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(54) **PARAFFINIC HYDROISOMERATE AS A WAX CRYSTAL MODIFIER**

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(57) **ABSTRACT**

Heavy fractions of paraffinic lubes produced over dewaxing catalysts are effective as wax crystal modifiers for being hydrocarbons notwithstanding that such heavy fractions have pour points above that of the liquid hydrocarbon.

FIGURE 1

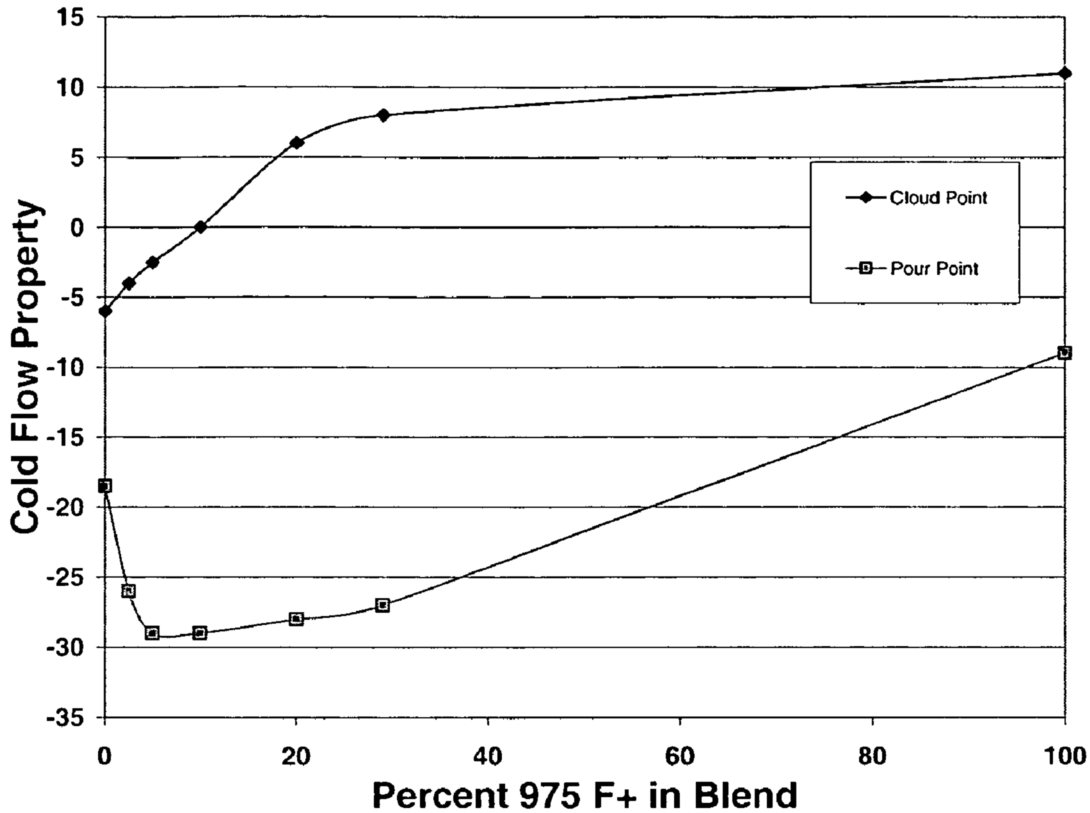
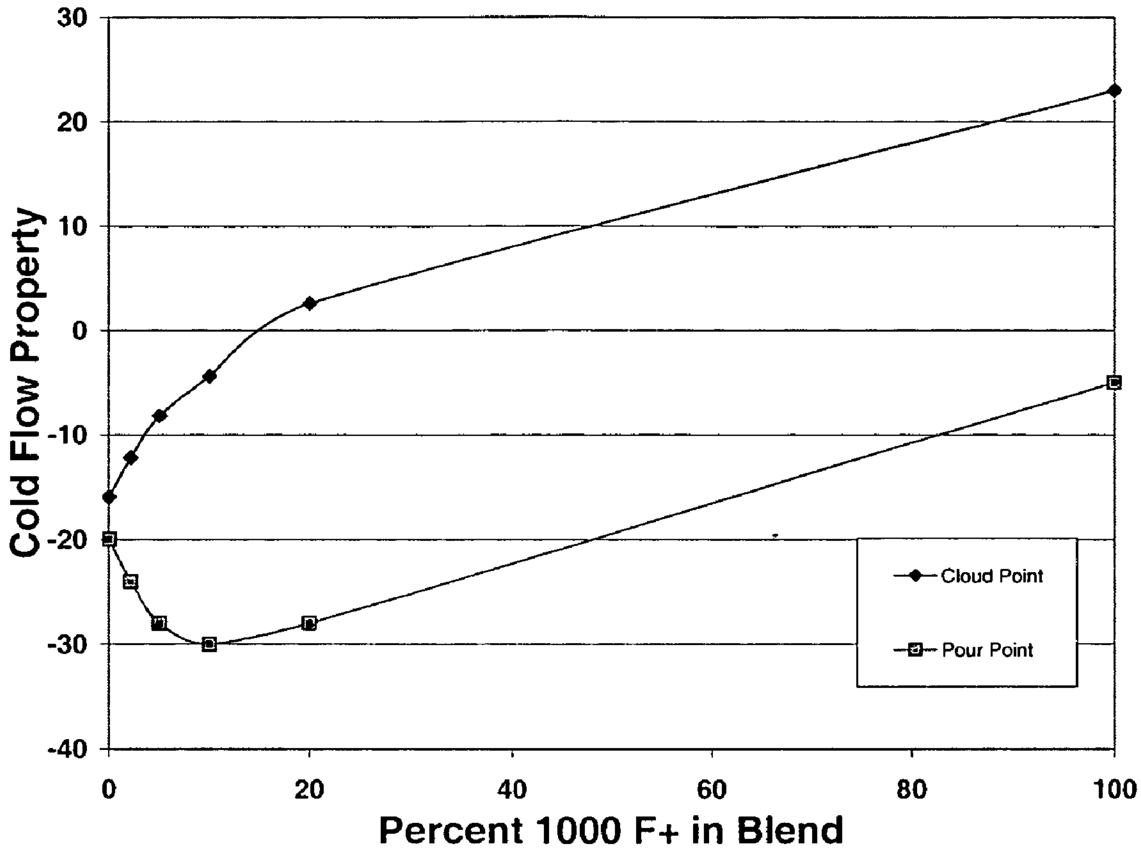

Cold Flow Property
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
0
20
40
60
80
100
Percent 975 F+ in Blend
Cloud Point
Pour Point

FIGURE 2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20
10
0
-10
-20
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-40
Cold Flow Property
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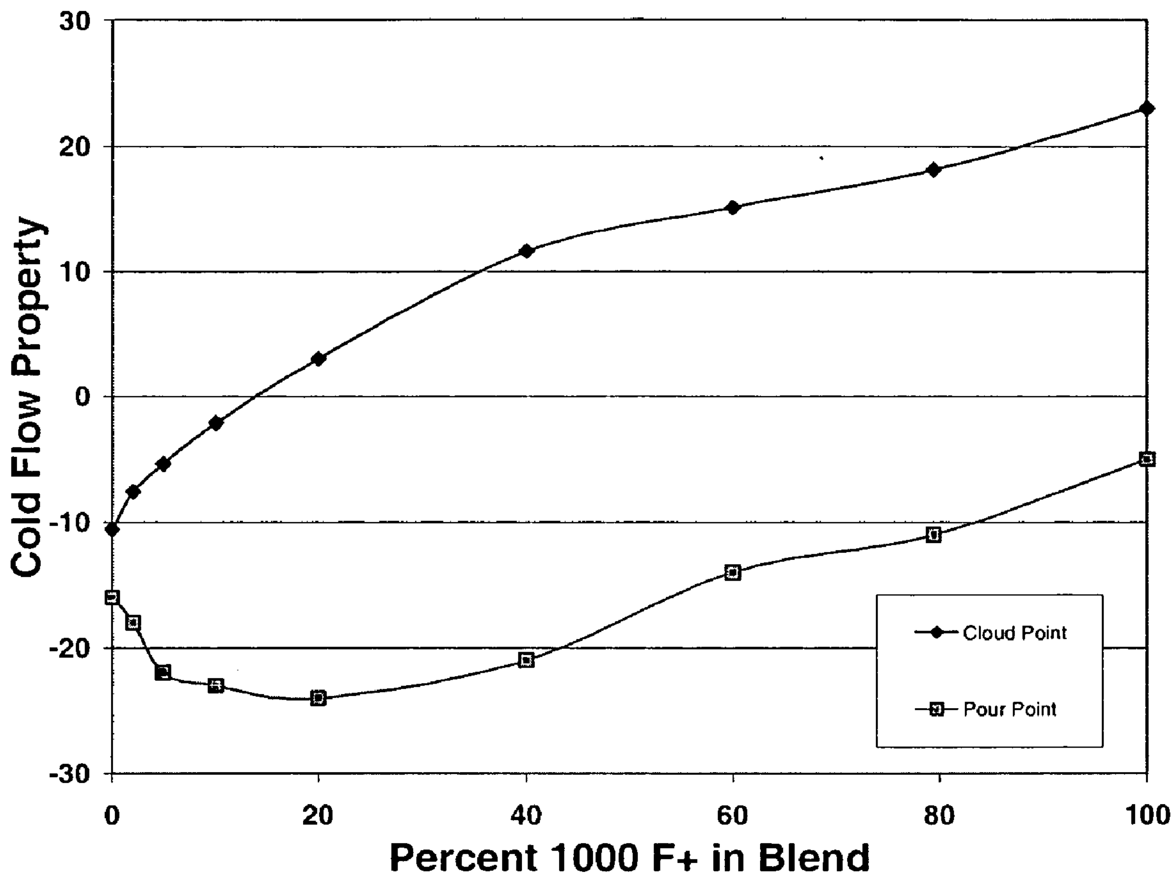
20
40
60
80
100
Percent 1000 F+ in Blend
Cloud Point
Pour Point

FIGURE 3


30
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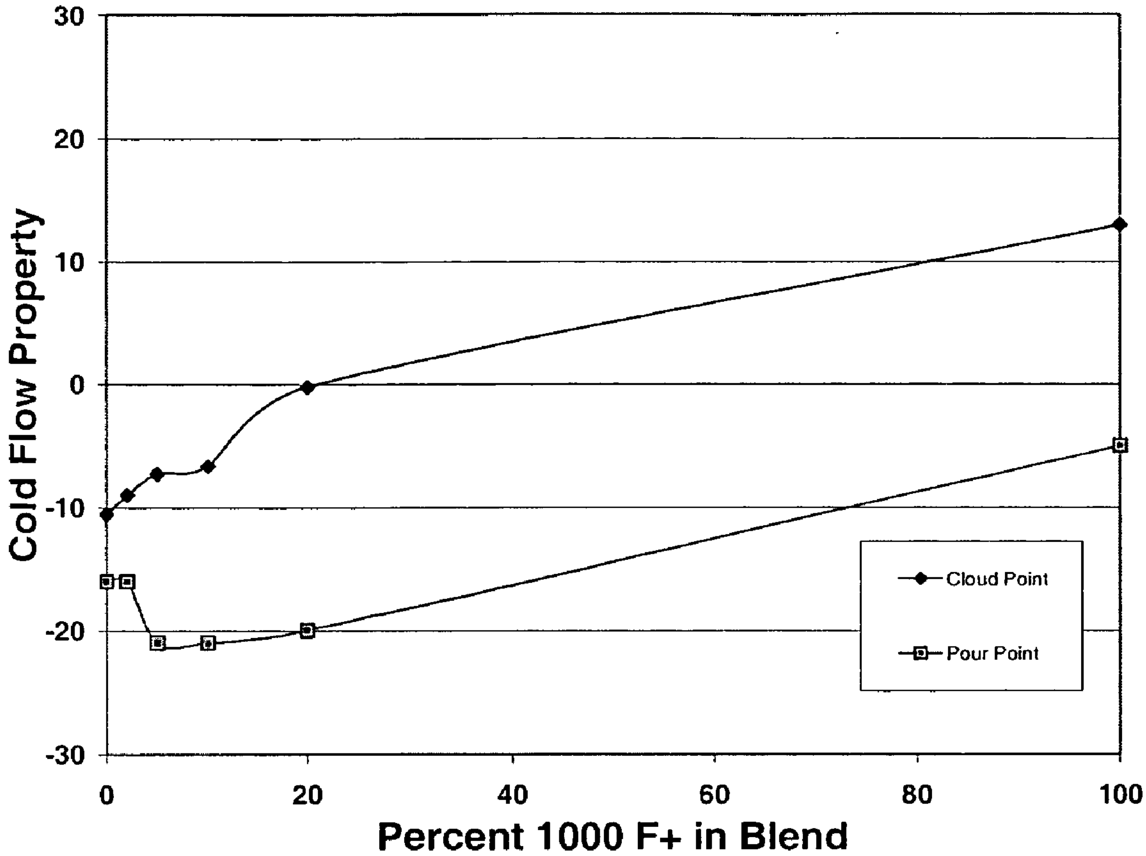
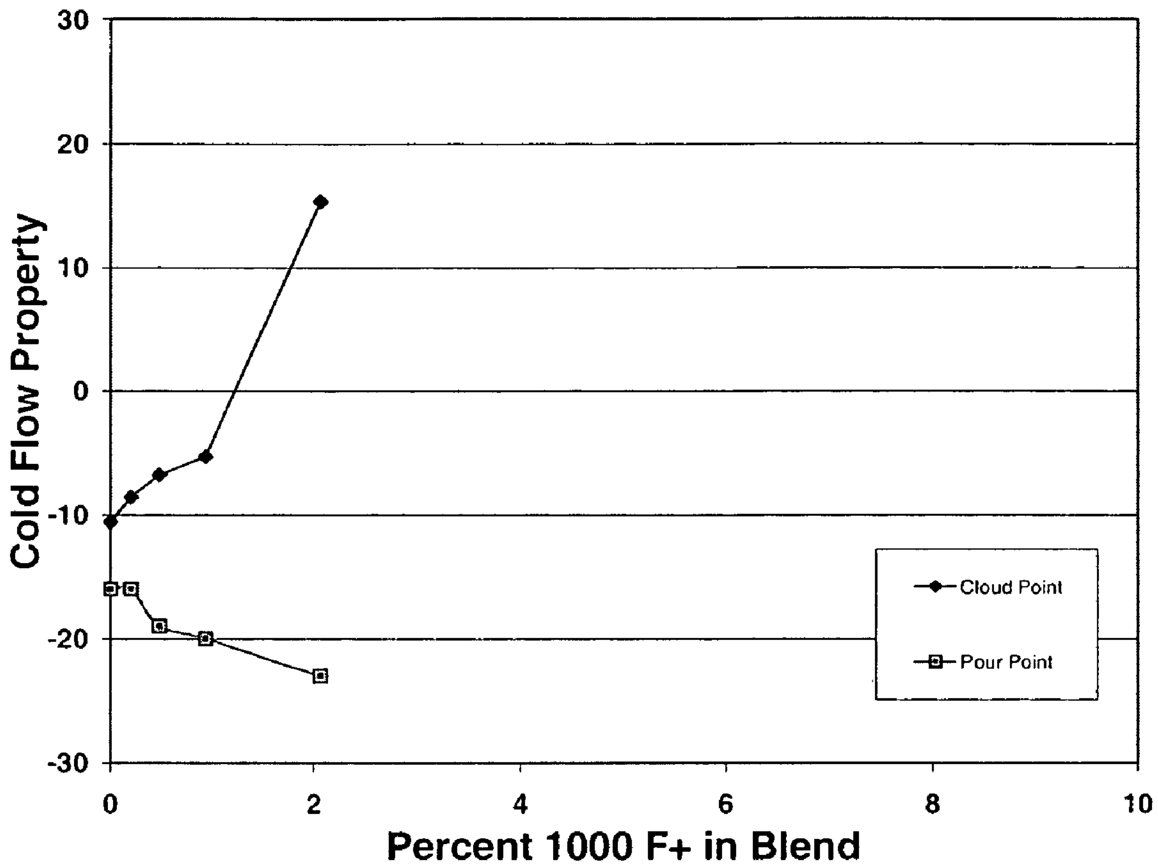
10
0
-10
-20
-30
Cold Flow Property
0
20
40
60
80
100
Percent 1000 F+ in Blend
Cloud Point
Pour Point

FIGURE 4



30
20
10
0
-10
-20
-30
Cold Flow Property
0
20
40
60
80
100
Percent 1000 F+ in Blend
Cloud Point
Pour Point

FIGURE 5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-30
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8
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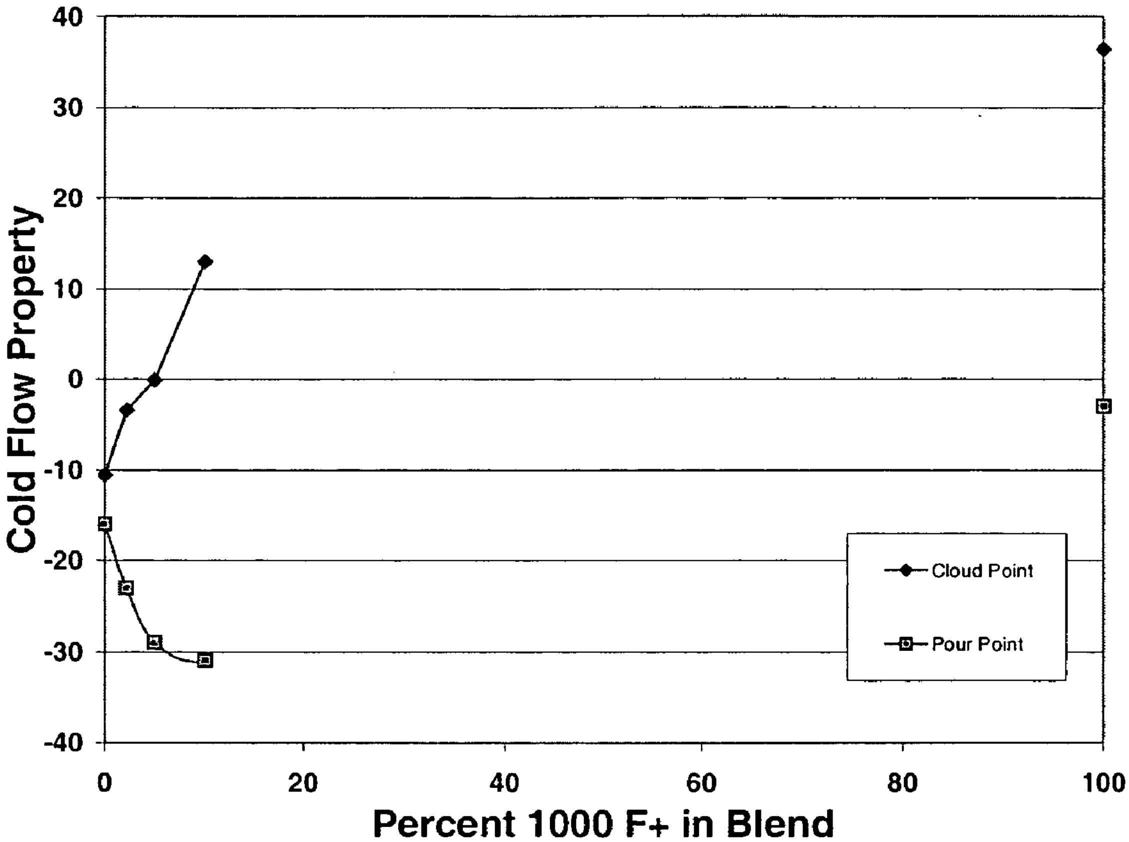
Percent 1000 F+ in Blend
Cloud Point
Pour Point

FIGURE 6


Cold Flow Property
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30
20
10
0
-10
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-30
-40
0
20
40
60
80
100
Percent 1000 F+ in Blend
Cloud Point
Pour Point

PARAFFINIC HYDROISOMERATE AS A WAX CRYSTAL MODIFIER

[0001] This application claims the benefit of U.S. Provisional Application No. 60/668,384 filed Apr. 5, 2005.

FIELD OF THE INVENTION

[0002] The present invention is concerned broadly with modifying the low temperature properties of hydrocarbon fluids and more particularly with the use of a heavy fraction of paraffinic lubes produced from a Fischer-Tropsch product as a wax crystal modifier.

BACKGROUND OF INVENTION

[0003] Wax crystal modifiers are additives used in the petroleum industry to improve the cold flow properties of numerous hydrocarbon fluids such as crude oils, diesel fuels, lubricating oils and the like. Basically, wax crystal modifiers function by modifying, in some way, the process by which wax crystals form in solutions when the solution temperature is lowered. For example, they may interact with paraffins in the hydrocarbon fluid to delay onset of crystallization, they may modify the morphology of the wax to a shape less likely to plug a filter or to form a gel; and they may operate to prevent fresh paraffin from adding to wax. Hence, wax crystal modifiers are used in lubricating oils as pour point depressants and in diesel fuels as cold filter plugging point depressants. They find use also as cloud point depressants in fuels and wax inhibitors in crude oils.

[0004] Wax crystal modifiers commonly employed include chlorinated hydrocarbons, polyolefins and ethylene-vinyl ester copolymers.

SUMMARY OF INVENTION

[0005] Surprisingly it has been discovered that heavy fractions of paraffinic lubes produced over dewaxing catalysts are effective as wax crystal modifiers. Indeed it has been discovered that when added to a base lube oil the aforesaid heavy fractions will lower the pour point of the base lube oil notwithstanding that the heavy fraction has a pour point well above that of the base oil.

[0006] By heavy fractions of dewaxed paraffinic lubes is meant those fractions having a final boiling point exceeding 850° F. (454° C.), preferably exceeding 950° F. (510° C.) and even exceeding 1000° F. (538° C.) after 95 mass percent of the lube has been removed. Typically, the lube will be one having an initial boiling point exceeding 700° F. (371 ° C.).

[0007] In a preferred embodiment of the invention the heavy fraction is derived from a Fischer-Tropsch product by catalytically hydroisomerizing the product to produce a lube oil and distilling the lube oil to obtain a high boiling, heavy fraction and a lower boiling fraction.

[0008] In one embodiment of the invention, the process by which wax crystals form in a first paraffinic containing hydrocarbon liquid is modified by adding to it a second lube containing greater amounts by weight of a heavy fraction than the first liquid, the second lube being added in an amount sufficient to modify the wax crystal formation process of the first liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIGS. **1** to **6** are graphical illustrations of various embodiments of the invention and also depict results of Examples 1 to 6 respectively.

DETAILED DESCRIPTION OF INVENTION

[0010] The wax crystal modifiers of the present invention comprise the heavy fractions of paraffinic lubes produced over dewaxing catalysts. Such paraffinic lubes include those lubes obtained from a mineral oil by hydrocracking, hydroisomerization, solvent extraction and hydroprocessing and combinations thereof, and lubes obtained from polyethylene and from Fischer-Tropsch paraffinic products. In a preferred embodiment of the invention the heavy fraction of a paraffinic lube suitable for use as a wax crystal modifier is derived from a Fischer-Tropsch product that has been catalytically dewaxed.

[0011] Preferably the Fischer-Tropsch product is obtained by conducting a Fischer-Tropsch process under conditions sufficient to produce products containing greater than 20 lbs. of 700° F.+(371° C.+) product per 100 lbs. CO converted and more preferably greater than 24 lbs. of 700° F.+(371° C.+) product per 100 lbs. CO converted. This can be achieved by at least one of (a) the appropriate selection of process operating conditions and (b) choice of catalyst.

[0012] Preferably, the Fischer-Tropsch process is conducted at temperatures no greater than 430° F. (221° C.), for example, from about 330° F. to about 430° F. (148° C. to 221° C.). More preferably the reaction is conducted at no greater than 410° F. (210° C.). Operating pressures typically are in the range of from about 10 to about 600 psia, preferably from about 250 to about 350 psia, and space velocities of about 1000 to 25,000 cc/cc/hour.

[0013] The Fischer-Tropsch process preferably is conducted in a slurry bubble column reactor. In slurry bubble column reactors catalyst particles are suspended in a liquid and gas is fed into the bottom of the reactor through a gas distributor. As the gas bubbles rise through the reactor the reactants are absorbed into the liquid and diffuse to the catalyst where they are converted to both gaseous and liquid products. Gaseous products are recovered at the top of the column and liquid products are recovered by passing the slurry through a filter which separates the solid catalyst from the liquid. An optimal method for operating a three phase slurry bubble column is disclosed in EP 0450860 B1 which is incorporated herein by reference in its entirety.

[0014] Suitable Fischer-Tropsch catalysts comprise one or more Group VIII metals such as Fe, Ni, Co, and Ru on an inorganic oxide support. Additionally, the catalyst may also contain a promoter metal. One suitable catalyst for the process of the invention is cobalt promoted with rhenium supported on titania having a Re:Co weight ratio in the range of about 0.01 to 1 and containing about 2 to 50 wt % cobalt. Examples of such catalysts can be found in U.S. Pat. No. 4,568,663; U.S. Pat. No. 4,992,406; and, U.S. Pat. No. 6,117,814.

[0015] Another suitable and preferred catalyst for the Fischer-Tropsch process comprises cobalt and especially cobalt and rhenium on a support comprising primarily titania and a minor amount of cobalt aluminate. In general the support will contain at least 50 wt % titania and preferably from 80 to about 97 wt % titania based on the total weight of the support. About 20 to 100 wt %, and preferably 60 to 98 wt % of the titania of the support is in the rutile crystalline phase with the balance being the anatase crystalline phase or amorphous phases. The amount of cobalt aluminate in the binder is dependent upon the amount of cobalt and aluminum compounds used in forming the support. Suffice it to say that sufficient cobalt is present in the support to provide a cobalt/aluminum atomic ratio greater than 0.25, preferably from 0.5 to 2, and more preferably about 1. Thus, at a Co/Al ratio of 0.25 about half the aluminum oxide is present as cobalt aluminate. At a Co/Al ratio of 0.5 substantially all the alumina oxide present is present as cobalt aluminate. At Co/Al ratios above 0.5 the support will contain cobalt titanate in addition to cobalt aluminate and be essentially free of alumina.

[0016] The support is typically formed by spray drying a suitable aqueous slurry of titania, alumina binder material and optionally silica binder material into a purged chamber with heated air at an outlet temperature of about 105° C. to 135° C. Spray drying produces a spherical support with a size range of about 20 to 120 microns. This spray dried support is then calcined at temperatures in the range of 400° C. to 800° C., preferably about 700° C. Next the calcined material is impregnated with an aqueous solution of a cobalt compound, preferably cobalt nitrate, in an amount sufficient to convert, upon calcination, at least part of the alumina to cobalt aluminate. Preferably sufficient cobalt compound is used to convert from 50% to 99+% of the alumina to cobalt aluminate. Therefore, the amount of cobalt compound added during the preparation of the support will correspond to an atomic ratio of Co:Al in the range of 0.25:1 to 2:1 and preferably 0.5:1 to 1:1. Indeed, it is especially preferred that the support produced be substantially free of alumina.

[0017] Calcination of the cobalt impregnated support preferably is conducted in air at temperatures in the range of about 700° C. to about 1000° C., preferably about 800° C. to about 900° C.

[0018] Typically the support will have a surface area in the range of from about 5 m^2/g to about 40 m^2/g and preferably from 10 m^2/g to 30 m^2/g. Pore volumes range from about 0.2 cc/g to about 0.5 cc/g and preferably from 0.3 cc/g to 0.4 cc/g.

[0019] In preparing the catalyst the cobalt and rhenium promoter are composited with the support by any of a variety of techniques well known to those skilled in the art, including impregnation (either co-impregnation with promoters or serial impregnation—either by spray drying or by the incipient wetness techniques). Since a preferred catalyst for fixed bed Fischer-Tropsch processes is one wherein the catalytic metals are present in the outer portion of the catalyst particle, i.e., in a layer no more than 250 microns deep, preferably no more than 200 microns deep, a preferred method of preparing the catalyst is the spray method which is described in U.S. Pat. No. 5,140,050, incorporated herein by reference or in EP 0 266 898, incorporated herein by reference. For slurry Fischer-Tropsch processes, catalysts are preferably made by incipient wetness impregnation of spray-dried supports. When using the incipient wetness impregnation technique, organic impregnation aids are optionally employed. Such aids are described in U.S. Pat. No. 5,856,260, U.S. Pat. No. 5,856,261 and U.S. Pat. No. 5,863,856, all incorporated herein by reference.

[0020] The amount of cobalt present in the catalyst will be in the range of 2 to 40 wt % and preferably 10 to 25 wt % while the rhenium will be present in weight ratios of about 1/20 to 1/10 of the weight of cobalt.

[0021] By selecting the appropriate Fischer-Tropsch reaction conditions, the appropriate catalyst, or both as described above the amount of high molecular weight waxy product formed is favored.

[0022] A 450° F.+(232° C.+) cut of the waxy product is separated from other hydrocarbons produced in the Fischer-Tropsch process and then is catalytically hydroisomerized. Suitable hydroisomerization catalysts typically include at least one Group VIII hydrogenating metal component selected from Pt, Pd, Rh, Ir and preferably at least Pt on a refractory metal oxide support, or preferably on a zeolite support. The catalyst typically contains from about 0.1 wt % to about 5 wt % metal. Examples of such catalysts include a noble metal, e.g., Pt on ZSM-23, ZSM-35, ZSM-48, ZSM-57 and ZSM-22.

[0023] A preferred catalyst is Pt on ZSM-48. The preferred preparation of ZSM-48 is disclosed in U.S. Pat. No. 5,075,269 incorporated herein by reference. The Pt is deposited on the ZSM-48 by techniques well known in the art such as impregnation, either dry or by incipient wetness techniques.

[0024] Isomerization is conducted under conditions of temperatures between about 500° F. (260° C.) to about 900° F. (482° C.), preferably 550° F. (288° C.) to 725° F. (385° C.), pressures of 1 to 10,000 psi H_2, preferably 100 to 2,500 psi H_2, hydrogen gas rates of 50 to 3,500 SCF/bbl, and a space velocity in the range of 0.25 to 5 v/v/hr, preferably 0.5 to 3 v/v/hr.

[0025] Following isomerization, the isomerate may be distilled into cuts of various ranges. The heavy fraction used as a wax crystal modifier typically will have a final boiling point after 95 mass percent has been distilled off of greater than 850° F. (454° C.), and preferably greater than 950° F. (510° C.), and even higher.

[0026] In an alternate embodiment of the invention the heavy fraction used as a wax crystal modifier may be obtained as the waxy fraction removed from a dehazed paraffinic oil. The waxy fraction may be removed by techniques known in the art such as filtration, precipitation, distillation, adsorption and the like.

[0027] In yet another embodiment of the invention the heavy fraction used as wax crystal modifier is obtained by catalytically hydroisomerizing a poly-ethylene wax and distilling the isomerate, taking as the heavy fraction the material boiling above 1050° F. (566° C.).

[0028] Low molecular weight polyethylene waxes are derived from high density polyethylene. They are hard, crystalline materials that melt to a low viscosity. They do not contain any chemical functional groups. A range of products may be obtained using different distillation conditions. Examples are the Polyflo® products available commercially from SasolWax. These polyethylene waxes may be catalytically hydroisomerized in a process similar to that described above for waxy Fischer-Tropsch feeds.

[0029] The heavy fraction or waxy material is added to the lube to be pour point depressed in an amount sufficient to lower the pour point of the oil. Typically this will be in the range of from about 0.01 to 30 wt % based on the weight of the lube oil.

[0030] Lube base oils that may have their pour point depressed with the additive of the invention include lube oils derived from paraffinic Fischer-Tropsch products and conventional lube oils prepared from petroleum feedstocks.

[0031] In one aspect of the invention, the heavy fraction may be added to the lube to be pour point depressed without having been separated from the dewaxed paraffinic lube of which it constitutes a fraction. Thus, a first base lube containing some or no heavy fraction may be blended with a second lube containing an amount of a heavy fraction greater than the first lube. The amount of second lube blended with the first lube will be an amount sufficient to lower the pour point of the first lube. In general, the amount of the second lube added to the first lube is that amount which will provide a lube blend containing between about 0.01 to 0.50 parts by weight of a heavy fraction, preferably between 0.01 and 0.30 and more preferably between 0.01 and 0.20.

[0032] In general, to provide a pour point depressing effect upon blending, the amount of the heavy fraction in the second lube will be at least 0.10 parts by weight of the second lube, preferably 0.20 parts by weight, more preferably 0.50 and most preferably 0.70 parts by weight of the second lube.

[0033] The fractional amounts of the heavy fraction, i.e., the material having a final boiling point of greater than 850° F. (454° C.) can be determined by any suitable method for determining boiling point distribution, such as, fractional distillation or by simulated boiling point distribution measurement by gas chromatographic distillation.

EXAMPLES

[0034] In these Examples the pour point was determined by test method ASTM D-5950 and the cloud point by ASTM D5773.

[0035] Also, the Pt/ZSM-48 catalyst used was prepared according to U.S. Pat. No. 5,075,269 by adding the Pt compound by impregnation followed by calcination and reduction.

Example 1

[0036] Fischer-Tropsch wax was processed over Pt/ZSM-48 in a wide cut mode. A wide boiling feed fraction, nominally 430° F. (221° C.) plus material was hydroisomerized under conditions sufficient to reduce the pour point and cloud point of the product. The wide boiling product from this process was fractionated into a 730-975° F. (388-524° C.) fraction and a 975° F.+(524° C.+) fraction. The pour point and cloud point for the 730-975° F. fraction were −18° C. and −6° C. respectively. The pour point and cloud point of the 975° F. fraction were −9° C. and 11° C. respectively. When the 975° F.+fraction was added to the 730-975° F. fraction it was observed that the pour point decreased dramatically with little increase in cloud point at low addition rates. The results are shown in **FIG. 1**.

[0037] As can be seen, at about 5% addition of 975° F.+a maximum pour point depressant effect is observed.

Example 2

[0038] A hazy Fischer-Tropsch lube was prepared by hydroisomerization of a nominal 430° F. (221° C.) fraction over Pt/ZSM-48 at approximately 610° F. (321° C.) at 250 psig H_2 and 1 LHSV. The resulting product was fractionated to produce the 1000° F.+fraction having a pour point of −5° C.

[0039] A conventional basestock produced from catalytic dewaxing having a viscosity of 4.33 cSt and a pour point of −20° C. was combined with the hazy fraction of Fischer-Tropsch lube, having a pour point of −5° C. and a cut point of 1000° F.+(538° C.). The pour point is significantly reduced from 20° C. to −30° C. with the addition of 10% by weight of the heavy GTL lube. The results are shown in **FIG. 2**.

Example 3

[0040] A conventional petroleum derived basestock produced from catalytic dewaxing having a viscosity of 5.98 cSt and a pour point of −16° C was combined with a hazy fraction of Fischer-Tropsch lube, having a pour point of −5° C., a cloud point of 23° C. and a cut point of 1000° F.+and prepared as described in Example 2. At about 20% addition of heavy FT oil, a maximum reduction in pour point from −16° C. to of −24° C. is obtained. The results are given in **FIG. 3**.

Example 4

[0041] A conventional petroleum derived basestock produced from catalytic dewaxing having a viscosity of 5.98 cSt and a pour point of −16° C. was combined with an of Fischer-Tropsch lube which had the haze selectively removed, having a pour point of −5° C., a cloud point of 13° C. and a cut point of 950° F.+(510° C.). In this example, at only 5-10 percent addition, the maximum pour point reduction was obtained of a change from −16° C. pour point to −21° C. pour point. The cloud point in this example was increased only slightly, from −10° C. to −7° C. In contrast with Example 3 where a hazy 1000° F.+(371° C.) oil was used for pour point depression, this example shows a smaller pour point depression response for the adsorbate de-hazed oil. The results are shown in **FIG. 4**.

Example 5

[0042] A conventional petroleum derived basestock produced from catalytic dewaxing having a viscosity of 5.98 cSt and a pour point of −16° C. was combined with the haze fraction removed from a sample of hazy Fischer-Tropsch lube prepared as described in Example 2. Before de-hazing the lube had a pour point of −5° C., a cloud point of 36° C. and a cut point of 950° F.+(510° C.). The haze removed from this lube had a cloud point of 50° C. and a pour point above room temperature. The results are given in **FIG. 5**.

Example 6

[0043] Polyethylene wax, with a MW of 1100 and a melting point of approximately 110° C. was converted in a batch reactor over a ZSM-48 catalyst for 2 hours at 655° F. (346° C.) at 500 psig hydrogen. The product produced from this catalytic reaction had the following boiling distribution. As can be seen from the GCD data, the isomerate product contains 67% 700° F.+(371° C.+) material.

GCD	Mass Percent Off
320° F.	4.47
500° F.	15.89
700° F.	32.31
850° F.	47.98
950° F.	59.65
1050° F.	72.08

[0044] The total liquid product from this process had a pour point of −3° C. and a cloud point of 36.4° C. This entire boiling range product was added to a conventional petroleum derived basestock produced from catalytic dewaxing having a viscosity of 5.98 cSt and a pour point of −16° C. The results of these blends are shown in **FIG. 6**. At low concentrations, the pour point of the resulting blend is significantly depressed relative to the starting base stock. Although this material has a lower initial boiling point, it is predominately 700° F. (371° C.) material. This concentration of heavy lube present in this wide boiling isomerate is sufficient to achieve the desirable pour point reduction response.

What is claimed is:

1. A method for modifying the process by which wax crystals form in a paraffinic containing hydrocarbon liquid when the temperature of the liquid is lowered comprising adding to the liquid an effective amount of a heavy fraction of a paraffinic lube produced over a dewaxing catalyst.

2. The method of claim 1 wherein the heavy fraction has a final boiling point above 850° F. (454° C.).

3. The method of claim 2 wherein the paraffinic lube is produced from a Fischer-Tropsch product.

4. The method of claim 2 wherein the heavy fraction is extracted as a waxy material from said paraffinic lubes.

5. The method of claim 2 wherein the paraffinic lube is produced from a polyethylene wax.

6. The method of claim 3 wherein the hydrocarbon liquid is a base lube oil and wherein the heavy fraction is added in a pour point lowering amount.

7. The method of claim 3 wherein the hydrocarbon liquid is a first base lube oil, and the heavy fraction is added in a pour point lowering amount in the form of a second base oil containing a greater fractional amount of the heavy fraction than that contained in the first lube oil.

8. The method of claim 7 wherein the second lube oil is added to the first lube oil in an amount sufficient to provide a blend containing from about 0.01 parts by weight to about 0.5 parts by weight of a heavy fraction.

9. The method of claim 8 wherein the amount of heavy fraction in the second lube is in the range of about 0.10 to about 0.70 parts by weight.

10. The method of claim 3 wherein the hydrocarbon liquid is a crude oil and the heavy fraction is added in an amount sufficient to lower the temperature for wax deposition.

11. The method of claim 3 wherein the hydrocarbon liquid is a diesel or heating fuel and the heavy fraction is in the form of a second base oil containing a greater fractional amount of the heavy fraction than that contained in the first lube oil, and second base oil is added in an amount to lower the cold filter plugging point.

12. The method of claim 11 wherein the second lube oil is added to the first lube oil in an amount sufficient to provide a blend containing from about 0.01 parts by weight to about 0.5 parts by weight of a heavy fraction.

13. The method of claim 12 wherein the amount of heavy fraction in the second lube is in the range of about 0.10 to about 0.70 parts by weight.

14. A fuel composition comprising a major amount of a diesel or heating fuel and a heavy fraction of a paraffinic lube produced over a dewaxing catalyst, the heavy fraction being in an amount sufficient to lower the cold filter plugging point of the fuel.

15. The method of claim 14 wherein the heavy fraction has a final boiling point above about 850° F. (454° C.).

16. A blend of a first paraffinic containing hydrocarbon liquid and a second paraffinic containing hydrocarbon liquid wherein the second liquid contains a heavy hydrocarbon fraction having a final boiling point greater than 850° F. (454° C.) in an amount greater than that in the first liquid and wherein the amount of the heavy fraction in the total blend is in the range of from about 0.01 to 0.5 parts by weight.

17. The blend of claim 16 wherein the second liquid contains from about 0.10 to 0.70 parts by weight of the heavy hydrocarbon fraction.

* * * * *