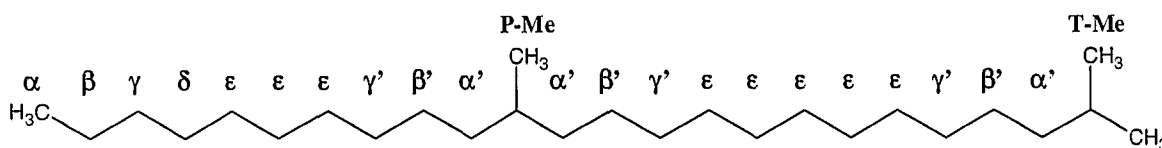
[0021] The Free Carbon Index (FCI) is then defined as the product of the carbon mole percent of epsilon methylenes measured from the overall carbon species in the  $^{13}\text{C}$  NMR spectrum of a basestock and, the average carbon Number (CN) of the basestock as calculated from the equation below:

$$\text{CN} = \frac{200}{\alpha - \text{PBu} + \text{TMe} + \text{TEt} + \text{TPr} + \text{TBu}}$$

where the values for  $\alpha$ ,  $\text{PBu}$ ,  $\text{TMe}$ ,  $\text{TEt}$ ,  $\text{TPr}$ , and  $\text{TBu}$  are in units of carbon mole percent.

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[0022] For example, the FCI can be further explained as follows. Since particular structural types have characteristic spectral features, the FCI method of data processing provides a description of the average molecular structure of the normal and branched paraffins in a sample. Among the figures of merit that result from this analysis are the average carbon number of the sample (CN), the number of side chains (NS), and the free carbon index (FCI). The FCI is defined as the number of carbons that are more than four carbons away from a chain end or more than three carbons away from a branch point on a hydrocarbon backbone; these carbons are also labeled as epsilon, ("ε") in the drawing below. In practice, FCI represents the product of the CN and the mole percentage contribution of epsilon to the NMR spectrum.



[0023] As an example, the above structure illustrates some of the nomenclature associated with this analysis. For this illustrative molecule, CN = 26, NS = 2, and FCI = 8. While the above molecule represents a pure compound, lube basestocks consist of extremely complex mixtures of molecules. However, since the structural components such as alpha, beta, gamma, etc. listed above (in addition to other structural pieces not included above) exhibit characteristic and repeatable spectral signals, NMR allows for a statistically averaged structural characterization of the ensemble. Epsilon and FCI represent the most pertinent features of the NMR analysis.

[0024] As stated above, the formulated lubricant compositions of the instant invention also comprise at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction

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additives, viscosity index improvers, pour point depressants, and foam inhibitors. The at least one component selected from the above described list, can be any of these components known. For example, dispersants suitable for use in the present formulated engine oils can be any dispersants used in formulated engine oils; detergents suitable for use in the present lubricant products can be selected from any detergents used in formulated oils, etc.

[0025] The formulated engine oils of the instant invention can also be described as possessing a Mini Rotary Viscometer ("MRV") viscosity less than 30,000 cP, preferably from about 10,000 cP to about 30,000 cP, more preferably from about 10,000 cP to about 25,000 cP and most preferably from about 12,000 cP to about 20,000 cP.

[0026] The lube oil basestock can be produced by a process comprising solvent dewaxing a lube oil boiling range feedstream under conditions effective at producing at least a partially dewaxed fraction. The partially dewaxed fraction is then contacted with a catalytic hydrodewaxing catalyst in the presence of hydrogen containing treat gas in a reaction stage operated under effective catalytic hydrodewaxing conditions thereby producing a reaction product comprising at least a gaseous product and liquid product comprising a lube basestock. A lube oil boiling range feed stream is first contacted in a first reaction stage with a hydroprocessing catalyst, in the presence of a hydrogen containing treat gas, under effective hydroprocessing conditions thereby producing at least a liquid hydroprocessed lube oil product. The hydroprocessed lube oil product is then conducted to the solvent dewaxing zone. Also, in some embodiments of the instant invention, separation stages are employed to separate gaseous and liquid reaction products, dewaxing solvent from the dewaxed product, etc.

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[0027] As stated above, the formulated oils comprise at least one lube oil basestock, and the lube oil basestocks suitable for use as a component in the presently claimed formulated oils are produced by a specific process. Lube oil boiling range feedstocks suitable for use in creating the at least one lube oil basestock are wax-containing feeds that boil in the lubricating oil range. These lube oil boiling range feedstocks typically having a 10% distillation point greater than 650°F (343°C), measured by ASTM D 86 or ASTM 2887, and are derived from mineral sources, synthetic sources, or a mixture of the two. Non-limiting examples of suitable lubricating oil feedstocks include those derived from sources such as oils derived from solvent refining processes such as raffinates, partially solvent dewaxed oils, deasphalted oils, distillates, vacuum gas oils, coker gas oils, slack waxes, foots oils and the like, dewaxed oils, Fischer-Tropsch waxes and GTL materials.

[0028] GTL materials are materials that are derived via one or more synthesis, combination, transformation, rearrangement, and/or degradation/deconstructive processes from gaseous carbon-containing compounds, hydrogen-containing compounds, and/or elements as feedstocks such as hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. GTL base stocks and base oils are GTL materials of lubricating viscosity that are generally derived from hydrocarbons, for example waxy synthesized hydrocarbons, that are themselves derived from simpler gaseous carbon-containing compounds, hydrogen-containing compounds and/or elements as feedstocks. GTL base stocks and base oils include wax isomerates, comprising, for example, hydroisomerized or isodewaxed synthesized waxy hydrocarbons, hydroisomerized or isodewaxed Fischer-Tropsch (F-T) material (i.e., hydrocarbons, waxy hydrocarbons, waxes and possible analogous oxygenates), preferably hydroisomerized or isodewaxed F-

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T waxy hydrocarbons or hydroisomerized or isodewaxed F-T waxes, hydroisomerized or isodewaxed synthesized waxes, or mixtures thereof. The term GTL base stocks and base oil further encompass the aforesaid base stock and base oils in combination with other hydroisomerized or isodewaxed materials comprising for example, hydroisomerized or isodewaxed mineral/petroleum-derived hydrocarbons, hydroisomerized or isodewaxed waxy hydrocarbons, or mixtures thereof, derived from different feed materials including, for example, waxy distillates such as gas oils, waxy hydrocracked hydrocarbons, lubricating oils, high pour point polyalphaolefins, foots oil, normal alpha olefin waxes, slack waxes, deoiled waxes, and microcrystalline waxes.

[0029] These lube oil boiling range feedstocks suitable may also have high contents of nitrogen- and sulfur-contaminants. Sulfur and nitrogen contents may be measured by standard ASTM methods D5453 and D4629, respectively.

[0030] The process used to produce lube basestocks suitable for use in the present formulated oils involves solvent extracting a lube oil boiling range feedstock in a solvent dewaxing stage operated under effective solvent dewaxing conditions thereby producing at least a partially dewaxed fraction. The solvent dewaxing step typically involves mixing a lube oil boiling range feedstock with a dewaxing solvent at atmospheric pressure, separating precipitated wax and recovering solvent for recycling. During the solvent dewaxing step, the lube oil boiling range feedstock is mixed with chilled solvent to form an oil-solvent solution and precipitated wax is thereafter separated by, for example, filtration. The temperature and solvent are selected so that the oil is dissolved by the chilled solvent while the wax is precipitated. Thus, one embodiment of the process used to create lube basestocks suitable for use herein involves separating, by any suitable separation means, the

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solvent and partially dewaxed fraction, recovering the partially dewaxed fraction and conducting the partially dewaxed fraction to a catalytic hydrodewaxing reaction stage. It should be noted that because solvent dewaxing typically occurs at atmospheric pressure, it may be necessary to pressurize the partially dewaxed fraction prior to the catalytic dewaxing step.

[0031] A particularly suitable solvent dewaxing step involves the use of a cooling tower where solvent is prechilled and added incrementally at several points along the height of the cooling tower. The lube oil boiling range feedstream-solvent mixture is agitated during the chilling step to permit substantially instantaneous mixing of the prechilled solvent with the lube oil boiling range feedstream. The prechilled solvent is added incrementally along the length of the cooling tower so as to maintain an average chilling rate at or below 10°F /minute, usually between about 1 to about 5°F/minute. The final temperature of the lube oil boiling range feedstream-solvent/precipitated wax mixture in the cooling tower will usually be between 0 and 50°F (-17.8 to 10°C). The mixture may then be sent to a scraped surface chiller to separate precipitated wax from the mixture.

[0032] Generally, effective solvent dewaxing conditions will include that amount of solvent that when added to the lube oil boiling range feedstream will be sufficient to provide a liquid/solid weight ratio of about 5/1 to about 20/1 at the dewaxing temperature and a solvent/oil volume ratio between 1.5/1 to 5/1. The solvent dewaxing of the lube oil boiling range feedstream typically results in a partially dewaxed fraction having a pour point from about +30°C to about -20°C. The benefits observed were seen whether the solvent dewaxing step was very mild and removed very little wax leaving a higher intermediate pour point stream or the solvent dewaxing step was more severe and removed most of the wax leaving a lower intermediate pour point stream.

[0033] Representative dewaxing solvents are aliphatic ketones having 3-6 carbon atoms such as methyl ethyl ketone and methyl isobutyl ketone, low molecular weight hydrocarbons such as propane and butane, and mixtures thereof. The solvents may be mixed with other solvents such as benzene, toluene or xylene. Further descriptions of solvent dewaxing process useful herein are disclosed in U.S. Patents 3,773,650 and 3,775,288, which are incorporated herein in their entirety.

[0034] The partially dewaxed fraction from the solvent dewaxing step is subjected to a catalytic dewaxing step to remove at least a portion of any wax remaining in the partially dewaxed fraction. This step is commonly used to further lower the pour point of the partially dewaxed fraction. The sequence of solvent dewaxing followed by catalytic dewaxing is designated as trim dewaxing when the catalytic dewaxing stage removes and isomerizes a relatively small amount of wax as opposed to the solvent dewaxing step.

[0035] During the catalytic hydrodewaxing step, the partially dewaxed fraction is contacted with a catalytic hydrodewaxing catalyst in the presence of a hydrogen containing treat gas in a reaction stage operated under effective catalytic hydrodewaxing conditions. Effective catalytic hydrodewaxing conditions as used herein includes temperatures between about 200°C to about 350°C, preferably about 250°C to about 325°C, more preferably 250 to 320°C, pressures between about 2,860 to about 20,786 kPa (about 400 to about 3,000 psig), preferably about 4,238 to about 17,338 kPa (about 600 to about 2,500 psig), preferably about 4,238 to about 10,443 kPa (about 600 to about 1,500 psig) hydrogen treat gas rates of about 89 to about 890 m<sup>3</sup>/m<sup>3</sup> (about 500 to about 5,000 SCF H<sub>2</sub>/B), preferably about 107 to about 445 m<sup>3</sup>/m<sup>3</sup> (about 600 to about 2,500 SCF H<sub>2</sub>/B), and liquid hourly space

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velocities ("LHSV") of about 0.1 to about 10 V/V/hr, preferably about 0.1 to about 5 V/V/hr, more preferably about 0.5 to about 2 V/V/hr. Operating the catalytic hydrodewaxing under these narrow, less severe, catalytic hydrodewaxing conditions, the catalytic hydrodewaxing stage reaction stage operates to convert trace paraffins that impair low temperature properties of the partially dewaxed fraction at a low yield loss while still maintaining the key lube basestock properties such as pour point, viscosity, viscosity index ("VI"), and volatility of the partially dewaxed fraction resulting from the solvent-dewaxing operation described herein. Therefore, effective catalytic hydrodewaxing conditions, as used herein, are to be considered those catalytic hydrodewaxing conditions as described above that result in a lube basestock having a VI within about 0 to about 30 points of the partially dewaxed fraction, a pour point within about 0 to about -50°C of the partially dewaxed fraction, and in a yield loss of about 0 to about 20 wt. In all cases the effective catalytic hydrodewaxing stage follows the solvent dewaxing stage.

**[0036]** Catalytic hydrodewaxing catalysts suitable for use in the trim dewaxing step may be either crystalline or amorphous. Amorphous catalytic hydrodewaxing catalysts include alumina, fluorided alumina, silica-alumina, fluorided silica-alumina. Such catalysts are described for example in US Patent Nos. 4,900,707 and 6,383,366.

**[0037]** Crystalline materials are molecular sieves that contain at least one 10 or 12 ring channel and may be based on aluminosilicates (zeolites) or on aluminophosphates such as silicoaluminophosphates (SAPOs) and MAPOs. Molecular sieves suitable for use herein contain at least one 10 or 12 channel. Examples of such zeolites include ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, ferrierite, ITQ-13, MCM-68 and MCM-71. Examples of aluminophosphates containing at least one 10 ring channel include ECR-42. Examples of molecular sieves containing 12 ring channels include zeolite

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beta, and MCM-68. Some molecular sieves suitable for use herein are described in US Patent Numbers 5,246,566, 5,282,958, 4,975,177, 4,397,827, 4,585,747, 5,075,269 and 4,440,871. MCM-68 is described in U.S. Patent 6,310,265. MCM-71 and ITQ-13 are described in PCT published applications WO 0242207 and WO 0078677. ECR-42 is disclosed in US 6,303,534. Suitable SAPOs for use herein include SAPO-11, SAPO-31, SAPO-41, and suitable MAPOs include MAPO-11. SSZ-31 is also a catalyst that can be effectively used herein.

**[0038]** It is preferred that the catalytic hydrodewaxing catalyst used herein be a zeolite. Preferred zeolite catalytic hydrodewaxing catalysts suitable for use herein include ZSM-48, ZSM-22 and ZSM-23. The molecular sieves are preferably in the hydrogen form.

**[0039]** Preferably, the catalytic hydrodewaxing catalyst selected would contain a metal hydrogenation component and be bifunctional, i.e., they are loaded with at least one metal hydrogenation component, which is selected from Group VI metals, Group VIII metals, and mixtures thereof. Preferred metals are selected from Group VIII metals. Especially preferred are Group VIII noble metals such as Pt, Pd or mixtures thereof. These metals are loaded at the rate of 0.1 to 30 wt.%, based on catalyst. Catalyst preparation and metal loading methods are described for example in U.S. Patent 6,294,077, and include for example ion exchange and impregnation using decomposable metal salts. Metal dispersion techniques and catalyst particle size control techniques are described in U.S. Patent 5,282,958. Catalysts with small particle size and well-dispersed metal are preferred.

**[0040]** The molecular sieves are typically composited with binder materials which are resistant to high temperatures which may be employed

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under hydrodewaxing conditions to form a finished catalytic hydrodewaxing catalyst or may be binderless (self bound). The binder materials are usually inorganic oxides such as silica, alumina, silica-aluminas, binary combinations of silicas with other metal oxides such as titania, magnesia, thoria, zirconia and the like and tertiary combinations of these oxides such as silica-alumina - thoria and silica-alumina magnesia. The amount of molecular sieve in the finished catalytic hydrodewaxing catalyst is from 10 to 100, preferably 35 to 100 wt.%, based on catalyst. Such catalysts are formed by methods such spray drying, extrusion and the like. The catalytic hydrodewaxing catalyst may be used in the sulfided or unsulfided form, and is preferably in the sulfided form for metal containing HDW catalyst..

**[0041]** The catalytic hydrodewaxing reaction stage used to produce lube basestocks suitable for the present invention can be comprised of one or more fixed bed reactors or reaction zones each of which can comprise one or more catalyst beds of the same or different catalyst. Although other types of catalyst beds can be used, fixed beds are preferred. Such other types of catalyst beds include fluidized beds, ebullating beds, slurry beds, and moving beds. Interstage cooling or heating between reactors, reaction zones, or between catalyst beds in the same reactor, can be employed. A portion of any heat generated during catalytic hydrodewaxing can be recovered. Where this heat recovery option is not available, conventional cooling may be performed through cooling utilities such as cooling water or air, or through use of a hydrogen quench stream. In this manner, optimum reaction temperatures can be more easily maintained.

**[0042]** Hydrogen-containing treat gasses suitable for use in the catalytic hydrodewaxing reaction stage can be comprised of substantially pure hydrogen or can be mixtures of other components typically found in refinery

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hydrogen streams. However, it is preferred that the hydrogen-containing treat gas stream contains little, more preferably no, hydrogen sulfide. The hydrogen-containing treat gas purity should be at least about 50% by volume hydrogen, preferably at least about 75% by volume hydrogen, and more preferably at least about 90% by volume hydrogen for best results.

[0043] The contacting of the partially dewaxed fraction with the catalytic hydrodewaxing catalyst results in a reaction product comprising at least a gaseous product and a liquid product, wherein the liquid product comprises a lube basestock suitable for use in the present invention. Thus, the process used to prepare lube basestocks suitable for use herein involves separating the catalytic hydrodewaxing stage reaction product into at least the gaseous product and the liquid product comprising a lube basestock and recovering the liquid product comprising a lube basestock. The means by which the catalytic hydrodewaxing stage reaction product is separated is not critical and may be performed by any means known to be effective at separating gaseous and liquid reaction products such as, for example, flash or knock-out drums or stripping.

[0044] The liquid product, comprising a lube basestock, recovered from the catalytic hydrodewaxing reaction stage can be fractionated, by either vacuum or atmospheric distillation, to provide various lube basestocks that are suitable for use in a variety of formulated oils.

[0045] A lube oil boiling range feedstream, to be dewaxed according to the preceding steps, may be treated in a number of processes. Hydroprocessing refers to processes in which hydrogen reacts with the lube oil boiling fraction under the influence of a catalyst. Non-limiting examples of hydroprocessing processes include hydrocracking; hydrotreating to remove

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heteroatoms, such as sulfur, nitrogen, and oxygen; hydrogenation of aromatics; hydroisomerization and/or catalytic dewaxing; and demetallation of heavy streams.

**[0046]** The process used to prepare the lube basestock suitable for use herein can further comprise solvent extracting a lube oil boiling range feedstock prior to the solvent dewaxing stage. Thus, in this example, the feedstream to the solvent dewaxing stage is an aromatics lean raffinate. A lubricating oil feedstock is extracted in a solvent extraction zone with an extraction solvent under conditions effective at producing an aromatics lean raffinate.

**[0047]** The solvent extraction process selectively dissolves the aromatic components in an aromatics-rich extract solution while leaving the more paraffinic components in the aromatics-lean raffinate solution. Naphthenes are distributed between the extract and raffinate phases. Typical solvents for solvent extraction include phenol, furfural and N-methyl pyrrolidone. By controlling the solvent to oil ratio, extraction temperature and method of contacting distillate to be extracted with solvent, one can control the degree of separation between the extract and raffinate phases. The solvent extraction process, solvent, and process conditions used herein are not critical to the instant invention and can be any solvent extraction process known.

**[0048]** The process used to prepare the one lube basestock suitable for use herein comprises first solvent extracting a lube oil boiling range feedstock prior to the first hydroprocessing reactor stage, as described above, and following this by the solvent dewaxing stage.

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[0049] The above description is directed to preferred embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0050] The following examples will illustrate the improved effectiveness of the present invention, but is not meant to limit the present invention in any fashion.

### **EXAMPLES**

#### **Example 1: Trim Catalytic Hydrodewaxing using Zeolite Catalysts**

[0051] The present invention was illustrated by comparing formulated engine oils comprising basestocks produced by the above-described processing sequence, i.e., solvent dewaxing followed by trim catalytic hydrodewaxing using a zeolite catalyst with no metal hydrogenation function to others employing only solvent dewaxing. This data illustrates the benefit of this invention using a zeolite catalyst to trim hydrodewax over the traditional approach of solvent dewaxing to lower target pour point. The properties of the catalysts used, and the amount employed, in the examples herein are outlined in Table 1 below. These catalysts included a non-metal HDW catalyst (H-ZSM-48/ $\text{Al}_2\text{O}_3$ ) ("Catalyst B"). Catalyst B was formed into 1/16" quadrulobe extrudates that contained 65% ZSM-48 crystals bound with 35% alumina. Catalyst C was formed using self-bound H-ZSM-5 extrudates.

**Table 1: Trim Catalytic Hydrodewaxing Zeolite Catalyst Properties**

| <b>Catalyst Name</b>                   | <b>Catalyst B</b>       | <b>Catalyst C</b> |
|----------------------------------------|-------------------------|-------------------|
| H/Pt                                   | N/A                     | N/A               |
| Support                                | H-ZSM-48                | H-ZSM-5           |
| Binder                                 | $\text{Al}_2\text{O}_3$ | N/A               |
| Surface Area ( $\text{m}^2/\text{g}$ ) | 239                     | N/A               |
| Alpha                                  | 20                      | 47                |

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|                      |    |    |
|----------------------|----|----|
| Catalyst Volume (cc) | 5  | 5  |
| Pre-sulfidation      | No | No |

### HDW Reactor Preparation and Operating Procedure

[0052] A solvent dewaxed feedstream having the properties outlined in Table 2 below was separately hydrodewaxed using Catalyst B and Catalyst C. The trim catalytic hydrodewaxing studies were performed using a continuous catalyst testing unit composed of a liquid feed system with an ISCO syringe pump, a fixed-bed tubular reactor with a three-zone furnace, liquid product collection, and an on-line MTI GC for gas analysis. 5-10 cc, as outlined in Table 1, of catalyst was charged in a down-flow 3/8" stainless steel reactor containing a 1/8" thermowell. After the unit was pressure tested, the catalyst was dried at 300°C for 2 hours with 250 cc/min N<sub>2</sub> at ambient pressure. If pre-sulfidation of the catalyst was required, 2% (vol) H<sub>2</sub>S in hydrogen was flowed through the catalyst bed at 100sccm for 1 hour. Upon completion of the catalyst treatment, the reactor was cooled to 150°C, the unit pressure was set to 1000 psig by adjusting the Mity-Mite back-pressure regulator and the gas flow was switched from N<sub>2</sub> to H<sub>2</sub>. The liquid solvent dewaxed feedstream described in Table 2 was introduced into the reactor at the desired liquid hourly space velocity (LHSV). Once the liquid solvent dewaxed feedstream reached the downstream knockout pot, the reactor temperature was increased to the target value. A material balance (MB) was initiated until the unit was lined out for 6 hours. The total liquid product (TLP) was collected in the MB dropout pot. Gas samples were analyzed with an on-line HP MTI gas chromatograph (GC) equipped with both TCD and FID detectors. A series of runs were performed to understand the catalyst activity/product properties as function of the process variables, such as LHSV and process temperature. The TLP product from each balance was cut at 370°C by batch distillation.

The properties of 370+°C dewaxed oil and wax were analyzed. The 370+°C dewaxed oil was then blended as described in the next section below.

**Table 2: Solvent Dewaxed Feedstream Properties**

|                                   |         |
|-----------------------------------|---------|
| Density , g/cc                    | 0.844   |
| Boiling Range 2% to 98% off, °F   | 690-910 |
| Kinematic Viscosity at 40°C, cSt  | 23.3    |
| Kinematic Viscosity at 100°C, cSt | 4.6     |
| Viscosity Index                   | 114     |
| Pour Point (ISL), °C              | -18     |
| UV Total Aromatics, mmol/kg       | 18.5    |
| Saybolt Color                     | > +30   |
| GCD Noack Volatility, wt%         | 15.2    |
| Sulfur, wppm                      | <10     |
| Nitrogen, wppm                    | <1      |

### Finished Oil Blending and Testing

[0053] The basestock produced by solvent dewaxing followed by catalytic hydrodewaxing as described above was then blended to make a 5W-30 engine oil. The above basestock was a lighter viscosity than required for the finished 5W-30 oil and hence a second basestock which was somewhat heavier was added to all the blends to hit a base oil desired viscosity target. A commercial additive package for GF-3 engine oils was then added to make the formulated oil. This package consists of a detergent inhibitor package, a viscosity modifier, and a pour point depressant. The package utilized and the second basestock were constants in all the blends, only the light basestock was varied.

[0054] To determine whether zeolite catalysts are effective as trim catalytic hydrodewaxing catalysts, it is useful to compare their performance against trim solvent dewaxing samples. These trim solvent dewaxing samples were processed by using the same feedstock and further solvent dewaxing to lower target pour points. In this way, a direct comparison is made between the efficacy of trim catalytic hydrodewaxing and trim solvent dewaxing. The

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feedstock itself which has already been commercially solvent dewaxed is also blended into the same 5W-30 package to show the benefits of additional dewaxing whether by solvent or catalytic hydrodewaxing. The data is shown in Table 3 below.

**Table 3. Trim Solvent and HDW Basestock and Formulated 5W-30 Engine Oil Properties (Catalyst B and C)**

| Physical Property                                 | Feed  | Full Solvent Dewaxing | HDW Basestock (Catalyst B) | HDW Basestock (Catalyst C) |
|---------------------------------------------------|-------|-----------------------|----------------------------|----------------------------|
| Density, g/cc                                     | 0.844 |                       | 0.811                      | 0.811                      |
| Kinematic Viscosity at 40C, cSt                   | 23.3  | 23.16                 | 23.34                      | 23.78                      |
| Kinematic Viscosity at 100C, cSt                  | 4.6   | 4.60                  | 4.61                       | 4.65                       |
| Viscosity Index                                   | 114   | 114.3                 | 113.1                      | 112.8                      |
| Pour Point (ISL), degC                            | -18   | -20                   | -19                        | -20                        |
| GCD Noack Volatility, wt%                         | 15.2  | 15.6                  |                            |                            |
| Kinematic Viscosity at 100C (formulated oil), cSt | 10.26 | 10.39                 | 10.35                      | 10.38                      |
| CCS (formulated 5W30 engine oil), cP              | 5790  | 4600                  | na                         | na                         |
| MRV (formulated 5W30 engine oil), Yield Stress    | <35   | <35                   | <35                        | <35                        |
| MRV (formulated 5W30 engine oil), cP              | 36211 | 33200                 | 29600                      | 31400                      |

[0055] As can be seen from the data, trim solvent dewaxing to about -20°C pour point is effective in lowering the MRV viscosity from 36,211 cP to 33,200 cP, a ~8% reduction in MRV viscosity. This shows that it is fairly difficult for a solvent refinery to dramatically impact the MRV viscosity using only a small change in target pour point. Large changes in target pour point, while more effective, also involve much greater yield debits and chilling costs.

[0056] Using trim catalytic hydrodewaxing with the zeolite catalysts provides larger benefits. Catalyst C lowered the MRV viscosity to 31,400 cP, a ~13% reduction in MRV viscosity. Catalyst B lowered the MRV to 29,600 cP, a ~18% reduction in MRV viscosity. Both of these zeolite catalysts show performance advantages over the trim solvent dewaxing approach. However, these advantages were still relatively small and the <sup>13</sup>C-NMR Free Carbon Index and Epsilon Carbon content were negligibly changed (as shown in

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Table 4). Decreases in the mole percent of total pendant groups and the increase in the free carbon index all indicate that decreased branching, most likely due to cracking, occurred.

**Table 4:  $^{13}\text{C}$  NMR Data of Trim-HDW Basestock (Catalyst B)**

| NMR Measurement              | Solvent Dewaxed Feedstream | Trim-HDW Basestock (Catalyst B) |
|------------------------------|----------------------------|---------------------------------|
| Epsilon Carbons, mole%       | 13.66                      | 13.64                           |
| Total Pendant Groups, mole % | 6.25                       | 6.17                            |
| # Side Chains / Molecule     | 2.3                        | 2.3                             |
| Carbon #                     | 36.7                       | 37.7                            |
| Free Carbon Index            | 4.31                       | 4.41                            |

[0057] Because it was sometimes difficult to exactly hit a target pour point experimentally in our pilot plant reactors, and also to look at trends, we dewaxed to a range of target pour points. Figure 1 shows the results over the range of solvent trim dewaxing studied and the range of trim catalytic hydrodewaxing using Catalyst B and C. These curves clearly indicate the advantage of trim catalytic hydrodewaxing over trim solvent dewaxing.

#### **Example 2: Trim Catalytic Hydrodewaxing using Bifunctional Catalysts**

[0058] The present invention was also illustrated by comparing formulated engine oils comprising basestocks produced by another of the above-described processing sequences, i.e., solvent dewaxing followed by trim catalytic hydrodewaxing using a bifunctional catalyst with a metal hydrogenation function, to others employing trim catalytic hydrodewaxing using the zeolite catalysts of Example 1. This data illustrates the further benefit of this invention using a bifunctional catalyst to trim hydrodewax over that shown in Example 1 of using a zeolite catalyst to trim hydrodewax. The

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properties of the catalysts used, and the amount employed, in the examples herein are outlined in Table 5 below.

**Table 5: Trim Catalytic Hydrodewaxing Bifunctional Catalyst Properties**

| Catalyst Name                    | Catalyst A                     |
|----------------------------------|--------------------------------|
| Pt loading (%)                   | 0.62                           |
| H/Pt                             | 1.16                           |
| Support                          | ZSM-48                         |
| Binder                           | Al <sub>2</sub> O <sub>3</sub> |
| Surface Area (m <sup>2</sup> /g) | 247                            |
| Alpha                            | 24                             |
| Catalyst Volume (cc)             | 10                             |
| Pre-sulfidation                  | Yes                            |

### Reactor Preparation and Operating Procedure

[0059] The same feed as shown in Table 2 of Example 1 was used in this example. The HDW reactor preparation and operating procedure is also as described above in Example 1 with the following conditions: T = 270-345°C, P = 1000 psig, liquid rate = 10 cc/hr, H<sub>2</sub> circulation rate = 2500 scf/bbl, and LHSV = 1 hr<sup>-1</sup>. The 370+ °C dewaxed oil was then collected and blended for testing.

[0060] The 370°C+ conversion of the solvent dewaxed feedstream was seen to increase with increasing reactor temperatures. A low yield loss (<10%) could be achieved at a temperature range of 270 to 310°C. For obvious reasons, it is highly desirable to improve basestock properties while maximizing lube yield. At mild process conditions (process temperature @ 290°C), the trim hydrodewaxed feedstream, sometimes referred to as a

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lubricating oil basestock herein, showed a marginal decrease in pour point from -18°C to -19°C, while 370°C+ product yield loss was only about 3%, based on the solvent dewaxed feedstream. In addition, the viscosity index ("VI") and viscosity remained nearly unchanged. An additional benefit of the present invention is that by using Catalyst A, a bifunctional catalyst, in the trim HDW mode is the aromatic saturation capability of the catalyst. The aromatics content of the trim HDW product is essentially zero. High saturate content, i.e., saturated aromatics, in the lube product provides better oxidation stability and increases the value of the lube oil basestock. Table 6 summarizes the physical properties of the lube fraction of the product with the highest 370°C+ yield.

**Table 6: Trim HDW Basestock Properties (Catalyst A)**

| Physical Property                 | Feed  | Trim-HDW Basestock (Catalyst A) |
|-----------------------------------|-------|---------------------------------|
| 370°C+ Yield, % on SDW feed       | 97.5  | 94.6                            |
| Kinematic Viscosity at 40°C, cSt  | 23.3  | 23.7                            |
| Kinematic Viscosity at 100°C, cSt | 4.6   | 4.7                             |
| Viscosity Index                   | 114   | 113                             |
| Pour Point (ISL), °C              | -18   | -19                             |
| UV Total Aromatics, mmol/kg       | 18.5  | 0                               |
| Saybolt Color                     | > +30 | >+30                            |
| GCD Noack Volatility, wt%         | 15.2  | 15.3                            |

### Finished Oil Blending and Testing

[0061] The basestock produced by solvent dewaxing followed by catalytic hydrodewaxing as described above was then blended to make a 5W-30 engine oil. The above basestock was a lighter viscosity than required for the finished 5W-30 oil and hence a second basestock which was somewhat heavier was added to all the blends to hit a base oil desired viscosity target. A commercial additive package for GF-3 engine oils was then added to make the formulated oil. This package consists of a detergent inhibitor package, a viscosity

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modifier, and a pour point depressant. The package utilized and the second basestock were constants in all the blends, only the light basestock was varied.

[0062] To assess the performance of bifunctional catalysts, they were compared to other trim samples including the trim catalytic hydrodewaxing samples of Example 1. The feedstock itself which has already been commercially solvent dewaxed is also blended into the same 5W-30 package to show the benefits of additional trim dewaxing. The data generated using the bifunctional Catalyst A is shown in Table 7 below. The pilot plant run was done twice; hence the first two columns used a basestock made in the first run and the third column used a basestock made in the second run.

**Table 7. Trim HDW Basestock and Formulated 5W-30 Engine Oil Properties (Catalyst A)**

| Physical Property                                 | Feed  | HDW (Catalyst A) | HDW (Catalyst A) | HDW (Catalyst A) |
|---------------------------------------------------|-------|------------------|------------------|------------------|
| Density, g/cc                                     | 0.844 | 0.810            | 0.810            |                  |
| Kinematic Viscosity at 40C, cSt                   | 23.3  | 23.65            | 23.65            | 23.73            |
| Kinematic Viscosity at 100C, cSt                  | 4.6   | 4.64             | 4.64             | 4.66             |
| Viscosity Index                                   | 114   | 113.1            | 113.1            | 113.6            |
| Pour Point (ISL), degC                            | -18   | -19              | -19              | -20              |
| GCD Noack Volatility, wt%                         | 15.2  |                  |                  |                  |
| Kinematic Viscosity at 100C (formulated oil), cSt | 10.26 | 10.33            | 10.36            | 10.12            |
| CCS (formulated 5W30 engine oil), cP              | 5790  | 5180             |                  |                  |
| MRV (formulated 5W30 engine oil), Yield Stress    | <35   | <35              | <35              | <35              |
| MRV (formulated 5W30 engine oil), cP              | 36211 | 19338            | 19536            | 19997            |

[0063] As can be seen from the data, trim catalytic hydrodewaxing to about -20°C pour point is surprisingly effective in lowering the MRV viscosity from 36,211 cP to an average value of 19,624 cP, a 46% reduction in MRV viscosity. This level of MRV viscosity reduction under such mild catalytic hydrodewaxing condition and with only small changes in basestock bulk properties was much greater than expected. As summarized in Table 6, minimal changes to basestock physical properties (viscosity, VI, pour point, volatility) were observed. Table 8 highlights the key <sup>13</sup>C NMR results of the

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feed versus trim HDW basestock.  $^{13}\text{C}$  NMR was used to show that mild trim catalytic hydrodewaxing isomerizes the trace paraffins that impair the low temperature, low-shear properties of solvent-dewaxed basestocks to provide exceptional improvements to formulated engine oil cold flow properties. A substantial reduction to the NMR Free Carbon Index from 4.31 to 4.02 was seen. Also a significant reduction to the NMR Epsilon Carbon content from 13.66 mole% to 13.04 mole% was obtained. This confirms that a significant change to the molecular structure of the lube molecules was achieved without significant alteration to standard basestock physical properties.

**Table 8:  $^{13}\text{C}$  NMR Data of Trim-Hydrodewaxed Basestock(Catalyst A)**

| NMR Measurement               | Feed  | Trim-HDW Basestock<br>(Catalyst A) |
|-------------------------------|-------|------------------------------------|
| Epsilon Carbons, mole%        | 13.66 | 13.04                              |
| Total Pendant Groups, mole %  | 6.25  | 6.58                               |
| Pendant Methyl Groups, mole % | 5.00  | 5.30                               |
| # Side Chains / Molecule      | 2.3   | 2.4                                |
| Carbon #                      | 36.7  | 36.5                               |
| Free Carbon Index             | 4.31  | 4.02                               |

[0064] This 46% decrease in MRV and 11% decrease in CCS were obtained with less than 3% yield loss in mild trim-HDW with Catalyst A. As noted above, the aromatic saturation benefit of using the Catalyst A in a trim HDW mode is clearly reflected by the negligible aromatics content of the trim hydrodewaxed product. The MRV improvement and yield loss associated with the trim HDW over Catalyst A are superior to the improvements observed in Example 1 where Catalyst B and C were employed in the trim HDW setup as demonstrated by the 46% MRV improvement with <3% yield loss. This was achieved through an effective molecular re-arrangement that was achieved with Catalyst A but not with Catalyst B and C as evidenced by

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the NMR measurements. This is discussed further below.

[0065] Increases in the mole percent of total pendant groups, mole percent of pendant methyl groups, and number of side chains and the decrease observed in the mole percent of epsilon carbons and free carbon index all indicate that increased branchiness of lube molecules, likely due to isomerization, has occurred. No significant changes in carbon number (CN) were observed. The trends shown in Table 8 indicate that isomerization is likely the key mechanism behind the extensive improvement observed in engine oil low temperature properties using Catalyst A in a mild trim catalytic hydrodewaxing. Thus, overall, the trends in Table 4 are quite opposite to the trends observed in Table 8. The trends shown in Table 4 indicate that cracking is the likely the key mechanism behind the 17% improvement in MRV observed in engine oil low temperature properties using the Catalyst B in a mild trim catalytic hydrodewaxing mode. Cracking is not as effective in altering the molecular structure as isomerization as evidenced by the NMR data. Cracking is also not as effective in improving the low temperature quality as shown by the MRV data discussed above.

[0066] Because it was sometimes difficult to exactly hit a target pour point experimentally in our pilot plant reactors, and also to look at trends, we dewaxed to a range of target pour points. Figure 2 shows the results over the range of trim catalytic hydrodewaxing using Catalysts A, B, C, D, and E. These curves clearly indicate the advantage of trim catalytic hydrodewaxing using a bifunctional catalyst such as Catalyst A over trim catalytic hydrodewaxing using a zeolite catalyst such as Catalyst B and C. This can be most readily seen by looking at the MRV viscosity obtained at similar pour points, especially those pour points closer to the feed such as around -20°C.

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[0067] This example illustrated the improvement in low-temperature properties achievable using trim catalytic hydrodewaxing of a solvent-dewaxed feedstream at mild conditions with Catalyst A. This example also demonstrates that although trim HDW using Catalyst B and C improved the low temperature property of the solvent dewaxed feedstream, the low temperature property improvement demonstrated by the present invention employing Catalyst A were superior to those obtained with Catalyst B.

[0068]  $^{13}\text{C}$  NMR was used to show that mild trim catalytic hydrodewaxing isomerizes the trace paraffins that impair the low temperature, low-shear properties of solvent-dewaxed basestocks to provide exceptional improvements to formulated engine oil cold flow properties. Table 9 highlights the key  $^{13}\text{C}$  NMR results of the feed versus trim HDW basestock.

**Table 9:  $^{13}\text{C}$  NMR Data of Trim-Hydrodewaxed Basestock(Catalyst A)**

| NMR Measurement               | Feed  | Trim-HDW Basestock<br>(Catalyst A) |
|-------------------------------|-------|------------------------------------|
| Epsilon Carbons, mole%        | 13.66 | 13.04                              |
| Total Pendant Groups, mole %  | 6.25  | 6.58                               |
| Pendant Methyl Groups, mole % | 5.00  | 5.30                               |
| # Side Chains / Molecule      | 2.3   | 2.4                                |
| Carbon #                      | 36.7  | 36.5                               |
| Free Carbon Index             | 4.31  | 4.02                               |

[0069] Increases in the mole percent of total pendant groups, mole percent of pendant methyl groups, and number of side chains and the decrease observed in the mole percent of epsilon carbons and free carbon index all indicate that increased branchiness of lube molecules, likely due to isomerization, has occurred. No significant changes in carbon number (CN) were observed. The trends shown in Table 6 indicate that isomerization is likely the key mechanism behind the extensive improvement observed in

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engine oil low temperature properties using Catalyst A in a mild trim catalytic hydrodewaxing. Thus, overall, the trends in Table 4 are quite opposite to the trends observed in Table 6. The trends shown in Table 4 indicate that cracking is the likely the key mechanism behind the 17% improvement in MRV viscosity observed in engine oil low temperature properties using the Catalyst B in a mild trim catalytic hydrodewaxing mode. Cracking is not as effective in altering the molecular structure as isomerization as evidenced by the NMR data. Cracking is also not as effective in improving the low temperature quality as shown by the MRV viscosity data discussed above.

**Example 3: Comparative example of HDW followed by SDW**

[0070] To further explore the potential for improving the low temperature quality of a finished lubricant, the study was extended beyond trim dewaxing. trim dewaxing utilizes a solvent dewaxing process to dewax a waxy feed so that the majority of wax is removed in this first process. The second step of trim dewaxing is then done on the nearly dewaxed feed and only removes or isomerizes small amounts of residual wax. To identify whether the balance of wax removal between the first process and second process could be modified, we extended the study to samples which had only been partially or mildly dewaxed in the first step leaving more residual wax for the second step to handle.

[0071] We also wanted to determine if catalytic hydrodewaxing first followed by solvent dewaxing as the second process would be effective. The degree of catalytic hydrodewaxing in the first stage was varied to also look at the impact of catalytic hydrodewaxing severity and solvent dewaxing severity. That is the subject of this third example. The catalytic hydrodewaxing catalyst used was Catalyst A.

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[0072] The HDW reactor preparation and operating procedure is same as described above in Example 1.

#### *SDW Lab Procedure*

The lab solvent dewaxings were conducted using a single stage batch filtration with the large Buchner funnel apparatus. This apparatus uses a 24-cm filtration area and has up to a 1.5 gallon oil/wax/solvent slurry capacity. The solvent was a mixture of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK).

[0073] As the filtration proceeds, the predominately wax component is left on the surface of the filtration media, with the filtrate (oil and solvent) passing through the filter into a collection flask. These two products are then stripped of their respective solvents using a rotary vacuum stripper to complete the filtration process. The DWO and wax were further analyzed to determine their individual physical properties.

[0074] The feed used in this case was a waxy light feedstream from the refinery and was a slightly lower viscosity grade than in Example 1 and 2.

**Table 10. HDW Followed by SDW Basestock and Formulated 5W-30  
Engine Oil Properties Using Various Degrees of HDW to SDW**

| Physical Property                                 | Base Case | HDW to 30,<br>SDW to -18 | HDW to 13,<br>SDW to -19 | HDW to -7,<br>SDW to -20 |
|---------------------------------------------------|-----------|--------------------------|--------------------------|--------------------------|
| Density, g/cc                                     | 0.844     |                          |                          |                          |
| Kinematic Viscosity at 40C, cSt                   | 23.3      | 18.91                    | 18.462                   | 17.82                    |
| Kinematic Viscosity at 100C, cSt                  | 4.6       | 4.09                     | 4.04                     | 3.97                     |
| Viscosity Index                                   | 114       | 117.1                    | 118.210086               | 120.6                    |
| Pour Point (ISL), degC                            | -18       | -18                      | -19                      | -20                      |
| GCD Noack Volatility, wt%                         | 15.2      |                          |                          |                          |
| Kinematic Viscosity at 100C (formulated oil), cSt | 10.26     | 10.28                    | 10.27                    | 10.26                    |
| CCS (formulated 5W30 engine oil), cP              | 5790      | 6483                     |                          | 5227                     |
| MRV (formulated 5W30 engine oil), Yield Stress    | <35       | <175                     | <175                     | <175                     |
| MRV (formulated 5W30 engine oil), cP              | 36211     | 103488                   | 102578                   | 92649                    |

[0075] In this comparative example, the formulated oil MRV viscosity values measured were undesirable (Shown in Table 10). The base case full

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solvent dewaxed sample to -18°C pour point gave a 5W-30 MRV viscosity of 36,211 cP with No Yield Stress (<35 Pa). The mildest HDW example was HDW to +30°C followed by SDW to -18°C, which is a very similar pour point to the base case. The 5W-30 MRV viscosity was 103,488 cP, much higher than base case, and a Yield Stress of <175 Pa was found. Thus this formulated oil fails the MRV viscosity specifications on both apparent viscosity and yield stress. The intermediate HDW example was HDW to +13°C followed by SDW to -19°C, which is a very similar pour point to the base case. The 5W-30 MRV viscosity was 102,578 cP, again much higher than the base case, and a yield stress of <175 Pa was found. Thus this formulated oil again fails the MRV viscosity specifications on both apparent viscosity and yield stress. The most severe HDW example was HDW to -7°C followed by SDW to -20°C, which is a very similar pour point to the base case. The 5W-30 MRV apparent viscosity was 92,649 cP, again much higher than the base case, and a yield stress of <175 Pa was found. Thus this formulated oil again fails the MRV viscosity specifications on both apparent viscosity and yield stress.

[0076] In all three cases, the NMR results help to explain the MRV viscosity results seen. The Free Carbon Index has risen to 4.85 to 5.02% and the Epsilon Carbon content has increased to 15.35 mole% to 16.30 mole%. This is a comparative example that shows that when the NMR Free Carbon Index and Epsilon Carbon contents exceed 4.3 and 14%, respectively, the low temperature quality of the finished oil as demonstrated by the MRV viscosity deteriorates.

[0077] Thus, it is shown that HDW followed by SDW to an acceptable pour point is unable to achieve acceptable finished oil low temperature quality. Even when the first HDW step is done to within about 11°C of the desired target, it is still not sufficient to generate good quality product.

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[0078] To look at trends going to lower pour points, the final SDW step was taken to lower target pour points and the data is plotted in Figure 3 below. It can be seen that even at lower final pour points of -23 and -24°C, HDW followed by SDW is still not competitive with full SDW performance.

#### **Example 4: SDW followed by HDW**

[0079] To further explore the potential for improving the low temperature quality of a finished lubricant, the study was extended beyond trim dewaxing. trim dewaxing utilizes a solvent dewaxing process to dewax a waxy feed so that the majority of wax is removed in this first process. The second step of trim dewaxing is then done on the nearly dewaxed feed and only removes or isomerizes small amounts of residual wax. To identify whether the balance of wax removal between the first process and second process could be modified, we extended the study to samples which had only been partially or mildly dewaxed in the first step leaving more residual wax for the second step to handle.

[0080] In this example, the first step is a Solvent Dewaxing Process to various intermediate pour points followed by Catalytic hydrodewaxing using Catalyst A to the final target pour points.

[0081] The feed used in this case was a waxy light feedstream from a refinery and was a slightly lower viscosity grade than in Example 1 and 2 and the same feedstream as used in Example 3.

**Table 11. SDW Followed by HDW Basestock and Formulated 5W-30 Engine Oil Properties Using Various Degrees of SDW to HDW**

| Physical Property                                 | Base Case | SDW to 10,<br>HDW to -21 | SDW to -2,<br>HDW to -19 |
|---------------------------------------------------|-----------|--------------------------|--------------------------|
| Density, g/cc                                     | 0.844     | 0.801                    | 0.803                    |
| Kinematic Viscosity at 40C, cSt                   | 23.3      | 18.28                    | 18.88                    |
| Kinematic Viscosity at 100C, cSt                  | 4.6       | 4.01                     | 4.09                     |
| Viscosity Index                                   | 114       | 117.5                    | 117.5                    |
| Pour Point (ISL), degC                            | -18       | -21                      | -19                      |
| GCD Noack Volatility, wt%                         | 15.2      |                          |                          |
| Kinematic Viscosity at 100C (formulated oil), cSt | 10.26     | 10.26                    | 10.28                    |
| CCS (formulated 5W30 engine oil), cP              | 5790      | 4950                     | 5126                     |
| MRV (formulated 5W30 engine oil), Yield Stress    | <35       | <35                      | <35                      |
| MRV (formulated 5W30 engine oil), cP              | 36211     | 17873                    | 22826                    |

**[0082]** In this example, the formulated oil MRV viscosity values were much better than the base case (shown in Table 11). The base case full solvent dewaxed sample to -18 °C pour point gave a 5W-30 MRV viscosity of 36,211 cP with no yield stress (<35 Pa). The milder SDW example was SDW to +10 °C followed by SDW to -21°C, which is a very similar pour point to the base case. The 5W-30 MRV viscosity was 17,873 cP, which is 51% lower than the base case with no Yield Stress (<35 Pa). The more intermediate SDW example was SDW to -2°C followed by HDW to -19°C, which is a very similar pour point to the base case. The 5W-30 MRV viscosity was 22,826 cP, which is 37% lower than the base case, and no Yield Stress (<35 Pa) was found. The most severe SDW example is the trim cases discussed in Examples 1 and 2. Example 2 also used Catalyst A and the 5W-30 MRV viscosity average value was 19,624 cP which was a 46% reduction and the benefit magnitude is very similar to what is shown here.

**[0083]** Again, in all three cases, the NMR results help to explain the MRV viscosity results seen. The Free Carbon Index has dropped to 4.09 to 4.29% and the Epsilon Carbon content has decreased to 13.67 mole% to 13.72 mole%. This shows that when the NMR Free Carbon Index and Epsilon Carbon contents decrease below 4.3 and 14%, respectively, the low

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temperature quality of the finished oil as demonstrated by the MRV viscosity improves.

[0084] Thus, it is shown that SDW followed by HDW to an acceptable pour point is a surprisingly effective means to achieve acceptable finished oil low temperature quality. This large benefit is seen independent of the relative amount of SDW to HDW. It seems critical that the final step be HDW but whether the SDW is run quite mild to higher pour points are run more severely to lower pour points does not impact how effective this processing approach is in impacting finished oil low temperature quality.

[0085] To look at trends going to lower pour points, the final HDW step was taken to lower target pour points and the data is plotted in Figure 4 below. It can be seen that as the final pour point is lowered, the benefits continue until a final MRV viscosity of 10,000 - 15,000 cP is reached.

**CLAIMS:**

1. A dewaxed lube basestock having a Free Carbon Index of less than 4.3 and an Epsilon Carbon mole% of less than 14%.
2. A dewaxed lube basestock having a Free Carbon Index of less than 4.1 and an Epsilon Carbon mole% of less than 13.3%.
3. A dewaxed lube basestock having a Free Carbon Index of from 3.0 to 4.3 and a Epsilon Carbon mole% from 10.0% to 14.0 %.
4. A dewaxed lube basestock according to claim 1 wherein the Pour Point is between -6 °C and -30 °C
5. A dewaxed lube basestock according to claim 2 wherein the Pour Point is between -6 °C and -30 °C
6. A dewaxed lube basestock according to claim 1 wherein the Pour Point is between -15 °C and -24 °C
7. A dewaxed lube basestock according to claim 2 wherein the Pour Point is between -15 °C and -24 °C
8. A dewaxed lube basestock according to claim 1 wherein the kinematic viscosity at 100 °C is between 3 cSt and 7 cSt, the Viscosity Index is between 95 and 150, and the Pour Point is between -6 °C and -30 °C.
9. A dewaxed lube basestock according to claim 1 wherein the kinematic viscosity at 100 °C is between 3 cSt and 7 cSt, the Viscosity Index is between 100 and 120, and the Pour Point is between -15 °C and -24 °C
10. A dewaxed lube basestock according to claim 2 wherein the kinematic viscosity at 100 °C is between 3 cSt and 7 cSt, the Viscosity Index is between 100 and 120, and the Pour Point is between -15 °C and -24 °C
11. A dewaxed lube basestock according to claim 1 wherein the kinematic viscosity at 100 °C is between 4 cSt and 5 cSt, the Viscosity Index is between 100 and 120, and the Pour Point is between -15 °C and -24 °C.
12. A dewaxed lube basestock having a Free Carbon Index of less than 4.3 and an Epsilon Carbon mole% of less than 14% prepared by a process comprising

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- a) solvent dewaxing a lube oil boiling range feedstream in a solvent dewaxing stage operated under effective solvent dewaxing conditions thereby producing at least a partially dewaxed fraction; and
  - b) contacting said partially dewaxed fraction with a hydrodewaxing catalyst in the presence of a hydrogen-containing treat gas in a reaction stage operated under effective hydrodewaxing conditions thereby producing a reaction product comprising at least a gaseous product and liquid product, wherein said liquid product comprises a dewaxed lube basestock.
- 13.A dewaxed lube basestock according to claim 12 wherein said hydrodewaxing catalyst is selected from ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, Beta, SSZ-31, SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, fluorided alumina, silica-alumina, fluorided silica alumina, synthetic Ferrierites, Mordenite, Offretite, Erionite, Chabazite, and mixtures thereof under effective catalytic dewaxing conditions.
- 14.A dewaxed lube basestock according to claim 13 wherein said hydrodewaxing catalyst comprises a zeolite selected from ZSM-48, ZSM-22 and ZSM-23.
- 15.A dewaxed lube basestock according to claim 14 wherein said hydrodewaxing catalyst further comprises at least one metal hydrogenation component, which is selected from Group VI metals, Group VIII metals, or mixtures thereof and contains at least one Group VIII noble metal.
- 16.A formulated oil comprising:
- a) a major amount of at least one dewaxed lube basestock according to claim 4,
  - b) at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors.

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17. A formulated oil according to claim 16 wherein the formulated oil is an engine oil.
18. An engine oil according to claim 17 wherein said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 30,000 cP.
19. An engine oil according to claim 17 wherein said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP.
20. An engine oil according to claim 17 wherein said engine oil has a Mini Rotary Viscometer viscosity from about 12,000 cP to about 20,000 cP.
21. An engine oil comprising:
- a) at least 60 % by weight of the total composition of a dewaxed lube basestock having a Free Carbon Index of from 3.0 to 4.3 and an Epsilon Carbon mole% from 10.0% to 14.0 % and wherein the kinematic viscosity at 100 °C is between 3 cSt and 7 cSt, the Viscosity Index is between 95 and 150, and the Pour Point is between -6 °C and -30 °C
  - b) at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors, and
- wherein the said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP.
22. An engine oil comprising:
- a) at least 60 % by weight of the total composition of a dewaxed lube basestock having a Free Carbon Index of from 3.0 to 4.3 and an Epsilon Carbon mole% from 10.0% to 14.0 % and wherein the kinematic viscosity at 100 °C is between 3 cSt and 7 cSt, the Viscosity Index is between 95 and 150, and the Pour Point is less than -6 °C and wherein said dewaxed lube basestock is prepared by a process comprising
    - (i) solvent dewaxing a lube oil boiling range feedstream in a solvent dewaxing stage operated under effective solvent dewaxing

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conditions thereby producing at least a partially dewaxed fraction;  
and

- (ii) contacting said partially dewaxed fraction with a hydrodewaxing catalyst in the presence of a hydrogen-containing treat gas in a reaction stage operated under effective hydrodewaxing conditions thereby producing a reaction product comprising at least a gaseous product and liquid product, wherein said liquid product comprises a dewaxed lube basestock.

- b) at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors, and

wherein the said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP.

23. An engine oil comprising:

- a) at least 60 % by weight of the total composition of a dewaxed lube basestock having a Free Carbon Index of from 3.0 to 4.3 and an Epsilon Carbon mole% from 10.0% to 14.0 % and wherein the kinematic viscosity at 100 °C is between 3 cSt and 7 cSt, the Viscosity Index is between 95 and 150, and the Pour Point is less than -6 °C and wherein said dewaxed lube basestock is prepared by a process comprising
  - (i) solvent dewaxing a lube oil boiling range feedstream in a solvent dewaxing stage operated under effective solvent dewaxing conditions thereby producing at least a partially dewaxed fraction;  
and
  - (ii) contacting said partially dewaxed fraction with a hydrodewaxing catalyst in the presence of a hydrogen-containing treat gas in a reaction stage operated under effective hydrodewaxing conditions thereby producing a reaction product comprising at least a gaseous

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product and liquid product, wherein said liquid product comprises a dewaxed lube basestock.

b) at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors, and

wherein the said engine oil has a Mini Rotary Viscometer viscosity from about 10,000 cP to about 25,000 cP.

24. A method of formulating an engine oil comprising blending a dewaxed lube basestock as characterized in claim 6 with at least one component selected from dispersants, detergents, wear inhibitors, antioxidants, rust inhibitors, demulsifiers, extreme pressure agents, friction modifiers, multifunction additives, viscosity index improvers, pour point depressants, and foam inhibitors.