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54 **Improved process for lowering pour and cloud points of hydrocracked lube oils.**

57 A two-step or combination process for preparing low pour point, low cloud point lube oils is set forth. The process involves subjecting a lube stock to a mild solvent dewaxing step so as to obtain high quality waxes and a lube stock having an intermediate pour point, recovering the waxes and subjecting said intermediate pour point lube stock to a hydrodewaxing step over a crystalline ZSM-23 zeolite to obtain a product having a pour point of less than -7°C. The catalytic dewaxing step preferably includes a noble metal small pore zeolite, such as Pd/ZSM-23, to give a high yield of low cloud point, high viscosity index lube oil.

EP 0 271 265 A1

IMPROVED PROCESS FOR LOWERING POUR AND CLOUD
POINTS OF HYDROCRACKED LUBE OILS

It is desired that the lube oil have a low pour point so that it can be used at low temperature. Excessive thickening at low temperatures is unacceptable.

It is known to carry out dewaxing by contacting hydrocarbon fractions with zeolites having pore sizes of about 5 Angstrom units to selectively remove normal paraffins.

The present invention is concerned with an improved process for dewaxing heavy hydrocracked lubes, which is more economical than conventional solvent dewaxing procedures or catalytic dewaxing procedures and which produces hydrocracked lube oils having low pour and cloud points.

The present process employs the use of a conventional solvent dewaxing step, but only to slightly reduce the pour point of the treated stock and obtain a product having an intermediate pour point. The product of intermediate pour point is unsuitable for use as a low temperature lubricant at this stage. In accordance with the invention, this intermediate product is then hydrodewaxed with ZSM-23 zeolite to yield a product having both low pour point and low cloud point.

It is to be noted that the sequence of steps of the present combination process is critical in order to achieve the maximum economic advantage. The solvent dewaxing must come first, followed by the catalytic hydrodewaxing step. This is so because the highest quality wax which is obtained from a given feed is that obtained in the initial stages of the solvent dewaxing. If the feedstock were first subjected to catalytic hydrodewaxing, the highest quality wax would be destroyed.

Additionally, it has been found that catalytic hydrodewaxing with a ZSM-23 catalyst is more effectively carried out with intermediate pour point product than with a conventional lube stock. Moreover, a noble metal small pore zeolite, such as Pd/ZSM-23, is preferred as a catalyst. Thus, the unique processing scheme of the present invention provides a maximization of desirable products from a given feedstock. This is an improvement over prior art processes utilizing ZSM-5-type catalysts.

U. S. Patent No. 3,255,138 claims a process for preparing low pour point lube oils by first solvent dewaxing and then hydrodewaxing over a ZSM-5-type zeolite containing a hydrogenation component.

It is also known to practice a two-step process in which hydrocracked stocks, including brightstock, are first solvent dewaxed to -18°C (0°F), then hydrodewaxed to -40°C (-40°F) over Ni/ZSM-5.

U. S. Patent Nos. 4,283,271 and 4,283,272 claim energy efficient all-catalytic lube processes using dewaxing catalysts, such as ZSM-5 and ZSM-11, in the dewaxing step.

U. S. Patent No. 4,414,097 teaches catalytic dewaxing using Pt/ZSM-23.

Despite the many improvements made, there is still a need for better dewaxing processes. Especially needed is a process to reduce the cloud point and the pour point heavy hydrocracked lube stocks.

Accordingly, the present invention provides A process for preparing low pour point and low cloud point lube oils from a hydrocracked petroleum feedstock characterized by solvent dewaxing to obtain a lube oil having a pour point of -12 to 10°C (10 to 50°F) and thereafter subjecting the solvent dewaxed product to catalytic hydrodewaxing in the presence of added hydrogen with a catalyst comprising ZSM-23 and a hydrogenation component to obtain a product having a pour point of less than -7°C (20°F).

Fig. 1 shows lube yield versus pour point for dewaxing a brightstock and

Fig. 2 shows viscosity index versus pour point for the stock of Fig. 1.

5 The feeds comprises a hydrocracked heavy hydrocracked lube oils boiling above 343°C (650°F) and particularly between 343 and 704°C (650°C and 1300°F).

10 The feed is then mildly solvent dewaxed, lube stock until it has a pour point of -12 to 10°C (10° to 50°F), and preferably from -7 to 7°C (20° to 45°F).

The solvent dewaxing step is conventional. Suitable solvents include methyl ethyl ketone-toluene, methyl ethyl ketone-methyl isobutyl ketone and the like.

15 The products from the solvent dewaxing step are high quality waxes which are recovered and an intermediate pour point stock which is then hydrodewaxed over ZSM-23 zeolite.

20 Zeolite ZSM-23 is described in U. S. Patent Nos. 4,076,842 and 4,104,151. The hydrogenation component may be associated with the ZSM-23, e.g., a metal(s) from Group VIII of the Periodic Table of Elements, alone or in combination, with a Group VI metal. Non-limiting examples of the metals from Group VIII for this purpose include platinum, palladium, iridium, ruthenium, cobalt and nickel. The Group VI metals are chromium, molybdenum and tungsten.

The reaction conditions for the dewaxing process are summarized in Table 1.

Table 1

		<u>Broad</u>	<u>Preferred</u>
5	Pressure, psig	200 - 3000	400 - 2500
	kPa	1500 - 21000	2900 - 17000
	Temperature, °F	300 - 900	500 - 800
	°C	149 - 482	260 - 427
	LHSV, *	0.2 - 20	0.5 - 5
10	H ₂ gas, SCF/bbl,	500 - 20,000	1000 - 5000
	nm ³ /m ³	90 - 3600	180 - 900

*LHSV = Liquid Hourly Space Velocity, i.e., Volume of Feed per Volume of Catalyst per Hour

15 nm³/m³ = normal cubic meters of H₂ per cubic meter of liquid feed

The ZSM-23 may be incorporated with a matrix or binder of a material resistant to the temperature and other process conditions.

Useful matrix materials include both synthetic and naturally occurring substances, as well as inorganic materials, such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays, or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used as mined or after calcination, acid treatment or chemical modification.

30 Matrix materials, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-

magnesia and silica-magnesia-zirconia may also be used. The matrix can be in the form of a cogel. The proportions of ZSM-23 and matrix, on an anhydrous basis, may vary widely, with the zeolite content ranging from 1 to 99 wt %, and more usually 5 to 80 wt % of the dry composite.

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The hydrogenation component, if any may be on the zeolite or on the matrix or both.

Examples

The chargestock in all the examples is a hydrocracked brightstock having the following properties:

	Gravity, °API	30.2
5	g/cc	0.8751
	Pour Point, °F/°C	+120/49
	KV at 100°C, cs	25.63

The apparatus used is conventional and described in U.S. Patents Nos. 4,283,271; 4,283,272; and 4,414,097.

10 Example 1 (Prior Art)Hydrodewaxing Alone Over Ni/ZSM-5 Catalyst

The chargestock is processed over 1% Ni/ZSM-5 extrudate (sulfided in situ), at 2900 kPa (400 psig), 1 LHSV, 450 nm³/m³ (2500 SCFB H₂ at several temperatures, with the following results:

15	<u>Run No.</u>	<u>1</u>	<u>2</u>
	Avg. Cat. Temp, °F/°C	658/348	660/349
	Material Balance, Wt %	97.5	101.9
	Yields, Wt %		
	C ₁ + C ₂	0.8	0.9
20	C ₃	6.7	7.4
	C ₄	10.6	12.3
	C ₅	6.6	9.0
	C ₆ -343°C (650°F)	14.9	13.3
	343°C (650°F ⁺) Lube	61.6	58.8
25	Lube Properties		
	Gravity, °API	29.3	30.5
	g/cc	0.8800	0.8735
	Pour Point, °F/°C	0/-18	+10/-12
	Cloud Point, °F/°C	+52/11	+62/17
30	KV at 40°C, cs	354.2	359.8
	KV at 100°C, cs	27.02	27.61
	Viscosity Index	101.8	103.5

At the target pour of -12°C ($+10^{\circ}\text{F}$), the cloud point of 17°C ($+62^{\circ}\text{F}$) is unacceptably high. A cloud point $5-6^{\circ}\text{C}$ (about 10°F) above the pour point is considered acceptable.

Example 2 (Prior Art)

5. Solvent Dewaxing Alone

The hydrocracked brightstock is subjected to conventional solvent dewaxing employing conventional solvent ratios, which are as follows on a volume-to-volume basis:

	Solvent, MEK/Toluene	50/50
	Dilution, Solvent/Oil	3.5/1
	Wash, Solvent/Oil (2X)	1/1
	Dewaxing Temp., °F/°C	-20/-29
5	Lube Yield, Wt %	65.4
	Lube Properties	
	Gravity, °API	29.0
	g/cc	0.8816
	Pour Point, °F/°C	+10/-12
10	Cloud Point, °F/°C	+15/-9
	KV at 40°C, cs	430.7
	KV at 100°C, cs	32.47
	Viscosity Index	109.4
15	Yield is about 6 wt % higher than in Example 1, and the cloud point is acceptable.	

Example 3 (Prior Art)Combination Solvent Dewaxing/Hydrowaxing Over Ni/ZSM-5

The hydrocracked brightstock is solvent dewaxed as in Example 2, except at a temperature of -7°C (+20°F), with results as follows:

	Lube Yield, Wt %	78.2
	Lube Properties	
	Gravity, °API	29.4
	g/cc	0.8794
25	Pour Point, °F/°C	+45/7
	Cloud Point, °F/°C	+50/10
	KV at 40°C, cs	385.5
	KV at 100°C, cs	30.04
	Viscosity Index	109.0

This material is then hydrodewaxed over Ni/ZSM-5 under the reaction conditions used in Example 1, at several temperatures, with the following results:

<u>Run No.</u>		<u>1</u>	<u>2</u>	<u>3</u>
5	Avg. Cat. Temp., °F	502	520	560
	°C	261	271	293
	Maternal Balance Wt %	98.9	99.0	99.7
Yields, Wt %				
10	C ₁ + C ₂	0.1	0.1	0.2
	C ₃	0.4	1.0	2.5
	C ₄	1.2	1.7	3.9
	C ₅	1.4	1.5	2.3
	C ₆ -343°C (650°F)	3.1	2.9	4.4
	343°C+ (650°F+) Lube	93.9	93.1	87.3
15	Lube Properties			
	Gravity, °API	29.3	29.4	28.8
	g/cc	0.8800	0.8794	0.8827
	Pour Point, °F/°C	+20/-7	+10/-12	-5/-21
	Cloud Point, °F/°C	+48/9	+22/-6	+6/-14
20	KV at 40°C, cs	357.3	411.2	457.4
	KV at 100°C, cs	27.66	29.93	31.1
	Viscosity Index	104.4	102.1	98.2
	Lube Yield, Overall	73	73	68

The cloud point at the target pour of 12°C (+10°F) is acceptable, and the overall lube yield from the two steps is 73 wt %, compared to 65 wt % for solvent dewaxing alone (Example 2), and 59 wt % for hydrodewaxing alone (Example 1).

Example 4 (Invention)

Combination Solvent Dewaxing/Hydrodewaxing Over Pd/ZSM-23

The same 7°C (+45°F) pour point solvent dewaxed stock described in Example 3 is processed over 1 wt % Pd/ZSM-23 extrudate (H₂ treated in situ at 482°C (900°F) for 1 hour) at 2900 kPa (400 psig), 0.5 LHSV, 450 nm³/m³ (2500 SCFB H₂) at several temperatures, with the following results:

Run No.	1	2	3
Avg. Cat. Temp., °F °C	549 287	600 316	599 315
Material Balance, Wt %	98.7	97.8	98.7
Yield, Wt %			
C ₁ + C ₂	0.1	0.2	0.1
C ₃	0.5	1.5	1.6
C ₄	0.9	2.3	2.3
C ₅	0.9	2.0	2.0
C ₆ -343°C (650°F)	2.0	5.0	3.4
343°C (650°F+) Lube	96.2	89.6	91.2
Lube Properties			
Gravity, °API	30.3	30.3	30.1
g/cc	0.8745	0.8745	0.8756
Pour Point, °F/°C	+10/-12	-25/-32	-15/-26
Cloud Point, °F/°C	+12/-11	- 8/-22	- 6/-21
KV at 40°C, cs	286.2	248.0	289.7
KV at 100°C, cs	24.10	21.58	23.98
Viscosity Index	106.2	104.0	104.1
Lube Yield, Overall	75	70	71

The cloud point at the target pour of -12°C ($+10^{\circ}\text{F}$) is excellent, -11°C ($+12^{\circ}\text{F}$), compared to -6°C ($+22^{\circ}\text{F}$) using Ni/ZSM-5 (Example 3). Also, lube yields and viscosity index are both significantly higher than those obtained using NiZSM-5.

5 5 Fig. 1 shows lube yield versus pour point for the brightstock solvent dewaxed to 7°C ($+45^{\circ}\text{F}$) pour point. Fig. 2 shows viscosity index versus pour point for the same stock.

10 The high cloud point of heavy hydrocracked lubes using standard catalytic dewaxing technology has been a problem development of the process. A very mild solvent dewaxing step, requiring little or no refrigeration, solves the problem.

Claims

1. A process for preparing low pour point and low cloud point lube oils from a hydrocracked petroleum feedstock characterized by solvent dewaxing to obtain a lube oil having a pour point of -12 to 10°C (10 to 50°F) and thereafter subjecting the solvent dewaxed lube oil to catalytic hydrodewaxing in the presence of added hydrogen with a catalyst comprising ZSM-23 and a hydrogenation component to obtain a product having a pour point of less than -7°C (20°F).
2. The process of Claim 1 further characterized in that the catalyst is Pd/ZSM-23.
3. The process of Claim 1 or 2 further characterized in that the solvent dewaxed product has a pour point of -7 to 7°C (20 to 45°F).

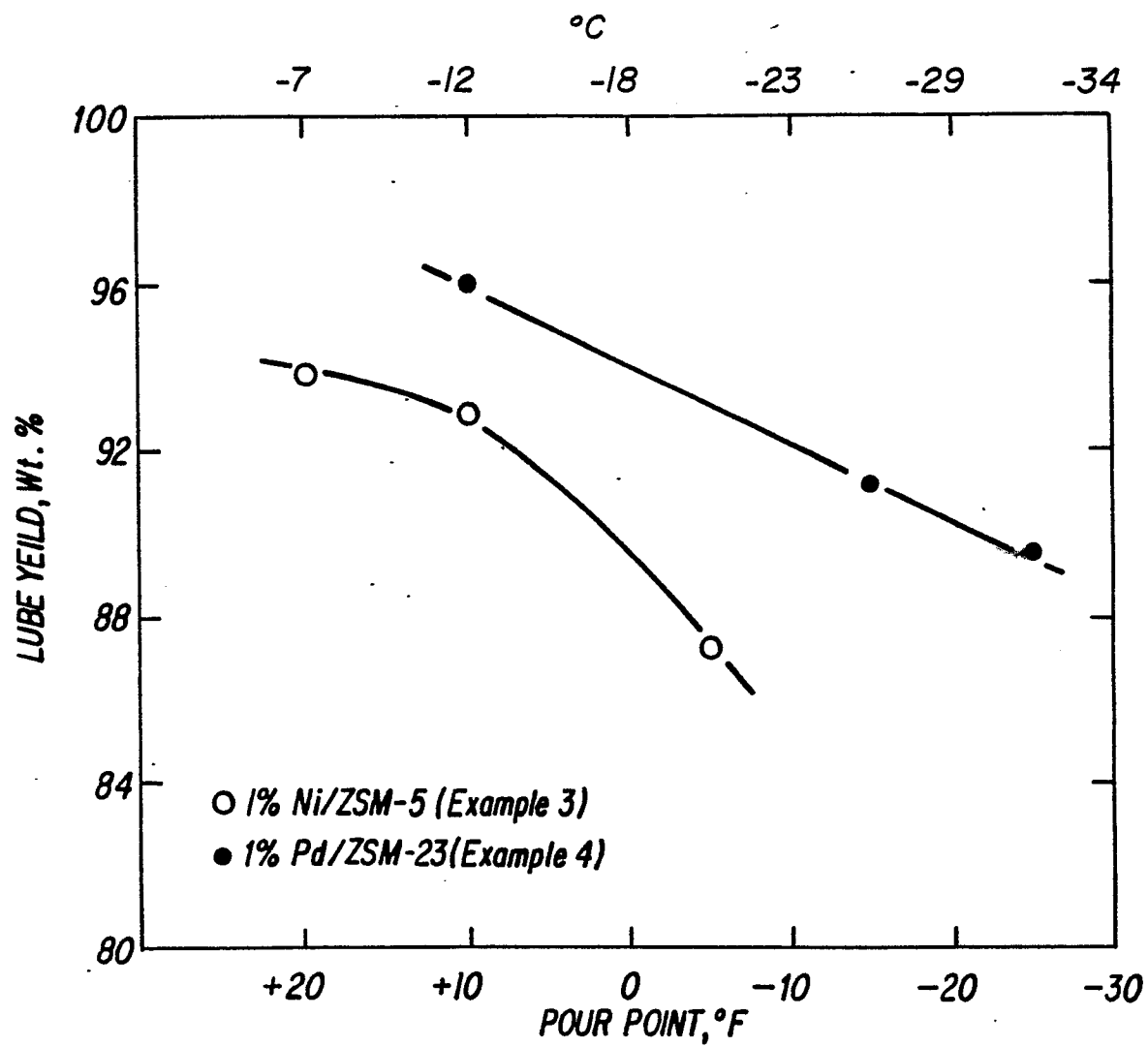


FIG. 1

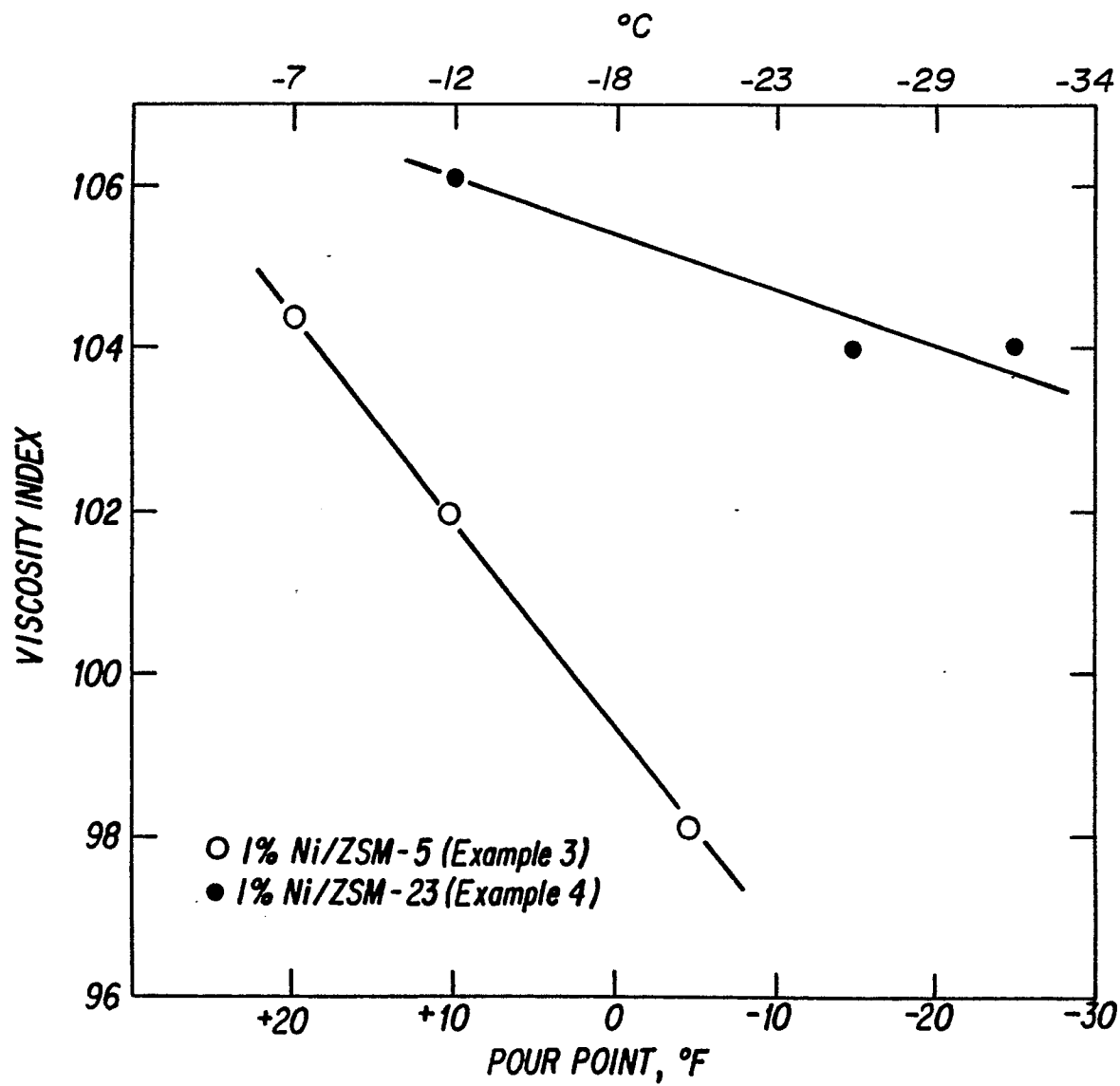


FIG.2



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 016 554 (MOBIL) * Abstract; page 5, line 27 - page 6, line 21; page 7, line 27 - page 8, line 9; claims 1-9 *	1-3	C 10 G 67/04 B 01 J 29/28 C 10 G 45/64
D,Y	EP-A-0 092 376 (MOBIL) * Abstract; pages 4,5; pages 8,9; example 4; claims 1-12 *	1-3	
A	EP-A-0 140 468 (MOBIL)		
D,A	US-A-4 104 151 (RUBIN et al.)		
D,A	US-A-3 755 138 (CHEN et al.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 G B 01 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25-02-1988	Examiner LO CONTE C.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			