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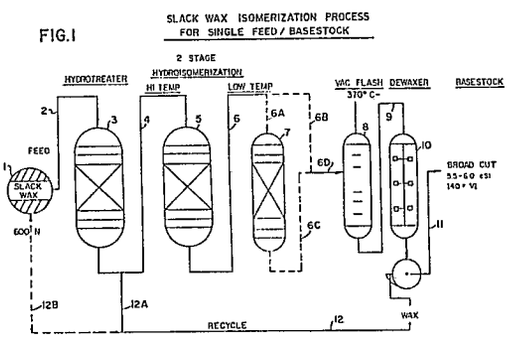
(54) Method for isomerizing wax to lube base oils.

(57) Slack waxes and synthetic wax (1) are isomerized and processed into high viscosity index (VI) and very low pour point lube base stock oils and blending stocks (11) by the process comprising the steps of optionally hydrotreating (3) the wax, if necessary, to remove heteroatom and polynuclear aromatic compounds and/or optionally deoiling the wax , if necessary, to an oil content between about 5-20% oil, isomerizing (5, 7) the wax over a catalyst of Group VI-Group VIII metal on a halogenated refractory metal oxide support, said isomerization being conducted to a level of conversion such that about 40% or less unconverted wax remains in the 330°C+ (preferably the 370°C+) fraction sent to the dewaxer. The total isomerate from the isomerization unit is fractionated (8) into a lube oil fraction (9) boiling at 330°C+, preferably 370°C+. This oil fraction is solvent dewaxed (10), preferably using MEK/MIBK at 20/80 ratio, and unconverted wax (12) is recycled (12A, 12B) to the isomerization unit. Operating in this manner permits one to obtain isomerate oil (11) of very high VI (in excess of 130) possessing a low pour point (-21°C, preferably -24°C, most preferably -27°C).

FIG.1



EP 0 321 307 A2

Description

METHOD FOR ISOMERIZING WAX TO LUBE BASE OILS

Brief Description of the Invention

A process is disclosed of the production of non-conventional lube oil base stocks or blending stocks of very low pour point, pour point of about -21°C or lower, preferably about -24°C or lower, said pour points being achieved by conventional dewaxing techniques without resort to deep dewaxing procedures, and very high viscosity index (VI), VI's of about 130, and higher, preferably 135 and higher by the isomerization of waxes over isomerization catalysts in an isomerization unit to a level of conversion such that about 40% or less, preferably 15-35%, most preferably 20-30%, unconverted wax remains in the fraction of the isomerate boiling in the lube boiling range sent to the dewaxing unit calculated as (unconverted wax)/(unconverted wax + dewaxed oil)X100. For the purposes of this application the amount of unconverted wax in the 370°C$^+$ oil fraction is taken to be the amount of wax removed or recovered from said oil fraction upon dewaxing. The total product from the isomerization (isom) unit is fractioned into a lube oil fraction boiling in the 330°C$^+$ range, preferably in the 370°C$^+$ range. This lube oil fraction is solvent dewaxed preferably using 20/80 mixture of MEK/MIBK and unconverted wax is recycled to the isomerization unit.

Operating the isomerization unit at a level of conversion such that the oil fraction sent to the dewaxer contains about 40% or less wax, preferably 15 - 35% wax, most preferably 20-30% unconverted wax goes against the conventional wisdom of isomerization operations. Lower levels of conversion, i.e. those levels at which a substantial portion of wax remains unconverted in the lube oil fraction sent to the dewaxer (and is subsequently recovered at the dewaxer for recycle) are typically seen as favoring maximization of lube oil production since operation at lower levels of conversion tend to favor the production of lube oil as compared to lower boiling fuels. The amount of wax present in the oil sent to the dewaxer normally should have no significant impact on the dewaxability of the oil or the pour point which can be achieved. There may be a point beyond which so much wax is present as to be beyond the ability of the dewaxer to handle the volume of waxy oil but this tradionally is a materials handling problem and does not affect the ability of the dewaxer to dewax oil to the desired pour point using conventional dewaxing techniques and temperatures. High levels of conversion however tend to produce larger quantities of fuels.

It has been discovered, that at low levels of conversion difficulty is encountered in producing a lube oil having a pour point of at least -21°C from wax isomerate. To produce a lube oil fraction which can be easily dewaxed to a pour point of at least-21°C it has been found that the isomerization unit should be run at a level of wax conversion such that about 40% or less, preferably 15-35%, most preferably 20-30% unconverted wax is in the lube fraction sent to the dewaxer.

Description of the Figures

Figure 1 is a schematic of the step sequences of the process of the present invention.

Figure 2 is a schematic of the step sequences of the process of the present invention including the optional step of waxy fractionator bottoms recycle.

Figure 3 illustrates the conversion behavior for three different Pt F/Al_2O_3 catalysts on a light slack wax (obtained from 600N raffinate) containing about 22% oil.

Detailed Description of the Invention

In Figure 3, the shape of the curves on the ternary diagram are a measure of the selectivity for converting wax into oil (e.g. 370°C$^+$ oil) and fuels (e.g. product boiling below 370°C-). These curves were generated by running the catalysts on a 600N wax feed at conditions of 1000 psi H_2, 0.9 V/V/hr, 5000 SCF/bbl, H_2, and temperatures ranging from 280-360°C.

The most selective catalysts produce higher oil yields and less fuel at any given residual wax level. Catalyst I (Catalyst 1 of Example 4 herein) produces a maximum once through oil yield of almost 55 wt.% on feed. Catalysts II (catalyst 8 of Example 5 herein) and III (comparison catalyst 1 of Example 5) produce maximum once-through oil yields of about 50 and about 45 wt.% respectively. Though the curves represent catalyst selectivity on a once through operation, they are a good guide to performance in a recycle-to-extinction process.

In principle a wax extinction process for maximizing lube yields would involve operation at a very low severity i.e. where conversion to fuels is at a minimum. Under these circumstances the amount of unconverted wax recycled to the isomerization reactor would be large and differences in catalyst selectivity would be less important.

In practice however, it is not possible to operate in a low conversion mode. Instead, the operating severity is governed by the need to make a low pour ($\leqq$ -21°C pour point) oil. It has been discovered that low pours cannot be achieved from isomerates made at low conversion. This is unexpected since with natural oils the amount of wax present did not affect the ability to dewax the oil to low target pour point. A critical determinant in reaching low pours is that the amount of wax remaining in the 370C+ fraction obtained from isomerization should not exceed 40% and for lower pour points may have to be as little as 25%. To maximize yield in this

situation the choice of catalyst becomes important.

As wax in 370C+ oil product declines from 50 to 25%, (Figure 3), the ratio of oil to fuels decreases. This trend is much more pronounced with the least selective catalyst III. This is also illustrated in the Table below. All yields are based on a once through operation.

Catalyst	I			II			III		
% Wax in oil product	25	40	50	25	40	50	25	40	50
Wax left (% of feed)	18.5	34	44.5	17	32	43	12	30	42
Oil yield (% of feed)	54.5	50	44.5	49.5	48	43	36	45	42
Fuels Yield (% of feed)	27.0	16	10	33.5	20	14	52	25	16

The full recycle oil yields for catalysts I, II and III, in which wax is recycled to extinction, can be predicted assuming the same conversion selectivity applies for recycled wax. On this basis, the yield distinctions between catalysts are even more pronounced.

Catalyst	-I-			-II-			-III-		
% Wax in oil (once-through)	25	40	50	25	40	50	25	40	50
Predicted extinction recycle yield of 370C+ oil	69	78	82	60	72	79	40	62	72

At a 25% wax in oil conversion level, Catalyst I is actually 70% more selective for oil than Catalyst III in an extinction recycle process. Thus small differences in catalyst selectivity identified in once through operations can translate into significant yield differences in a recycle process.

Another way to express the different performance of each catalyst is to determine the reaction severity required to achieve a particular target oil yield in a full recycle operation. For the target of 70% oil yield shown in Figure 3, catalyst I converts much more wax into oil than does catalyst III (i.e. there is less unconverted wax remaining in catalyst I product). In this case, catalyst III cannot simultaneously meet a target yield of 70% oil and a target of $\leqq$ -21°C pour point, since the amount of unreacted wax in oil exceeds 40%.

The wax which is isomerized may come from any of a number of sources. Synthetic waxes from Fischer-Tropsch processes may be used, as may be waxes recovered from the solvent or autorefrigerative dewaxing of conventional hydrocarbon oils as well as mixtures of these waxes. Waxes from dewaxing conventional hydrocarbon oils are commonly called slack waxes and usually contain an appreciable amount of oil. The oil content of these slack waxes can range anywhere from 0 to 45% or more, usually 5 to 30% oil. For the purposes of this application, the waxes are divided into two categories: (1) light paraffinic waxes boiling in the range about 300-580°C and (2) heavy micro waxes having a substantial fraction (>50%) boiling above 600°C.

Isomerization is conducted over a catalyst containing a hydrogenating metal component typically one from Group VI or Group VIII or mixtures thereof, preferably Group VIII, more preferably noble Group VIII most preferably platinum on a halogenated refractory metal oxide support. The catalyst typically contains from 0.1-5.0 wt.% metal, preferably 0.1 to 1.0 wt.% metal, most preferably 0.2-0.6 wt.% metal. The refractory metal oxide support is typically a transition e.g. gamma or eta alumina and the halogen is most usually fluorine.

A preferred catalyst contains a hydrogenation metal component which is a Group VIII metal or mixtures thereof, preferably noble Group VIII metal, most preferably platinum on a fluorided alumina or material containing alumina, preferably alumina or material consisting predominantly (i.e. >50%) of alumina, most preferably gamma or eta alumina wherein said catalyst in its as introduced to waxy feed form is characterized by possessing (1) a hydrate level of 60 or less, preferably 10 to 60 determined as the relative amount of hydrate represented by a peak in the X-ray diffraction (XRD) pattern at 20 = 5.66Å when a hydrate level of 100 corresponds to the XRD peak height exhibited by a standard material constituting 0.6 wt% Pt on 150 m^2/g γ

alumina containing 7.2 wt% F wherein the fluorine has been deposited using an aqueous solution containing a high concentration of HF, i.e. 10 wt% HF and greater, preferably 10 to 15 wt% HF and the material dried at 150°C for 16 hrs; (2) a surface nitrogen content N/Al ratio of 0.01 or less, preferably 0.007 or less, most preferably 0.004 or less as determined by X-ray photoelectron spectroscopy (XPS); (3) a bulk fluorine concentration of about 2 to 10 wt% and (4) a surface fluorine present in a layer extending from the surface of the particle (e.g. 1/16 inch extrudates) to a depth of 1/100 inch, of less than 3 wt%, preferably less than 1 wt%, most preferably less than 0.5 wt% fluorine in that zone provided that the surface fluoride concentration is less than the bulk fluoride concentration.

The fluoride content of the catalyst can be determined in a number of ways.

One technique analyzes the fluorided catalyst using oxygen combustion methodology which is well established in the literature. Approximately 8-10 mgs of sample is mixed with 0.1 g benzoic acid and 1.2 gms of mineral oil in a stainless steel combustion capsule which is mounted in a 300 mL. Parr oxygen combustion bomb. The "sample" is purged of air and subsequently combusted under 30 Atms of pure oxygen. Combustion products are collected in 5 mL. of deionized water. Once the reaction has gone to completion (about 15 minutes), the absorbing solution is quantitatively transferred and made to fixed volume.

Fluoride concentration of the sample is determined by ion chromatography analysis of the combustion product solution. Calibration curves are prepared by combusting several concentrations of ethanolic KF standards (in the same manner as the sample) to obtain a 0-10 ppm calibration range. Fluoride concentration of the catalyst is calculated on an ignition-loss-free-basis by comparison of the sample solution response to that of the calibration curve. Ignition loss is determined on a separate sample heated at 800 degrees F for at least 2 hours. Ion chromatographic analysis uses standard anion conditions.

Another procedure employs the use of fluoride distillation with a titrimetric finish. Fluorides are converted into fluorosilicic acid (H_2SiF_6) by reaction with quartz in phosphoric acid medium, and distilled as such using super heated steam. This is the Willard-Winter-Tananaev distillation. It should be noted that the use of super heated, dry (rather than wet) steam is crucial in obtaining accurate results. Using a wet steam generator yielded results 10-20% lower. The collected fluorosilicic acid is titrated with standardized sodium hydroxide solution. A correction has to be made for the phosphoric acid which is also transferred by the steam. Fluoride data are reported on an ignition-loss-free-basis after determination of ignition loss on a sample heated to 400 degree C for 1 hour.

Another preferred catalyst is a catalyst prepared by a process involving depositing a hydrogenation metal on an alumina or material containing alumina support, calcining said metal loaded support typically at between 350 to 500°C, preferably about 450 to 500°C for about 1 to 5 hrs, preferably about 1 to 3 hrs and fluoriding said metal loaded support using a high pH fluorine source solution to a bulk fluorine level of about 8 wt% or less (e.g., 2 to 8 wt%), preferably about 7 wt% or less, said high pH source solution being at a pH of 3.5 to 4.5 and preferably being a mixture of NH_4F and HF followed by rapid drying/heating in a thin bed or rotary kiln to insure thorough even heating in air, oxygen containing atmosphere or an inert atmosphere to a temperature between about 350 to 450°C in about 3 hours or less, preferably 375 to 400°C and holding at the final temperature, if necessary, for a time sufficient to reduce the hydrate and nitrogen content to the aforesaid levels, e.g. holding for 1 to 5 hours or using a low pH fluorine source solution having a pH or less than 3.5 to a bulk fluorine level of about 10 wt% or less (e.g., 2 to 10 wt%), preferably about 8 wt% or less followed by drying/heating in a thin bed or rotary kiln to a temperature of about 350 to 450°C, preferably 375 to 425°C and holding, if desired, at that temperature for 1 to 5 hours, in air, an oxygen containing atmosphere, or inert atmosphere. The alumina or alumina containing support material is preferably in the form of extrudates and are preferably at least about 1/32 inch across the longest cross sectional dimension. If the catalyst is first charged to a unit, heating a dense bed charge of catalyst will be for a longer period, longer than 5 hours, preferably longer than 10 hours and preferably at temperatures of 400 to 450°C.

The above catalysts typically contain from 0.1 to 5.0 wt% metal, preferably 0.1 to 1.0 wt% metal, most preferably 0.2 to 0.6 wt% metal.

The dried/heated catalyst has a surface nitrogen content N/Al of 0.01 or less by X-ray photo-electron spectroscopy (XPS), preferably an N/Al of 0.007 or less, most preferably an N/Al of 0.004 or less by XPS.

The catalyst, following the above recited heating step, can be charged to the isomerization reactor and brought quickly up to operating conditions. Alternatively following the above recited heating step the catalyst prepared using the pH 3.5 - 4.5 solution technique can be activated preferably in pure or plant hydrogen (60-70 vol% H_2) at 350 to 450°C, care being taken to employ short activation times, from 1 to 24 hours, preferably 2 to 10 hours being sufficient. Long activation times (in excess of 24 hours) have been found to be detrimental to catalyst performance. By way of comparison, catalysts made using solutions of pH less than 3.5 can be activated in pure or plant hydrogen at 350 to 500°C for from 1 to 48 hours or longer. In fact, if catalysts prepared using solutions of pH 3.5 or less are not heated first, then it is preferred that they be subsequently activated at more severe conditions, i.e. for longer times and/or at higher temperatures. On the other hand, if they are heated first, then moderate activation procedures similar to those employed with catalysts made from the higher pH solution treatment will suffice.

A typical activation profile shows a period of 2 hours to go from room temperature to 100°C with the catalyst being held at 100°C for 0 to 2 hours then the temperature is raised from 100 to about 350 over a period of 1 to 3 hours with a hold at the final temperature of from 1-4 hours. Alternatively the catalyst can be activated by heating from room temperature to the final temperature of 350-450°C over a period of 2-7 hours with a hold at

the final temperature of 0-4 hours. Similarly activation can be accomplished by going from room temperature to the final temperature of 350-450°C in 1 hour.

It is possible to dispense with a separate activation procedure entirely, (provided the catalyst has first been heated in air). In these instances, the calcined catalyst is simply charged to the reactor, heated to just above the melting point of the wax feed, feed and hydrogen introduced onto the catalyst, and thereafter the unit brought quickly up to operation conditions.

Another preferred catalyst comprises a hydrogenating metal on fluorided alumina or material containing alumina support made by depositing the hydrogenation metal on the support and fluoriding said metal loaded support using acidic fluorine sources such as HF by any convenient technique such as spraying, soaking, incipient wetness, etc. to deposit beween 2-10%F preferably 2-8%F. Following halogenation the catalyst is dried, typically at 120°C and then crushed to expose inner surfaces, the crushed catalyst and is double sized to remove fines and uncrushed particles. This sieved catalyst is 1/32 inch and less and typically from 1/64 to 1/32 inch in size across its largest cross-sectional dimension.

The starting particle or extrudate may be of any physical configuration. Thus particles such as cylinders, trilobes or quadri lobes may be used. Extrudates of any diameter may be utilized and can be anywhere from 1/32 of an inch to many inches in length, the length dimension being set solely by handling considerations. It is preferred that following sizing the particle have a length smaller than the initial extrudate diameter.

Following deposition of the hydrogenation metal and the fluoriding of the particle or extrudate, the particle or extrudate is crushed or fractured to expose inner surfaces.

The crushing is conducted to an extent appropriate to the particle or extrudate with which one is starting. Thus, an extrudate which is 1 foot long and 1/16 inch in diameter would be sized into pieces which range anywhere from 1/64 to 1/32 inch across its longest cross-sectional dimension. Similarly, if the extrudate is only 1/16 inch to begin with it will be enough simply to break it in half, into two 1/32 inch pieces, for example.

Alternatively, one can take a metal loaded support particle which is already about 1/32 inch in size or smaller and fluoride it as described above using HF.

Generally, therefore, the sized material will range in size between about 1/64 to 1/32 inch in size.

The uncalcined sized catalyst is activated in a hydrogen atmosphere such as pure hydrogen or plant hydrogen containing 60 to 70 vol% hydrogen by heating to 350 to 500°C, preferably 350 to 450°C for from 1 to 48 hours or longer. The hydrogen activation profiles described above may similarly be employed here.

This sized catalyst is unexpectedly superior for wax isomerization as compared to the uncrushed particle or extrudate starting material. It has also been discovered that 370°C$^+$ oil products made using the sized catalyst as compared to the uncrushed or extrudate material starting with wax possessing about 5-10% oil exhibit higher VI's than do 370°C$^+$ oil products made starting with wax possessing 0% oil (on the one hand) and about 20% oil (on the other). Therefore, to produce products having the highest VI one would isomerize wax having from 5-15% oil, preferably 7-10% oil using the "sized" catalyst produced using HF.

As one would expect isomerization catalysts are susceptible to deactivation by the presence of heteroatom compounds (i.e. N or S compounds) in the wax feed so care must be exercised to remove such heteroatom materials from the wax feed charges. When dealing with high purity waxes such as synthetic Fischer-Tropsch waxes such precautions may not be necessary. In such cases subjecting such waxes to very mild hydrotreating may be sufficient to insure protection for the isomerization catalyst. On the other hand waxes obtained from natural petroleum sources contain quantities of heteroatom compounds as well as appreciable quantities of oil which contain heteroatom compounds. In such instances the slack waxes should be hydrotreated to reduce the level of heteroatoms compounds to levels commonly accepted in the industry as tolerable for feeds to be exposed to isomerization catalysts. Such levels will typically be a N content of about 1 to 5 ppm and a sulfur content of about 1 to 20 ppm, preferably 2 ppm or less nitrogen and 5 ppm or less sulfur. Similarly such slack waxes should be deoiled prior to hydrotreating to an oil content in the range of 0-35% oil, preferably 5-25% oil. The hydrotreating step will employ typical hydrotreating catalyst such as Co/Mo, Ni/Mo, or Ni/Co/Mo on alumina under standard, commercially accepted conditions, e.g., temperature of 280 to 400°C, space velocity of 0.1 to 2.0 V/V/hr, pressure of from 500 to 3000 psig H_2 and hydrogen gas rates of from 500 to 5000 SCF/b.

In the present invention isomerization of waxes over the above particularly recited isomerization catalysts is conducted to a level of conversion which optimizes the conversion of wax to lube range materials while minimizing production of fuels range materials (i.e. 370°C$^-$ products) yet producing an overall lube oil product which does not contain more unconverted wax than can be efficiently handled by the solvent dewaxing unit i.e. 25-40% wax to the dewaxer.

Isomerization is conducted under conditions of temperatures between about 270 to 400°C, preferably 300-360°C, pressures of 500 to 3000 psi H_2, preferably 1000-1500 psi H_2, hydrogen gas rates of 1000 to 10,000 SCF/bbl, and a space velocity in the range 0.1-10 v/v/hr, preferably 1-2 v/v/hr.

Following isomerization the isomerate is fractioned into a lubes cut and fuels cut, the lubes cut being identified as that fraction boiling in the 330°C$^+$ range, preferably the 370°C$^+$ range or even higher. This lubes fraction is then dewaxed to a pour point of about -21°C or lower. Dewaxing is accomplished by techniques which permit the recovery of unconverted wax, since in the process of the present invention this unconverted wax is recycled to the isomerization unit. It is preferred that this recycle wax be recycled to the main wax reservoir and be passed through the hydrotreating unit to remove any quantities of entrained dewaxing solvent which solvent could be detrimental to the isomerization catalyst. Alternatively, a separate stripper can be used

to remove entrained dewaxing solvent or other contaminants. Since the unconverted wax is to be recycled dewaxing procedures which destroy the wax such as catalytic dewaxing are not recommended. Solvent dewaxing is utilized and employs typical dewaxing solvents. Solvent dewaxing utilizes typical dewaxing solvents such as C_3-C_6 ketones (e.g. methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C_6-C_{10} aromatic hydrocarbons (e.g. toluene) mixtures of ketones and aromatics (e.g. MEK/toluene), autorefrigerative solvents such as liquified, normally gaseous C_2-C_4 hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof, etc. at filter temperature of -25 to -30° C. The preferred solvent to dewax the isomerate especially isomerates derived from the heavier waxes (e.g. bright stock waxes) under miscible conditions and thereby produce the highest yield of dewaxed oil at a high filter rate is a mixture of MEK/MIBK (20/80 v/v) used at a temperature in the range -25 to -30° C. Pour points lower than -21° C can be achieved using lower filter temperatures and other ratios of said solvents but a penalty is paid because the solvent-feed systems becomes immiscible, causing lower dewaxed oil yields and lower filter rates. Further, when dewaxing isomerate made from a microwax, e.g. Bright Stock slack wax it is preferred that the fraction of the isomerate which is sent to the dewaxer is the "broad heart cut" identified as the fraction boiling between about 330 to 600° C, preferably about 370-580° C. After such fractionation the fraction sent to the dewaxer has about 40% or less unconverted wax. The heavy bottoms fraction boiling above about 580 to 600° C contains appreciable wax and can be recycled to the isomerization unit directly. However if any hydrotreating or deoiling is deemed necessary or desirable then the fractionation bottoms are reisomerized by being first sent to the fresh feed reservoir and combined with the wax therein.

It has also been found that prior to fractionation of the isomerate into various cuts and dewaxing said cuts the total liquid product (TLP) from the isomerization unit can be advantageously treated in a second stage at mild conditions using the isomerization catalyst or simply noble Group VIII on refractory metal oxide catalyst to reduce PNA and other contaminants in the isomerate and thus yield an oil of improved daylight stability.

In that embodiment the total isomerate is passed over a charge of the isomerization catalyst or over just noble Gp VIII on e.g. transition alumina. Mild conditions are used, e.g. a temperature in the range of about 170-270° C, preferably about 180 to 220° C, at pressures of about 300 to 1500 psi H_2, preferably 500 to 1000 psi H_2, a hydrogen gas rate in the range of from abut 500 to 10,000 SCF/bbl and a flow velocity of about 0.25 to 10 v/v/hr., preferably about 1-4 v/v/hr. Temperatures at the high end of the range should be employed only when similarly employing pressures at the high end of their recited range. Temperatures in excess of those recited may be employed if pressures in excess of 1500 psi are used, but such high pressures may not be practical or economic.

The total isomerate can be treated under these mild conditions in a separate, dedicated unit or the TLP from the isomerization reactor can be stored in tankage and subsequently passed through the aforementioned isomerization reactor under said mild conditions. It has been found to be unnecessary to fractionate the 1st stage product prior to this mild 2nd stage treatment. Subjecting the whole product to this mild second stage treatment produces an oil product which upon subsequent fractionation and dewaxing yields a base oil exhibiting a high level of daylight stability and oxidation stability. These base oils can be subjected to subsequent hydrofinishing using conventional catalysts such as KF-840 or HDN-30 (e.g. Co/Mo or Ni/Mo on alumina) at conventional conditions to remove undesirable process impurities to further improve product quality.

Figures 1 and 2 present schematic representations of preferred embodiments of the wax isomerization process.

In Figure 1, slack wax feed, derived from, for example a lighter oil such as 600N oil or lighter is fed from reservoir (1) to a hydrotreater (3) via line 2 wherein heteroatom compounds are removed from the wax. This hydrotreated slack wax is then fed via line 4 to the isomerization unit (5) after which the total liquid product is fed either directly via lines 6, 6B and 6D to the separation tower (unit 8) for fractionation into a lubes fraction boiling above about 370° C^+ and a light fraction boiling below about 370° C^- or, in the alternative the TLP from the isomerization unit is fed first via lines 6 and 6A to a low temperature, mild condition second stage treating unit (unit 7) wherein the TLP is contacted with the isomerization catalyst or simply a noble Group VIII metal on alumina catalyst to produce a stream which is then sent via lines 6C and 6D to the fractionation tower (unit 8). In either case the lube steam boiling in the 370° C^+ range is then forwarded via line 9 to the solvent dewaxer (unit 10) for the separation of waxy constituents therefrom, the dewaxed oil fraction being recovered via line-11 and if necessary forwarded to other conventional treatment processes normally employed on base stock or blending stock oils. The recovered wax is recycled either directly via line 12 and 12A to the slack wax stream being fed to the isomerization unit or it is recycled to the wax reservoir (1) via line 12B for passage through the hydrotreater prior to being recycled to the isomerization unit.

In Figure 2 the wax processing stream is much like that of Figure 1, the main differences being that Figure 2 represents the scheme for handling heavier slack wax feeds, such as a wax feed derived from Bright Stock oil. In such a case the wax from reservoir 1 is fed via line 2 to the hydrotreater (3) prior to being sent via line 4 to the isomerization unit (unit 5) after which it is either fed via lines 6 and 6A to a low temperature mild condition second stage treating unit (unit 7) wherein it is contacted with a further charge of isomerization catalyst or simply noble Group VIII metal on alumina and fed via lines 6C and 6D to the fractionator tower (unit 8), or fed directly via lines 6, 6B and 6D to the fractionation tower (unit 8). In the fractionation tower the isomerate made using the heavy wax is fractionated into a light fraction boiling in the 370° C^- (a fuels cut) a lube cut boiling in the 370° C^+ range and a bottoms fraction boiling in the 580° C^+ range. The lubes fraction, a broad cut boiling in

the 370°C to 580°C range is sent via line 9 to the dewaxer (unit 10) as previously described. The 580°C$^+$ bottoms fraction contains appreciable wax and is recycled via line 13, 13A, 13B and 4 to the isomerization unit (5). This bottoms fraction optionally can be combined via line 13 and 13C with the wax in line 12 recovered from the dewaxing unit (10) in which case this total recycled stream can be fed directly to the isomerization unit via lines 12A, 13B and 4 or it can be sent to the wax reservoir (1) via lines 12B for treatment in the hydrotreater prior to being fed to the isomerization unit.

The invention will be better understood by reference to the following examples which either demonstrate the invention or are offered for comparison purposes.

EXAMPLES

Example 1

Catalyst 1

A synthetic hydrocarbon synthesis wax (a Fischer-Tropsch wax), characterized as being 100% 370°C+ material possessing a melting point in the range 104 to 110°C, a mean carbon number (from viscosity data) of about 65 carbons, a boiling range of about 450-650°C (initial to 70 LV% off by GCD) and a kinematic viscosity of 9.69, was isomerized over a 14/35 meshed platinum on fluorided alumina catalyst made by first fluoriding a platinum loaded 1/16" alumina extrudate (0.6 wt.% platinum) using a 11.6 wt% aqueous HF solution (by soaking) after which the fluorided metal loaded extrudate was washed with 10 fold excess water and dried at 150C in vac. oven. The metal loaded fluorided extrudate was not calcined. It was crushed to produce particles of about 1/30" (meshed to 14/35). Catalyst 1 had a fluorine content of 8.3 wt%.

The sized catalyst, Catalyst 1, was activated by heating to 450°C in 50 psi flowing H_2 in the following manner: room temperature to 100°C in 2 hours, hold at 100°C for 1 hour; heat from 100°C to 450°C in 3 hours, hold at 450°C for 1 hour.

Table 1

DEWAXING FISCHER-TROPSCH SYNTHETIC WAX HYDROISOMERATES (370°C+)

	(LOW)	(HIGH)
Isomerization, Conditions		
Pressure, psi H_2	1000	1000
space velocity(v/v/hr)	1.0	1.0
gas treat rate (SCF/bbl, H_2)	7500	7500
Temp., °C	375-378	380.5
Time on stream (hrs)	4082-4584	4981-5287
Conversion Level		
Wt% 370°C-	13	19
Waxy Product Properties		
Cloud °C	98	86
Dewaxing Conditions		
Solvent:	40/60 V/V MEK/TOLUENE	
Dilution:	4 V/V on Waxy Feed	
Filter Temperature, °C	-30	-30
Viscosity, cSt @100°C	7.3	6.5
Dewaxed Oil Properties		
Pour, °C	-13	-20
Pour-Filter DT°C	17	10
Viscosity, cST @40°C	39	33.8
Viscosity, cST @100°C	7.5	6.7
Viscosity Index	163	159
Wt% Wax Recovered from 370°C+ Oil	48	30

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It is apparent that at low levels of conversion, where large quantities of unconverted wax remain in the 370°C+ oil to the dewaxer, it is not possible to achieve a low pour (i.e. about -21°C) using typical dewaxing solvents under standard conditions (i.e. filter temperature of -30°C). Lower pour point could be achieved if one were to go to extremely low filter temperature such as -40°C, but this puts strains on the refrigeration capability of the plant as well as possibly being beyond the metallurgical limitations of most plants. Operating at higher levels of conversion (e.g. 30% wax in the 370°C+ fraction to the dewaxer) is seen to facilitate achieving a low pour point while still being within the typical operating parameters of standard dewaxing plants.

Example 2

Catalyst 1

Slack wax from 600N oil was isomerized over Catalyst 1 described in Example 1 to three levels of conversion.

The slack wax was first hydrotreated over HDN-30 catalyst (a conventional Ni/Mo on alumina catalyst) at 350°C, 1.0 v/v/hr., 1500 SCF/BBL, H_2, 1000 psi (H_2). The catalyst had been on stream for 1447-1577 hours. The hydrotreated slack wax had sulfur and nitrogen contents of less than 1 ppm and contained about 23% oil.

TABLE 2

DEWAXING OF ISOMERATES DERIVED FROM 600N SLACK WAX (370°C+)

Isomerization Conditions			
Pressure, psi	1000	1000	1000
Space Velocity (v/v/hr)	0.9	0.9	0.9
Gas treat rate (SCF/bbl, H_2)	5000	5000	5000
Temp. °C	318	324	327
Conversion Level	(Low)	(Medium)	(High)
Wt%370°C-	11.8	20	25.8
Dewaxer Feed Cloud, °C	60	54	49
Dewaxing Conditions (Batch Conditions)			
Solvent:		100% MIBK	
Dilution Solvent/Feed/ v/v	5.1	3.5	3.4
Filter Temperature, °C	-25	-25	-25
Viscosity,CS @ 100°C	5.63	5.03	4.61
Dewaxed Oil Properties			
Pour Point, °C	-14	-19	-23
Pour-Filter T°C	11	6	2
Viscosity, cST @ 40°C	27.6	22.8	20.7
Viscosity, cST @ 100°C	5.63	5.03	4.61
Viscosity Index	149	147	144
Wt.% Wax recovered from 370°C+ oil fraction	56	39	30

From this it is seen that even for isomerates obtained by isomerizing waxes from a natural petroleum source, the ability to dewax the isomerate to the desired low pour point of at least about -21°C is dependent upon the level of conversion. Low conversion levels produce isomerate which cannot be dewaxed to a low

target pour using conventional dewaxing solvents under typical dewaxing filter temperature conditions.

EXAMPLE 3 (Comparative)

It has been discovered that waxy isomerates behave differently than waxy conventional oils when being dewaxed. With waxy conventional oils the wax content of the oil (usually a solvent extracted distillate) has virtually no impact on the pour point of the dewaxed oil nor on the ease with which that pour point can be achieved. In Table 3 below two typical oils, 150 neutrals having viscosities of about 5.4 cSt @100°C, viscosities very similar to those of the isomerates described in the present text, were solvent dewaxed using ketone solvents. The difference between the two natural oil stocks is wax content; one stock from a South Louisiana crude contains about 9-10% wax, the other stock from a North Louisiana crude contains about 19-22% wax. Both stocks were processed under nearly identical conditions as shown in the Table. Despite the differences in wax content the pour points of the dewaxed oils obtained by dewaxing under nearly identical conditions were identical. Both natural oil stocks were dewaxed in a dewaxing plant employing MEK/MIBK under DILCHILL conditions as described in U.S. Patent 3,773,650 to a temperature of -6°C. Further chilling to the filtration temperature was done employing laboratory scraped surface chilling apparatus. While feed filter rates and wax cake liquids/solids differed, both oils could be dewaxed to about the same pour point using nearly indentical dewaxing conditions.

This is to be compared with the results obtained in the prior example wherein dewaxing isomerate of different wax contents under nearly identical dewaxing conditions gave dewaxed oils of different pour points, thus showing the unexpected effect that the wax content of the isomerate has on dewaxing performance.

Table 3

Dewaxing of Conventional Stocks

150 - 5.4 cSt @ 100°C tube fraction

Feed Crude Source	DWO VI(I)	Filtration Temp °C	Dewaxer Feed Wax Content %	Pour Point °C	Cloud Point °C	Feed Filter Rate m^3/m^2d	Wax Cake L/S v/v	Dilution Ratio v/v	MEK/MIBK v/v
South La.	90	-20	9-10	-18	28	6.6	8.8	2.5	40/60
North La.	105	-21	19-22	-18	31	11.0	4.6	2.8	40/60

(1) Both stocks extracted using N-methyl pyrolidone to the maximum possible Viscosity Index.
(2) Solvent composition required for miscible filtration at the filtration temperatures shown are typically MEK/MIBK, 60/40 for both stocks.

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EXAMPLE 4

Catalysts 2 to 7

In the following runs the isomerate was made from slack wax obtained by solvent dewaxing a 600N oil. The slack wax was hydrotreated over HDN-30 catalyst at 350°C, 1.0 v/v/hr. 1500 SCF/bbl, H_2, 1000 psi H_2 or over KF-840 at 340°C, 0.5 v/v/hr., 1000 psi, 1500 SCF/bbl. These hydrotreated waxes had oil contents ranging from 21 to 23%, S ranging from 3 to 10 (ppm), N $\leqq$1-(ppm).

This wax feed was contacted with platinum on fluorided alumina produced in the following way.

Catalyst 2

One sixteenth inch γ alumina extrudates impregnated with platinum were obtained from the commercial supplier containing 0.6 wt.% platinum and 1% chlorine on the extrudate. The metal loaded extrudate was then fluorided using a 10 fold excess 11.6 wt% aqueous HF by immersion for 16 hrs. at ambient temperature. The resulting catalyst was washed with 2 fold excess H_2O and dried at 150°C in vacuum for 16 hrs. The fluoride content was 8.0 wt.%. The sample of Catalyst 2 as charged to the 200 cc unit was activated in 300 psi H_2 at 6.3 SCF H_2/hr as follows: heat from room temperature to 100°C at 35°C/hr; hold at 100°C for 6 hrs; heat from 100°C to 250°C at 10°C/hr; hold at 250°C for 12 hrs; heat to 400°C at 10°C/hr; hold at 400°C for 3 hrs. The sample of Catalyst 2 as charged to the 3600 cc unit was activated as follows: at 300 psi H_2 at 11 SCF H_2/hour per pound of catalyst, heat from room temperature to 100°C at 10°C/hour; hold at 100°C for 24 hours; heat from 100°C to 250°C at 10°C per hour; hold at 250°C for 15 hours; then at 22 SCF H_2/hour per pound of catalyst, heat from 250 to 400°C in 31 hours; hold at 400°C for 3 hours.

Catalyst 3

was prepared using 1/16 inch γ alumina extrudates impregnated with 0.6 wt% platinum and containing 1.0% chlorine as received from the commercial supplier. The metal loaded extrudate was then fluorided using 5:1 volume excess of 11.6 wt% aqueous HF by immersion for 6 hours at ambient temperature ($\sim$ 25°C). The resulting material when washed with two-fold excess H_2O and dried at about 120°C for $\sim$6 hrs as designated Catalyst 3. The bulk fluorine content was 7.2 wt%. Catalyst 3 was activated in atmospheric pressure H_2 by heating from room temperature to 343°C in 4 hours followed by a hold at 343°C for 2 hours.

Catalyst 4

is the same as catalyst 3 in all respects except that prior to the hydrogen activation step the material was heated at 400°C in air for 3 hours.

Catalyst 5

One sixteenth inch alumina extrudates impregnated with platinum were obtained from a commercial supplier containing 0.6 wt.% platinum and 1% chlorine. The metal loaded extrudate was fluorided using a solution of NH_4F/HF at pH 4.2 by soaking. The soaked material was washed, then dried/heated for 2 hours at 400°C in air. Fluorine content was found to be 7.0 wt%, and the surface N/Al = .0037 by X-ray photo spectroscopy. Catalyst 5 was activated by heating in 50 psi flowing H_2 as follows: room temperature to 100°C in 2 hrs., hold for 1 hr., 100°C to 450°C in 3 hrs., hold for 4 hrs. For the sample of catalyst 5 charged to the small unit (b) used in the reported Table 4, the final activation condition was 400°C for 0.75 hours.

Catalyst 6

was prepared by meshing the dried/heated form of Catalyst 5 to a particle size of 1/30" (14/35 mesh). After meshing to a particle size of 1/30" (14/35 mesh), Catalyst 6 was activated in flowing hydrogen by heating from room temperature to 100°C over a 2 hour period, holding at 100°C for 1 hour, heating from 100 to 450°C over a 3 hour period, holding at 450°C for 1 hour. Activation pressure was 50 PSI.

Catalyst 7

1/16" Al_2O_3 extrudates were impregnated with chloroplatinic acid to a level of 0.26% pt. The extrudates were then sized and screened to 1/30" mesh and subsequently fluorided using a 10 fold excess of 11.6 wt% aqueous HF by immersion for 4 hrs at ambient temp. The resulting catalyst was washed in a 30 fold excess of H_2O and dried at 130°C for 16 hrs. The catalyst was not calcined. The fluorine content was found to be 8.5 wt%. Activation procedure was the same as employed for Catalyst 1 (See Example 1).

Table 4 presents comparisons of these catalysts on slack wax from 600M oil. Conditions are recited under which the catalysts were run. Dewaxed oil yields were determined by using the test method ASTM D-3235 on the 370°C$^+$ fraction.

This example demonstrates that Catalyst 1 is unexpectedly superior to the extrudate form of the HF treated catalyst (Catalyst 2), even when Catalyst 2 is run at high mass velocity.

The importance of using the low pH halogenation media is also demonstrated, compare Catalyst 4 with Catalyst 6, when each was run in a small unit in the down flow mode, clearly, sizing down the particles does not always improve selectivity; it is only an advantage if fluoriding was originally performed at low pH (e.g. <4) using for example HF. The performance of Catgalyst 7 of Table 4 also illustrates that the catalyst can be sized

before fluoriding. Good selectivity again results when the low pH fluoriding media is used.

Table 4 also demonstrates the importance of the catalyst having a hydrate level of 60 or less. Catalyst 3 possesses a hydrate level of about 66 and is seen to be inferior to catalyst 4 which is identical except that the hydrate level is lower (57). Catalyst 4 produces a higher yield of 370°C$^+$ oil than does Catalyst 3.

TABLE 4

Catalyst	1	1	2	2	3	4	5	5	6	7
Unit*	(a)	(b)	(a)	(a)	(a)	(a)	(a)	(b)	(b)	(b)
Cat Charge (cc)	200	80	3600	200	50	50	200	80	80	80
Flow	Up	Down	Down	Up	Up	Up	Up	Up	Down	Down
Catatlyst Inspections										
N/Al by XPS					0.0012	0.0013				
Hydrate level					100	60				
N/Al level (after activation)					0.0011	0.0013				
Hydrate level (after activation)					66	57				
Isomerization Conditions										
Temp °C	347	320	323	318	313	315	340	320	310	320
Pressure(psi H_2)	1000	1000	1000	1000	1000	995	1000	1000	1000	1000
LHSV (v/v/h)	0.9	0.9	1.0	1.0	0.45	0.45	0.9	0.9	0.9	0.9
Gas rate (SCF/bbl, H_2)	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
Dewaxed 370°C+ Oil Yield (Wt.% on feed)	56.0	52.0	51.0	45.0	47.1	51.7	50.0	48.0	39.0	51
370°C-, Conversion (wt.% on feed)	29.0	22.0	29.0	29.0	36.1	18.7	23.8	20.7	37.3	28.7

* (a) = continuous pilot unit

(b) = small lab unit.

Example 5

Catalysts 8 and 9 and Comparison Catalysts 1,2,3 and 4

In these Examples the hydrotreated 600N slack waxes are those previously described in Example 4. Following isomerization in an upflow once through mode of operation the isomerate was fractionated to obtain the 370°C$^+$ lube fraction.

Dewaxed oil yields were determined using the ASTM Test D-3235 method on the 370°C$^+$ fraction.

In this Example a series of catalysts was prepared using the NH_4F/HF fluoriding procedures described above. Examples of superior catalysts made using the NH_4F/HF fluoriding procedures were seen to have surface fluorine content in the low recited desirable range. Results for these catalysts are shown in Table 5. Less satisfactory catalysts made using NH_4F/HF treatment are shown in Table 6. These catalysts all contained high levels of surface fluorine resulting from initial excessive loading of bulk fluorine when using ph 4 or greater. In the case of comparison Catalyst 3, while the bulk fluorine level is within the desired range and surface fluorine was initially low in the as charged catalyst, the excessively severe activation conditions employed subsequently increased the surface fluorine level of the catalyst. This we believe is the reason for its poorer selectivity. All catalysts were dried and heated as reported in Tables 5 and 6.

Table 5

Examples of Good Catalysts in the Process of the Invention			
Catalyst	8	9	9
Catalyst Charge (cc)	50	50	200
Method of fluoride treat	NH_4F/HF	NH_4F/HF	NH_4F/HF
Drying conditions °C	400 (muffle)	400	400 rotary kiln
Catalyst Inspections			
N/Al by XPS	0.0037	0.0021	0.0021
Hydrate level	29	24	24
F. (wt%) (bulk)	6.9	7.0	7.0
F wt% (surface)	1.7	2.0	2.0
Hydrogen Activation Times, hrs.			
Rt. to final temp	7	4	7
Time at T	2	2	2
Final T, °C	343	343	350
Hydrogen Activation Pressure			
	ambient	ambient	50 psi

Isomerization Conditions			
Temp. °C	310	312	309
LHSV (v/v/h)	0.45	0.45	1.0
Press. PSI H_2	1000	1000	1000
Gas rate (SCF/B, H_2)	5000	5000	5000
Max 370° C^+ oil Dewaxed oil yield, (wt% on feed)	50(1)	49.8	49.3
Conversion to 370° C^- (wt% on feed)	28	24.5	35.2

(1) Interpolated data

Table 6

Performance of Comparative Catalysts

Catalyst	Comparison 1	Comparison 2	Comparison 3	Comparison 4
Unit Type			Continuous Pilot Unit	
Method Treat	NH_4F/HF	NH_4F/HF	NH_4F/HF	NH_4F/HF
drying conditions, °C	400 (rotary kiln)	400 (muffle)	400 (rotary kiln)	400 (muffle)
Catalyst Inspections				
N/Al by XPS	0.010	0.013	0.0021	0.0040
F. wt%	6.8	5.6	7.0	6.9
F, wt% (surface)	~10	~5	*	7
Hydrate level	39	<10	24	<10
Hydrogen Activation Times, hr.				
RT to 100°C, @100°C	2,1	2,1	3,6	2,1
to final temp (T)	2	2	42	2
time at T	1	1	3	1
Final T°C	350	350	400	350
Hydrogen Activation pressure #	50	50	300	50
Isomerization Conditions				
Temp., °C	310	300	305	310
LHSV (v/v/hr)	0.90	0.90	1.0	0.90
Pressure psi H_2	1000	1000	1000	1000
Gas rate (SCF H_2/bbl)	5000	5000	5000	5000
Dewaxed Oil yield, (wt% on feed)	44.0	45.0	45	48.5
370°F (wt% on feed)	26.1	24.1	21.8	30.1
Unconverted Wax (wt% on feed)	29.9	30.9	33.2	21.4

* F. at surface measured 2.0 before activation and approximately 7 after activation

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EXAMPLE 6

The presence of oil in the wax has been found to produce an enhanced VI product as compared to oil free wax when isomerization is performed utilizing the preferred "sized" catalyst made employing HF. The amount of oil in the wax, however, must fall within a particular range as previously described, if this enhanced VI phenomenon is to be obtained.

A meshed platinum on fluorided alumina catalyst (Catalyst 1 from Example 1) was used to isomerize a slack wax obtained from 600N oil. The wax samples had oil contents of $<1\%$, about 7% and about 23%. The wax containing less than about 1% oil was made by recrystallizing a 600N slack wax by warm-up deoiling then hydrotreating. This 1% oil wax has 99% saturates, 0.8% aromatics and 0.2% polar compounds (as determined by silica gel separation). It had an initial boiling point of 382° C and a 99% off boiling point of 588° C, as determined by GCD. Subsequently, isomerized products were dewaxed to between -18 to -21° C pour. Fractionation of the products showed that at the higher viscosity range the isomerate made from wax possessing about 7% oil exhibited an unexpected VI enhancement as compared to the other wax samples having $<1\%$ and 23% oil. This is to be compared with the results obtained using an extrudate Pt/FAl_2O_3 catalyst.

Comparison Catalyst 4 was used to isomerize slack waxes obtained from 600N oil, which slack waxes contained $<1\%$, 10.9% and 22% oil under conditions selected to achieve the levels of conversion indicated in Table 7. Comparing the results obtained using Catalyst 1 with those obtained using Comparison Catalyst 4 one sees that isomerization utilizing the meshed catalyst (Catalyst 1) exhibits an unexpected VI enhancement when the wax feed employed contains about 7% oil.

From the above it is clear that the sized catalyst is preferred for use in the isomerization process described herein. Reference to Figure 3 shows that Catalyst 1 has the highest selectivity for oil production making it a preferred catalyst (Catalyst I of the Figure).

TABLE 7

Example of Unexpected VI Enhancement using **Meshed Catalyst** on Wax Containing ~ 10% oil

Catalyst	Oil Content of Wax	Conv. to 370C-	Vis.@100°C	VI
1	<1	13	4.8	148
	[7]	24	4.8	[150]
	23	12.8	4.8	135
	23	25.8	4.8	137
Comparison Cat 4	<1	19.3	4.8	147
		35.0	4.6	142
	[10.9]	26.8	4.9	[143]
	22	28.8	5.0	139
		48.6	4.6	136

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Example 7

Slack wax from Bright Stock containing 15% oil was hydrotreated over Cyanamid's HDN-30 catalyst at 399°C, 0.5 v/v/h, 1000 psi H_2 and 1500 SCF/B, H_2, yielding a hydrotreated slack wax with the following properties:

Wax Oil content: 22.8 wt%
Sulfur = 3ppm
Nitrogen = < 1ppm

Distillation Data

GCD % off at °C.	ibp,255
10	363
20	436
30	481
40	515
50	541
60	564
70	590
80	656

The hydrotreated slack wax was then isomerized over Catalyst 1 described in Example 1 to produce the following isomerate products:

Isomerization Conditions:	Run 1	Run 2
Temperature, °C	332	332
Pressure psi H_2	1000	1000
Gas rate SCF/B, H_2	5000	5000
LHSV (v/v/h)	0.9	0.9

Isomerate Product	A	B
Max 370°C$^+$ Dewaxed oil yield (wt% on feed) (by ASTM D3235 method)	54.6	54.9
Conversion to 370°C$^-$,(wt% on feed)	28.4	27.6

The isomerate products A and B made from the Bright Stock slack wax were fractionated into a broad heart cut (from product A) and a narrow cut (from product B) and dewaxed using MEK/MIBK under conventional dilution chilling dewaxing conditions. This was a DILCHILL dewaxing operation run at 150 cm/sec. agitation top speed (2 inch agitator) at an outlet temp. of -13°C. Indirect chilling was then employed to get down to the filter temperature. From review of the data presented in Tables 8 and 8A it is apparent that fractionating the isomerate into a heart cut boiling between 370-582°C not only facilitated dewaxing the oil to the target pour point but permitted the dewaxing to be more efficient (i.e. higher filter rates) than with the narrow fraction. Higher yields of oil were obtained at good dewaxed oil filter rates on the broad heart cut as compared to narrow cut or 370°C$^+$ topped fractions dewaxed under the same conditions. (Compare runs 1 and 2 Table 8 with runs A, B and I, Table 8A). This shows the advantage of dewaxing the heart cut when dealing with isomerate obtained from very heavy, high boiling wax fractions since operating on the heart cut permits dewaxing to be conducted under miscible conditions. Only when dealing with a broad heart cut can low pour points, high yields and good filter rates be simultaneously achieved.

TABLE 8

COMPARISON OF NARROW VERSUS BROAD HEART CUT DILUTION CHILLING DEWAXING PERFORMANCE FOR BRIGHT STOCK ISOMERATES

Isomerate Boiling Range, °C:	Broad Heart cut 370-582					
Run	1	2	3	4	5	6
Dewaxing Conditions:						
Solvent Type:	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK
Sovent Ratio, v/v	10/9	20/80	20/80	20/80	30/70	0/100
Dilution, Solv/Feed, v/v		4.3	4.1	4.1	4.3	-
Filter Temperature, °C	-25	-25	-30	-35	-35	-25
Miscibility	Miscible	Miscible	Borderline	Immiscible	Immiscible	Miscible
Feed Filter Rate, M3/M2 Day	3.8	3.8	4.2	3.7	4.8	3.4
Wax Cake Liquids/Solids, W/W	7.7	9.4	8.4	10.5	10.5	8.3
Wash/Feed,W/W	-	1.0	1.1	1.0	0.88	-
% Oil in Wax	22	42	37	56	66	33
Unconverted wax content, wt%	-	21	23	25	25	21
Theoretical DWO Yield, (100-WC), wt%	-	79	77	75	75	79
Dewaxed Oil Yield, wt.%	73.1	63.8	63.5	43.2	26.5	68.7
Dewaxed Oil Filter Rate, M3/M2 Day	2.8	2.6	2.6	1.6	1.3	2.3
Dewaxed Oil Inspections:						
Viscosity, cSt						
@ 40°C	25.5	25.30	25.75	24.49	22.67	25.7
@ 100°C	5.31	5.28	5.34	5.15	4.87	5.34
Viscosity Index	147	147	147	146	143	147
Pour, °C	-20	-20	-26	-32	-32	-20
Cloud, °C	-17	-17	-22	-28	-31	-16

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TABLE 8A

COMPARISON OF NARROW VERSUS BROAD HEART CUT DILUTION CHILLING DEWAXING PERFORMANCE FOR BRIGHT STOCK ISOMERATES

Isomerate	Narrow Cut					Topped 370°C+
Boiling Range, °C:			495-582			
Run	A	B	C	D	E	I
Solvent Type:	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK
Solvent Ration, v/v	10/90	20/80	30/70	0/100	5/95	10/90
Dilution, Ratio,Solv/Feed,V/V	4.3	4.5	3.9			4.2
Filter Temperature, °C	-25	-25	-25	-25	-25	-25
Miscibility	Miscible/Borderline	Immiscible	Immiscible	Miscible	Borderline	Miscible/Borderline
Feed Filter Rate, M3/M2 Day	3.2	3.8	6.6	3.1	3.0	2.9
Wax Cake Liquids/Solids, W/W	5.1	6.9	6.8	6.1	5.6	5.9
Wash/Feed, W/W	1.19	1.08	0.87	-	-	-
% Oil in Wax	18	52	62	-	-	24
Wax Content, wt.%	29	29	30	-	-	28
Theoretical DWO Yield, (100-WC), wt%	71	71	70	-	-	72
Dewaxed Oil Yield, wt.%	64.6	39.6	21.1	65.3	65.8	63.2
Dewaxed Oil Filter Rate, M3/M2 Day	2.1	1.5	1.4	2.0	2.0	1.8
Dewaxed Oil Inspeotions:						
Viscosity, cst						
@ 40°C	56.1	51.3	49.6	48.7	53.6	34.9
@ 100°C	9.18	8.83	8.63	8.37	9.13	6.63
Viscosity Index	145	152	152.5	148	152	148
Pour, °C	-20	-21	-22	-15	-15	-20
Cloud, °C	-15	-14	-17	-	-	-18

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Example 8

Slack wax derived from a 600N oil was hydrotreated over KF-840, a Ni/Mo on alumina hydrotreating catalyst at 370°C, 0.33 LHSV, 1500 SCF H_2/bbl, 1000 psi H_2. The hydrotreated wax had a sulfur content of 6 wppm, a nitrogen content of < 1 wppm, an oil content of 18.7 wt%, an initial boiling point of 233°C and a 95% off boiling point of 338°C.

The slack wax was isomerized over Catalyst 2 in three runs at high mass velocity as described in Table 9.

Table 9

	Run 1	Run 2	Run 3
Pressure (psi)	1200	1200	1200
LHSV	1.0	1.0	1.0
gas rate SCF/bb,H_2	2500	2500	2500
Temp °C	329	328.9	327.1
Yield (wt%)			
370°C$^-$	37.5	37.8	22.0
Max 370°C$^+$ Oil* residual wax	49.8	50.5	52.5
	12.7	11.8	25.5

* Oil yield determined using ASTM D-3235 test method

Isomerate from these three runs was combined to produce a feed to the dewaxer having a 370°C$^-$ wt% on feed of 26.6. The feed was fractionated into a 370°C$^+$ fraction and 420°C$^+$ fraction and dewaxed under simulated DILCHILL conditions in the laboratory using the procedure described in Example 7. DILCHILL dewaxing was performed using two different solvent systems on the two above described fractions. The results are presented in Table 10, below:

Table 10

DILCHILL Dewaxing of 600 Neutral Slack Wax Isomerates
Comparison of Two Solvent Systems

Isomerate Fraction, °C	370°C		420°C+	
Solvent	MEK/MIBK	MEK/Toluene	MEK/MIBK	MEK/Toluene
Composition, v/v	20/80	50/50	20/80	50/50
Feed Cloud, °C	49	49	52	52
Viscosity, cSt @ 100°C	5.2	5.2	5.2	5.2
Filter Temp. °C	-27	-30	-27	-30
Wt.% Wax Removed	27.4	26.4	30.5	29
Dewaxed Oil Properties				
Pour, °C	-24	-21	-24	-21
Cloud, °C	-20	-18	-21	-18
Pour-Filter dT, °C	3	9	3	9
Cloud-Filter dT, °C	7	12	6	12
Viscosity, cSt @				
40°C	22.9	23.2	28.5	28.9
100°C	4.92	4.94	5.68	5.72
Viscosity Index	144	144	143	144
Feed Filter Rate, m3/m2, day	4.7	4.4	5.3	4.7
Wax Cake Liquids/ Solids, w/w	6.8	7.3	5.8	6.1
Dewaxed Oil Filter rate m3/m2 day	2.9	2.7	2.9	2.7

Average Solvent/Feed dilution on all runs was 3.4 v/v on feed.

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From this it can be seen that to achieve extremely low pour points, it is preferred to use MEK/MIBK as the dewaxing solvent.

NOTES

- Temperature in °F is converted to equivalent °C by subtracting 32 and then dividing by 1.8.
- Length in inch(") is converted to cm by multiplying by 2.54.
- 1 SCF = 28.316 liter.
- 1 B = 159.0 liter.
- Pressure in psi is converted to equivalent kPa by multiplying by 6.895.
- Mesh sizes are of the Tyler series.

Claims

1. A process for producing lube oil base stocks or blending stocks having a pour point of about -21°C or lower and a viscosity index of about 130 and higher by the isomerization of wax said process comprising (1) isomerizing the wax in an isomerization unit over an isomerization catalyst to a level of conversion such that about 40% or less unconverted wax, calculated as (unconverted wax)/(unconverted wax + dewaxed oil) X100 remains in the fraction of the isomerate boiling in the lube boiling range sent to the dewaxing unit, fractionating the total product from the isomerization zone into a lube fraction boiling in the lube boiling range and solvent dewaxing said fraction and (2) recovering a lube oil product having a VI of at least 130 and a pour point of -21°C or lower.

2. The process of claim 1 wherein the level of conversion is between about 15 to 35% (e.g. 20 to 30%) unconverted wax.

3. The process of claim 1 or claim 2 wherein the isomerization process is conducted over a catalyst containing a hydrogenating metal (e.g., Group VI and/or Group VIII) component supported on a halogenated (e.g., fluorided) refractory metal oxide (e.g., alumina).

4. The process of any one of claims 1 to 3 wherein the isomerization step is conducted at a temperature in the range of from about 270 to 400°C, a pressure of from 500 to 3000 psi (3.45 to 20.69 MPa) H_2, a gas rate of 1000 to 10,000 SCF/b (178.1 to 1780.9 liter gas/liter oil), and a space velocity in the range 0.1 to 10 v/v/hr.

5. The process of any one of claims 1 to 4 wherein the wax which is fed to the isomerization unit is a slack wax which has been hydrotreated so as to contain about 1 to 5 ppm nitrogen, about 1 to 20 ppm sulfur and has been deoiled to contain 0 to 35 wt% oil.

6. The process of any one of claims 1 to 5 wherein the isomerate from the isomerization zone is fractionated into a lube oil fraction boiling in the 330°C+ range, preferably 330 to 600°C range (e.g., 370°C+.

7. The process of any one of claims 1 to 6 wherein the solvent dewaxing step is practiced using C_3-C_6 ketones, C_6-C_{10} aromatic hydrocarbons, mixtures of C_3-C_6 ketones, mixtures of C_3-C_6 ketones and aromatic hydrocarbons, liquified, normally gaseous C_2-C_4 hydrocarbons.

8. The process of any one of claims 1 to 7 wherein the solvent dewaxing step is practiced using a mixture of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) in a ratio of 20/80 at a temperature in the range -25 to -30°C.

9. The process of any one of claims 1 to 7 wherein the solvent dewaxing step is practiced using methyl-isobutyl ketone.

10. The process of any one of claims 1 to 9 wherein unconverted wax recovered in the drawing step and/or the fraction boiling above 600°C is recycled to be further isomerized.

FIG. 1

SLACK WAX ISOMERIZATION PROCESS
FOR SINGLE FEED / BASESTOCK

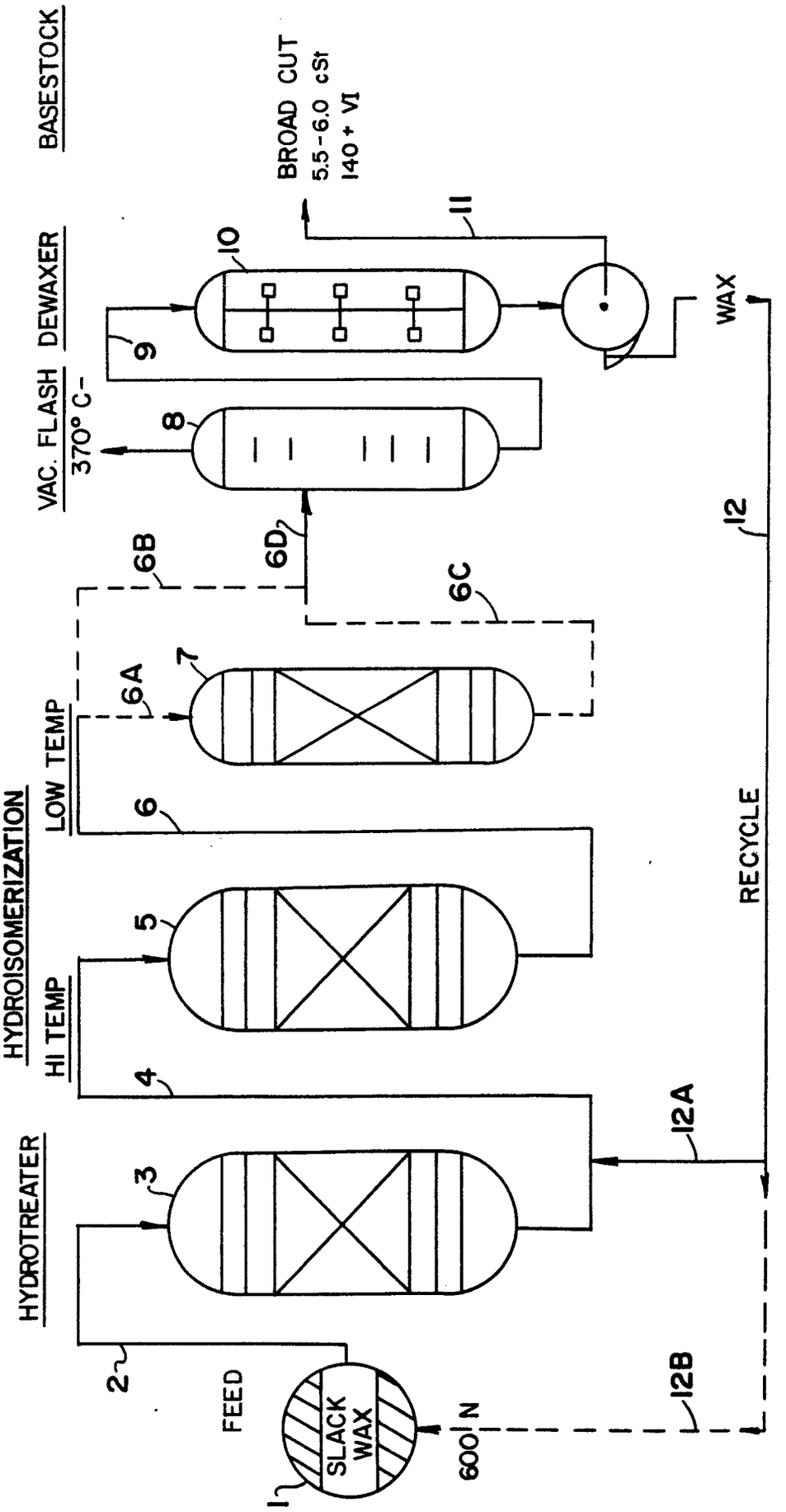
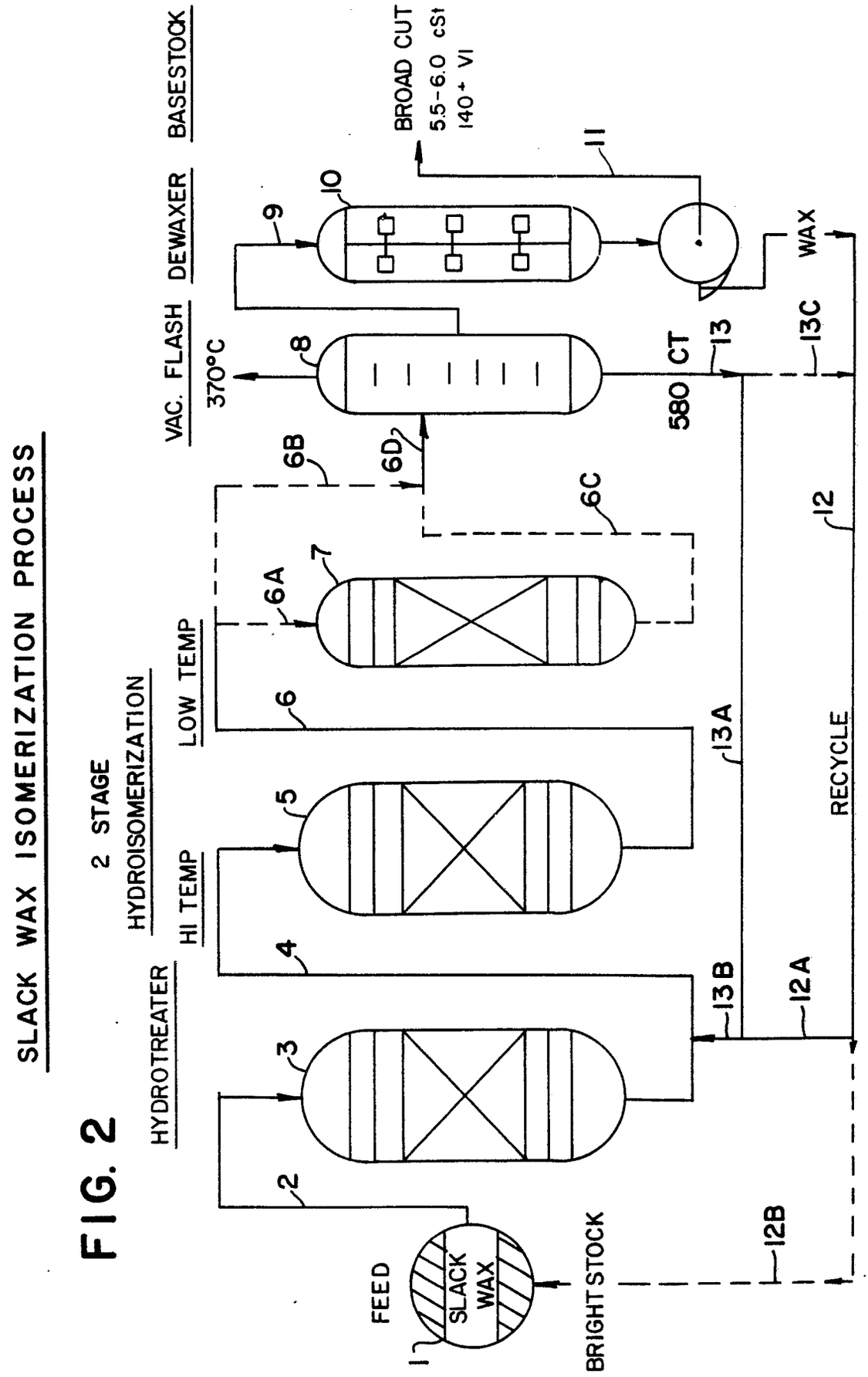


FIG. 2


SLACK WAX ISOMERIZATION PROCESS
2 STAGE
HYDROISOMERIZATION
HYDROTREATER
HI TEMP
LOW TEMP
VAC. FLASH
DEWAXER
BASESTOCK
FEED
SLACK WAX
BRIGHT STOCK
BROAD CUT
5.5-6.0 cSt
140+ VI
WAX
RECYCLE
370°C
580 CT
1
2
3
4
5
6
6A
6B
6C
6D
7
8
9
10
11
12
12A
12B
13
13A
13B
13C

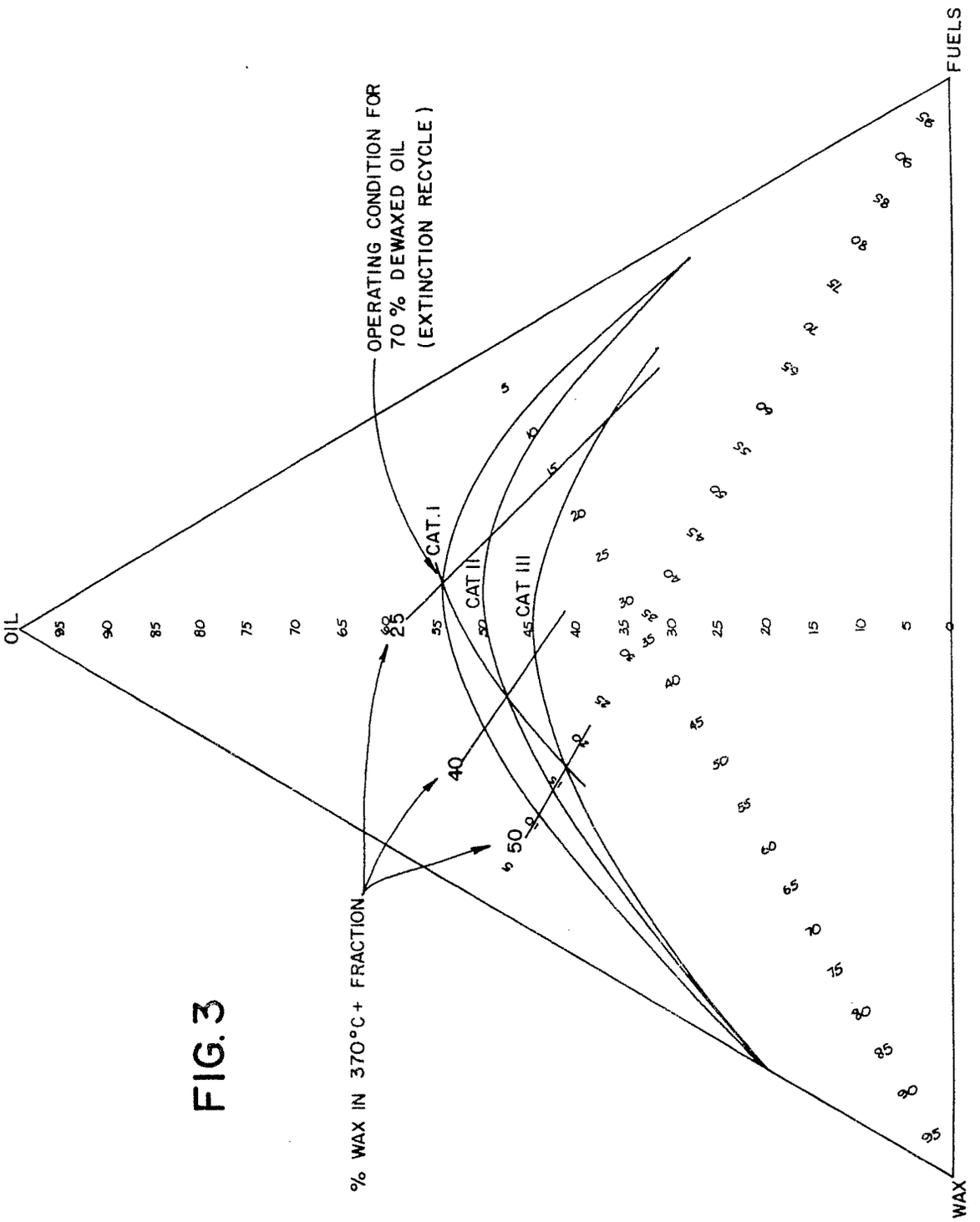

OIL
FUELS
WAX
OPERATING CONDITION FOR
70 % DEWAXED OIL
(EXTINCTION RECYCLE)
CAT. I
CAT II
CAT III
% WAX IN 370°C+ FRACTION

FIG. 3