

466126-1 205

This Sheet Has Been Replaced



-1-

REPLACED SHEETS		SG
☒	Description : paged 1 to paged 23	
☒	Claim(s) : paged 24 to paged 27	
☐	Drawing(s) : paged to paged	
☒	Abstract : paged 28 to paged 7	
DATE OF RECEIPT		

01 A PROCESS FOR PRODUCING HEAVY LUBRICATING
02 OIL HAVING A LOW POUR POINT

03
04 Technical Field

05
06 This invention relates to a process for reducing the pour
07 point of a waxy refinery stream using a medium pore
08 aluminosilicate, SSZ-32.

09
10 BACKGROUND OF THE INVENTION

11
12 Recent advances in the development of catalysts used for
13 catalytic dewaxing have made it possible to produce low
14 pour point lubricating oil base stock from waxy feeds at
15 high yield. Dewaxing is required when highly paraffinic
16 oils are to be used in products which need to remain
17 mobile at low temperatures, e.g., lubricating oils,
18 heating oils and jet fuels. The straight chain normal
19 and slightly branched paraffinic substituents which are
20 present in oils of this kind are waxes which cause high
21 pour points and high cloud points in the oils. In heavy
22 oils, cyclic paraffins and aromatics having paraffinic
23 side chains re also present as wax. If adequately low
24 pour points are to be obtained, these waxes must be
25 wholly or partly removed, or converted to non-waxy
26 analogues. In the past, various solvent removal
27 techniques such as propane dewaxing and MEK dewaxing were
28 used, but these techniques are costly and time consuming.

29
30
31 Catalytic dewaxing has been used to overcome the
32 deficiencies of commercial solvent wax removal processes.
33 U.S. Patent No. 4,222,855 issued September 16, 1980, to
34 Pelrine et al. describes a process for dewaxing a waxy
hydrocarbon fraction boiling between 450°F and 1050°F
(about 232-566°C) using ZSM-23 or ZSM-35. U.S. Patent

01 No. 4,414,097 issued November 8, 1983, to Chester et al.
02 discloses dewaxing hydrocrackate with ZSM-23, where the
03 hydrocrackate is derived from hydrocracking a hydrocarbon
04 feedstock boiling above 343°C. The zeolite used in the
05 present process has essentially the same X-ray
06 diffraction pattern as ZSM-23, described in U.S. Patent
07 No. 4,076,842. In the present invention the aluminum
08 content is higher than previously described. The X-ray
09 diffraction lines are quite broad due to the very small
10 crystal size.

11

12 Catalytic dewaxing processes using conventional catalysts
13 remove waxes by selectively cracking waxy components to
14 produce lower molecular weight products, some of which
15 may be removed by distillation. For example, waxy
16 paraffins may be cracked to lighter n-paraffins,
17 including butane, propane, ethane and methane, which do
18 not contribute to the waxy nature of the oil. Because
19 these lighter products are generally of lower value than
20 the higher molecular weight materials, it would be
21 desirable to limit the degree of cracking which takes
22 place during a catalytic dewaxing process.

23

24 Recent advances in processes for reducing the pour and
25 cloud points of refinery streams have provided medium
26 pore molecular sieves for isomerization and
27 hydroisomerization of the paraffinic components in the
28 refinery streams. Isomerization of wax, which converts
29 wax to non-waxy components boiling in the same range as
30 the wax, is preferred to the cracking reactions described
31 above.

32

33 U.S. Patent No. 4,734,539 discloses a method for
34 isomerizing a naphtha feed using an intermediate pore
size zeolite catalyst, such as an H-offretite catalyst.
U.S. Patent No. 4,518,485 discloses a process for



01 dewaxing a hydrocarbon feedstock containing paraffins by
02 a hydrotreating and isomerization process.

03

04 In U.S. Patent No. 4,814,543 issued March 21, 1989, Chen
05 et al. teaches paraffin isomerization of a 330-650°F
06 (about 166-343°C) boiling range feedstock having a
07 paraffinic content with not more than 20 carbon atoms and
08 containing at least 20 ppm nitrogen impurities. ZSM-22,
09 ZSM-23 or ZSM-35 are suggested as alternative
10 hydroisomerization catalysts for this application. These
11 catalysts are taught as being resistant to nitrogen
12 poisoning under isomerization conditions in the
13 conversion of distillate range feedstock.

14

15 U.S. Patent Nos. 4,689,138; 4,859,311; 4,921,594; and
16 5,149,421, the disclosures of which are incorporated
17 herein by reference, teach silicoaluminophosphate
18 molecular sieves for isomerizing waxy hydrocarbon
19 components.

20

21 The present invention is directed to a process for
22 dewaxing a specific type of oil, which contains wax
23 having a low proportion of normal alkanes. Dewaxing oils
24 of this type requires a highly selective catalyst in
25 order to maintain a high yield of lubricating oil base
26 stock product. The present invention provides such a
27 catalyst. A medium pore aluminosilicate zeolite, SSZ-32,
28 is the catalyst used in the present process. SSZ-32 has
29 been shown in co-assigned U.S. Patent No. 5,053,373,
30 issued 10/01/91 to S.I. Zones, to dewax hydrocarbon feeds
31 by selectively removing straight chain paraffins. Feeds
32 to the dewaxing process include light gas oil, heavy gas
33 oils and reduced crudes boiling above 350°F (about
34 177°C). The SSZ-32 hydrodewaxing catalyst of '373 may
optionally contain a hydrogenation metal. The present
process is particularly directed to heavy refinery



01 streams containing a high proportion of non-normal
02 paraffin waxes, and to the process for reducing the pour
03 point of these streams at high selectivity and at high
04 yield.

05

06

07

SUMMARY OF THE INVENTION

08

09 In accordance therefore with the present invention, a
10 process is set forth for converting a high boiling, high
11 pour point oil to a relatively lower pour point oil.

12 More particularly, a process is provided for producing a
13 lubricating oil base stock from a heavy wax-containing
14 oil, said process comprising contacting said heavy oil
15 under mild cracking and isomerization conditions with a
16 catalyst comprising

17

18 (a) a zeolite having a mole ratio of silicon oxide
19 to aluminum oxide greater than about 20:1 to
20 less than 40:1, and having the X-ray
21 diffraction lines of Table 1; and

22

23 (b) at least one Group VIII metal,

24

25 wherein said wax is a naphthenic wax, and wherein the
26 pour point of said lubricating oil base stock is reduced
27 relative to the pour point of said heavy oil.

28

29 As used herein, naphthenic wax is wax containing a
30 substantial portion of naphthenic wax components, ie. wax
31 components which are not normal alkanes.

32

33 Among other factors, the present invention is based on
34 our discovery that SSZ-32 selectively isomerizes small
amounts of normal paraffins in the presence of high
concentrations of waxlike non-normal paraffins. This



01 property of SSZ-32 provides a highly selective process
02 for lowering the pour point of heavy feeds which contain
03 naphthenic wax at high yield of lubricating oil base
04 stock.

05

06

07

DETAILED DESCRIPTION OF THE INVENTION

08

09 In the present process, a heavy oil containing naphthenic
10 wax is converted under mild cracking and isomerization
11 conditions to a low pour point oil. Oils which contain a
12 high wax content, up to and including essentially pure
13 wax, and oils containing a minor amount of wax may both
14 be treated in the present process. As used herein,
15 naphthenic wax is contrasted from paraffin wax in that
16 naphthenic wax is a petroleum derived wax containing a
17 substantial amount of hydrocarbons other than normal
18 alkanes. In general, naphthenic waxes are composed of C₃₀
19 and larger hydrocarbon molecules. Less than about
20 50 weight percent, preferably less than about 40 weight
21 percent, and more preferably less than 35 weight percent
22 of the molecules are normal alkanes (ie. normal
23 paraffins), the remainder being largely isoparaffins,
24 noncondensed cycloparaffins and condensed cycloparaffins.
25 There may also be small amounts of benzenes and
26 naphthalenes. Each or all of these may have normal
27 paraffin substituent groups to increase the waxlike
28 character of the particular molecular species.

29

30 When determining the composition of the naphthenic wax,
31 it is frequently necessary to separate the wax from oil
32 containing the wax or contained in the wax. Methods are
33 available in the art for both removing a major amount of
34 oil from a minor amount of wax, and for removing a minor
amount of oil from a major amount of wax. The oil



01 content of the naphthenic waxes may be determined, for
02 example, using method ASTM D721.

03

04 There are a number of methods known in the art for
05 quantifying the normal alkane content of a naphthenic
06 wax, including gas chromatographic methods, and mass
07 spectroscopic methods. It is preferred that the
08 naphthenic wax to be analyzed for normal alkanes contain
09 no more than about 25 weight percent oil, and more
10 preferably no more than about 15 weight percent, most
11 preferably no more than about 5 weight percent oil.

12

13 Examples of feeds which may be treated in the present
14 process include, for example, crude oils, reduced crude
15 oils, gas oils, lubricating oil stocks, foots oils, slack
16 wax, deoiled waxes, waxy bright stock and
17 microcrystalline wax. The total wax content of the oil,
18 including normal alkane and naphthenic waxes, depends on
19 the crude from which it is produced. Oil having a total
20 wax content ranging from about 0.5 weight percent to
21 100 weight percent can be dewaxed in the present process.
22 The benefit of the present process increases with wax
23 content. Thus, oils containing greater than 5 weight
24 percent total wax are preferred, and oils containing
25 greater than 10 weight percent total wax are particularly
26 preferred. The oil will have a pour point of at least
27 0°C, preferably at least 10°C, and more preferably at
28 least 20°C. Typically, at least 80 volume percent of the
29 heavy oil will boil at a temperature greater than about
30 800°F (about 427°C), preferably greater than about 850°F
31 (about 454°C).

32

33 Heavy gas oil boiling in the range of about 800°F to
34 about 1050°F (about 427°C-566°C) is a specific example of
a heavy oil which can be treated using the present
process. Bright stock is another specific example.



01 Bright stock is a deasphalted residuum fraction from a
02 crude distillation column. The deasphalted residuum used
03 to prepare the waxy bright stock has a normal boiling
04 range on the order of from about 900°F to about 1300°F
05 (about 482°C-704°C), and preferably in the range from
06 about 1000°F to about 1250°F (about 530°C-677°C).

07

08 Before being treated according to the present process,
09 the hydrocarbon feed may be treated in one or more prior
10 treating steps, including hydrotreating, hydrocracking,
11 solvent refining or deasphalting. These pretreatment
12 processes may remove sulfur, oxygen and nitrogen
13 heteroatoms from the feed and increase the viscosity
14 index of the feed. The nitrogen content of the heavy oil
15 depends on a number of factors, including the source of
16 the oil, the boiling range of the oil, and the processing
17 steps encountered by the oil before being treated in the
18 present process. In the present process the nitrogen
19 content of the heavy oil will be generally less than
20 about 100 ppm, though it is preferred to maintain the
21 nitrogen level below about 50 ppm, and more preferred
22 below about 10 ppm, where ppm represents parts per
23 million parts by weight.

24

25 As stated above, heavy oils containing a major amount of
26 wax may also be treated in the present process. These
27 highly waxy oils include oils containing greater than
28 about 50 weight percent total wax. Oils consisting of up
29 to 100% wax may be treated in the present process.

30

31 Slack wax from heavy gas oil and heavy microcrystalline
32 wax are two specific examples of naphthenic wax which can
33 be treated in the present process. Slack wax is
34 recovered from heavy gas oil by methods known to the art
such as, for example, by solvent dewaxing. Heavy
microcrystalline wax is generally differentiated from



01 paraffin wax by the size of the wax crystals in the solid
02 wax mass, by the difficulty of separating
03 microcrystalline wax from the oil liquid in which it is
04 found, and by certain characteristic physical properties,
05 including refractive index, melting point and molecular
06 weight. Heavy microcrystalline wax is largely composed
07 of C₄₀ and larger hydrocarbons, with less than 10% C₃₉ and
08 smaller hydrocarbons. In general, a heavy
09 microcrystalline wax has a refractive index greater than
10 1.434 measured at 98.9°C and a melting point of greater
11 than about 145°C. Chapters 1 and 2 of H. Bennett,
12 Industrial Waxes, Volume I, Chemical Publishing Company,
13 Inc., 1975, and Kirk-Othmer: Encyclopedia of Chemical
14 Technology, John Wiley and Sons, Third Edition, Vol. 24,
15 p. 473-476 includes a description of microcrystalline
16 waxes.

17
18 The present process is contrasted from conventional
19 processes for dewaxing heavy oil by the high yield of
20 high viscosity index lubricating oil base stock having
21 the same boiling range as that of the feed. However, the
22 present process is not to be limited to products boiling
23 in the same range as the feed. Depending on process
24 conditions and the type of feed processed, lubricating
25 oil base stocks having boiling ranges well below that of
26 the feed may be produced, including base stocks boiling
27 at or below 650°F. The lubricating oil base stock which
28 is the product of the present process has a pour point
29 below that of the heavy oil feed. Preferably, the
30 lubricating oil base stock has a pour point of less than
31 about -10°C. Ultra-low pour points of less than -25°C
32 are also possible with the present process. The present
33 process is particularly suited to the preparation of high
34 viscosity index base stocks. Thus, when heavy waxy oils
are treated in the present process, the viscosity index
of the base stock product will generally be greater than



01 95. When the waxy oil is essentially pure wax, or an oil
02 containing high percentages of wax, the viscosity index
03 of the base stock product may be greater than 115, and,
04 depending on the type of oil treated, may be as high as
05 140 and above.

06
07 SSZ-32
08

09 The zeolite useful in the present process is termed
10 SSZ-32. Novel SSZ-32 zeolites, as synthesized, have a
11 crystalline structure whose X-ray powder diffraction
12 pattern shows the following characteristic lines:
13

14 TABLE 1
15

16	<u>d/n</u>	<u>Int. I/I₀</u>
17	11.05	26
18	10.05	10
19	7.83	17
20	4.545	71
21	4.277	71
22	3.915	100
	3.726	98

23 The X-ray powder diffraction patterns were determined by
24 standard techniques. The radiation was the
25 K-alpha/doublet of copper and a scintillation counter
26 spectrometer with a strip-chart pen recorder was used.
27 The peak heights I and the positions, as a function of 2θ
28 where θ is the Bragg angle, were read from the
29 spectrometer chart. From these measured values, the
30 relative intensities, $100 I/I_0$, where I_0 is the intensity
31 of the strongest line or peak, and d, the interplanar
32 spacing in Angstroms corresponding to the recorded lines,
33 can be calculated. The X-ray diffraction pattern of
34 Table 1 is characteristic of novel SSZ-32 zeolites. The
zeolite produced by exchanging the metal or other cations
present in the zeolite with various other cations yields



01 substantially the same diffraction pattern although there
02 can be minor shifts in interplanar spacing and minor
03 variations in relative intensity. Minor variations in
04 the diffraction pattern can also result from variations
05 in the organic compound used in the preparation and from
06 variations in the silica-to-alumina mole ratio from
07 sample to sample.

08

09 Calcination can also cause minor shifts in the X-ray
10 diffraction pattern. Notwithstanding these minor
11 perturbations, the basic crystal lattice structure
12 remains unchanged.

13

14 Methods of preparing SSZ-32 zeolites are disclosed in
15 U.S. Patent No. 5,053,373, the disclosure of which is
16 incorporated herein by reference.

17

18 The synthetic zeolites can be used as synthesized or can
19 be thermally treated (calcined). Usually, it is
20 desirable to remove the alkali metal cation by ion
21 exchange and replace it with hydrogen, ammonium, or any
22 desired metal ion. The zeolite can be leached with
23 chelating agents, e.g., EDTA or dilute acid solutions, to
24 increase the silica:alumina mole ratio. The zeolite can
25 also be steamed; steaming helps stabilize the crystalline
26 lattice to attack from acids. The zeolite can be used in
27 intimate combination with hydrogenating components, such
28 as tungsten, vanadium, molybdenum, rhenium, nickel,
29 cobalt, chromium, manganese, or a noble metal, such as
30 palladium or platinum, for those applications in which a
31 hydrogenation-dehydrogenation function is desired.

32

33 Typical replacing cations can include metal cations,
34 e.g., rare earth, Group IIA and Group VIII metals, as
well as their mixtures. Of the replacing metallic
cations, cations of metals such as rare earth, Mn, Ca,



01 Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co are
02 particularly preferred. High conversions can be obtained
03 with zeolite SSZ-32 in the hydrogen form.

04
05 The hydrogen, ammonium, and metal components can be
06 exchanged into the zeolite. The zeolite can also be
07 impregnated with the metals, or the metals can be
08 physically intimately admixed with the zeolite using
09 standard methods known to the art. And, the metals can
10 be occluded in the crystal lattice by having the desired
11 metals present as ions in the reaction mixture from which
12 the SSZ-32 zeolite is prepared.

13
14 Typical ion exchange techniques involve contacting the
15 synthetic zeolite with a solution containing a salt of
16 the desired replacing cation or cations. Although a wide
17 variety of salts can be employed, chlorides and other
18 halides, nitrates, and sulfates are particularly
19 preferred. Representative ion exchange techniques are
20 disclosed in a wide variety of patents including U.S.
21 Patent Nos. 3,140,249; 3,140,251; and 3,140,253. Ion
22 exchange can take place either before or after the
23 zeolite is calcined.

24 Following contact with the salt solution of the desired
25 replacing cation, the zeolite is typically washed with
26 water and dried at temperatures ranging from 65°C to
27 about 315°C. After washing, the zeolite can be calcined
28 in air or inert gas at temperatures ranging from about
29 200°C to 820°C for periods of time ranging from 1 to 48
30 hours, or more, to produce a catalytically active product
31 especially useful in hydrocarbon conversion processes.

32
33 Regardless of the cations present in the synthesized form
34 of the zeolite, the spatial arrangement of the atoms
which form the basic crystal lattice of the zeolite
remains essentially unchanged. The exchange of cations



01 has little, if any, effect on the zeolite lattice
02 structures.

03

04 It is preferred that relatively small crystal size
05 zeolite be utilized in practicing the invention.
06 Preferably, the average crystal size is not greater than
07 about 0.5 microns, more preferably no more than about 0.1
08 microns and still more preferably not more than about
09 0.05 microns.

10

11 The shape selectivity of SSZ-32 is manifested by
12 Constraint Index values (as defined in J. Catalysis 67,
13 page 218), after calcination and in the hydrogen form, of
14 preferably greater than 12, and more preferably 13 or
15 greater. Determination of Constraint Index is also
16 disclosed in U.S. Patent No. 4,481,177.

17

18 The "constraint index" is determined by passing
19 continuously a mixture of an equal weight of normal
20 hexane and 3-methylpentane over a sample of zeolite at
21 atmospheric pressure according to the following
22 procedure. A zeolite sample is prepared in the form of
23 pellets. The pellets are lightly crushed, and the 20-40
24 mesh fraction is dried in flowing air at 1000°F (about
25 538°C) for at least 30 minutes. A reactor tube is
26 charged with 0.47 grams of the dried zeolite sample.
27 Helium at 9.4 cc/min is introduced to the catalyst
28 charge, and the charge is heated at 800°F. A 1:1 weight
29 ratio blend of normal hexane and 3-methylpentane is then
30 passed over the zeolite at 8 μ l/min. Effluent samples
31 are analyzed by on-line gas chromatography to determine
32 the fraction remaining unchanged for each of the two
33 hydrocarbons.

34

This Sheet Has Been Replaced



01 The "constraint index" is calculated as follows:

02

03
$$\text{Constr. Index} = \frac{\log_{10}(\text{fraction of n-hexane remaining})}{\log_{10}(\text{fraction of 3-methylpentane remaining})}$$

04

05

06

07

08 The aluminosilicate can be formed into a wide variety of
09 physical shapes. Generally speaking, the zeolite can be
10 in the form of a powder, a granule, or a molded product,
11 such as an extrudate having a particle size sufficient to
12 pass through a 2-mesh (Tyler) screen and be retained on a
13 400-mesh (Tyler) screen. In cases where the catalyst is
14 molded, such as by extrusion with an organic binder, the
15 aluminosilicate can be extruded before drying, or dried
16 or partially dried and then extruded. The zeolite can be
17 composited with other materials resistant to the
18 temperatures and other conditions employed in organic
19 conversion processes. Such matrix materials include
20 active and inactive materials and synthetic or naturally
21 occurring zeolites as well as inorganic materials such as
22 clays, silica and metal oxides. The latter may occur
23 naturally or may be in the form of gelatinous
24 precipitates, sols, or gels, including mixtures of silica
25 and metal oxides. Use of an active material in
26 conjunction with the synthetic zeolite, i.e., combined
27 with it, tends to improve the conversion and selectivity
28 of the catalyst in certain organic conversion processes.
29 Inactive materials can suitably serve as diluents to
30 control the amount of conversion in a given process so
31 that products can be obtained economically without using
32 other means for controlling the rate of reaction.
33 Frequently, zeolite materials have been incorporated into
34 naturally occurring clays, e.g., bentonite and kaolin.
These materials, i.e., clays, oxides, etc., function, in
part, as binders for the catalyst. It is desirable to
provide a catalyst having good crush strength, because in



01 petroleum refining the catalyst is often subjected to
02 rough handling. This tends to break the catalyst down
03 into powders which cause problems in processing.

04

05 Naturally occurring clays which can be composited with
06 the synthetic zeolites of this invention include the
07 montmorillonite and kaolin families, which families
08 include the sub-bentonites and the kaolins commonly known
09 as Dixie, McNamee, Georgia and Florida clays or others in
10 which the main mineral constituent is halloysite,
11 kaolinite, dickite, nacrite, or anauxite. Fibrous clays
12 such as sepiolite and attapulgite can also be used as
13 supports. Such clays can be used in the raw state as
14 originally mined or can be initially subjected to
15 calcination, acid treatment or chemical modification.

16

17 In addition to the foregoing materials, the SSZ-32
18 zeolites can be composited with porous matrix materials
19 and mixtures of matrix materials such as silica, alumina,
20 titania, magnesia, silica-alumina, silica-magnesia,
21 silica-zirconia, silica-thoria, silica-beryllia,
22 silica-titania, titania-zirconia as well as ternary
23 compositions such as silica-alumina-thoria,
24 silica-alumina-zirconia, silica-alumina-magnesia and
25 silica-magnesia-zirconia. The matrix can be in the form
26 of a cogel.

27

28 The SSZ-32 zeolites can also be composited with other
29 zeolites such as synthetic and natural faujasites (e.g.,
30 X and Y), erionites, and mordenites. They can also be
31 composited with purely synthetic zeolites such as those
32 of the ZSM series. The combination of zeolites can also
33 be composited in a porous inorganic matrix.

34

The SSZ-32 hydrodewaxing catalyst contains a Group VIII
hydrogenation component of the type commonly employed in



01 dewaxing catalysts. The hydrogenation component may be
02 selected from one or more metals of Group VIII, including
03 the salts, complexes and solutions containing such
04 metals. The preferred hydrogenation catalyst is at least
05 one of the group of metals, salts and complexes selected
06 from the group consisting of at least one of platinum,
07 palladium, rhodium, iridium and mixtures thereof.
08 Reference to the catalytically active metal or metals is
09 intended to encompass such metal or metals in the
10 elemental state or in some form such as an oxide,
11 sulfide, halide, carboxylate and the like.

12
13 The hydrogenation component is present in an effective
14 amount to provide an effective hydrodewaxing catalyst,
15 and preferably in the range of from about 0.1 to 5% by
16 weight.

17 Process Conditions

18
19
20 The conditions under which the isomerization/dewaxing
21 process of the present invention is carried out generally
22 include a temperature which falls within a range from
23 about 392°F (about 200°C) to about 887°F (about 475°C),
24 preferably from about 482°F (about 250°C) to about 842°F
25 (about 450°C). The pressure ranges from about 15 to
26 about 3000 psig, preferably from about 200 to about 3000
27 psig, and more preferably from about 200 to about 2000
28 psig. The liquid hourly space velocity during contacting
29 is generally from about 0.1 to about 20 hr⁻¹, more
30 preferably from about 0.2 to about 10 hr⁻¹. The
31 contacting is preferably carried out in the presence of
32 hydrogen. The hydrogen to feed is typically between
33 about 500 and about 30,000 SCF/bbl (standard cubic feet
34 per barrel), preferably about 1,000 to about 20,000
SCF/bbl.



01 The process of the invention may also be employed in
02 combination with conventional dewaxing processes to
03 achieve a lube oil having particular desired properties.
04 For example, the process of the invention can be used to
05 reduce the pour point of a lube oil to a desired degree.
06 Further reduction of the pour point can then be achieved
07 using a conventional dewaxing process. Under such
08 circumstances, immediately following the isomerization
09 process of the invention, the lube oil may have a pour
10 point greater than about 15°F. Further, the pour point
11 of the lube oil produced by the process of the invention
12 can be reduced by adding pour point depressant
13 compositions thereto.

14
15 It is often desirable to use mild hydrogenation referred
16 to as hydrofinishing after dewaxing to produce more
17 stable lubricating oils. Hydrofinishing also can be
18 carried out prior to the dewaxing step. Hydrofinishing
19 is typically conducted at temperatures ranging from about
20 190°C to about 340°C, at pressures from about 400 psig to
21 about 3000 psig at space velocities (LHSV) from about 0.1
22 hr⁻¹ to about 20 hr⁻¹, and hydrogen recycle rates of from
23 about 400 to about 1500 SCF/bbl. The hydrogenation
24 catalyst employed must be active enough not only to
25 hydrogenate the olefins, diolefins and color bodies
26 within the lube oil fractions, but also to reduce the
27 aromatic content. The hydrofinishing step is beneficial
28 in preparing an acceptably stable lubricating oil.

29
30 Suitable hydrogenation catalysts include conventional
31 metallic hydrogenation catalysts, particularly the
32 Group VIII metals such as cobalt, nickel, palladium and
33 platinum. The metals are typically associated with
34 carriers such as bauxite, alumina, silica gel,
silica-alumina composites, and crystalline
aluminosilicate zeolites. Palladium is a particularly



01 preferred hydrogenation metal. If desired, non-noble
02 Group VIII metals can be used with molybdates. Metal
03 oxides or sulfides can be used. Suitable catalysts are
04 disclosed in U.S. Patent Nos. 3,852,207; 4,157,294;
05 3,904,513; and 4,673,487.

06

07 The invention will be further clarified by the following
08 examples, which are intended to be purely exemplary of
09 the invention.

10

11

EXAMPLES

12

13 The wax content of the oil set forth in the following
14 Examples was determined as follows: 300 g of oil was
15 diluted 50/50 by volume with a 4:1 mixture of methyl
16 ethyl ketone and toluene which was cooled to -20°C in a
17 refrigerator. The mixture was filtered through a Coors
18 funnel at -15°C using Whatman No. 3 filter paper. The
19 wax was removed from the filter and placed in a tarred 2
20 liter flask. The solvent was removed on a hot plate and
21 the wax weighed.

22

23 The normal paraffin analysis of a naphthenic wax set
24 forth in the following Examples was determined using the
25 following gas chromatographic (GC) technique. A baseline
26 test is made to determine the retention times of a known
27 mixture of C₂₀ to C₄₀ normal paraffins. To make the
28 determination, approximately 5 ml of carbon disulfide is
29 added to a weighed amount of the known mixture in a
30 2-dram vial. Two microliters of the CS₂/known sample are

31

32

33

34

This Sheet Has Been Replaced



01 injected into an HP-5711 gas chromatograph, which is
02 operated using the following parameters:

03

04	Carrier gas - helium	Column - 15 m X 0.32 mm ID
05	Splitter flow - 50 ml/min	fused silica capillary
06	Inlet pressure - 30 psig	coated with DB-1.
06	Make-up gas - nitrogen	Available from J&W
07	Make-up flow - 25 ml/min	Scientific.
07	(@ 8 psig)	
08	FID hydrogen - 20 ml/min	Oven Temperature Program -
08	(@ 16 psig)	(150 °C initial, 4 min.
09	FID air - 300 ml/min	delay, 4°C/min rate, 270°C
10	(40 psig)	final temp, 26-min final
11	Injector Temperature - 350°C	temp hold.
11	Detector Temperature - 300°C	

12

13 The peaks in the resulting GC trace are correlated with
14 the identity of each of the normal paraffins in the known
15 mixture.

16

17 The gas chromatographic analysis is then repeated on a
18 sample of the unknown wax. A weighted amount of the
19 unknown wax is dissolved in 5 ml of CS₂ and the solution
20 injected into the gas chromatograph, which is operated
21 using the parameters listed above. The resulting GC
22 trace is analyzed as follows:

23

24 (a) Each peak attributable to each normal paraffin
25 C_x present in the wax is identified.

26

27 (b) The relative area of each normal paraffin peak
28 is determined by standard integration methods.
29 Note that only the portion of the peak directly
30 attributable to the normal paraffin, and
31 excluding the envelope at the base of the peak
32 attributable to other hydrocarbons, is included
33 in this integration.

34

(c) The relative area representing the total amount
of each hydrocarbon C_n (both normal and non



normal) in the wax sample is determined from a peak integration from the end of the C_{n-1} normal paraffin peak to the end of the C_n peak. The weight percentage of each normal paraffin in the wax is determined by relating the area of the normal paraffin peak to the total area attributable to each carbon number component in the wax.

The normal paraffin content of waxes boiling at temperatures beyond the range of the gas chromatograph were estimated from literature references to waxes having similar physical properties.

EXAMPLE 1

1400 ml of water and 56.5 grams KOH were mixed in a Hastelloy C lined 1-gallon autoclave, which was stirred with an overhead paddle-blade stirrer. 23.3 grams of Reheis F2000 alumina (50 wt% Al_2O_3) were added, and the mixture stirred until clear. 62 grams of isobutylamine and 200 millimoles of N,N' Diisopropylimidazolium hydroxide (1M aqueous solution) were then added. 253 grams of Cabosil M-5 were then added in increments with stirring. After an additional 30 minutes of stirring, the pH of the mixture was 13.2-13.3.

The reaction mixture was stirred at 75 RPM and heated to 170°C for 5 days. After washing and drying the reaction product, the product was analyzed by X-ray diffraction and found to be SSZ-32.

The uncalcined zeolite was bound with alumina as follows: 180 grams of zeolite was blended with 97 grams Catapal alumina in a Baker Perkins mixer. To the mixing powders was added 8.3 g of 70% HNO_3 in sufficient water so that



01 the total of water in the zeolite, in the alumina, and
02 with the HNO_3 was 269 g. The mixing powders containing
03 the nitric acid was mixed for 30 minutes at a total
04 volatiles content of approximately 45%, and was then
05 extruded with a 0.113 in die. The extrudates were dried
06 at 250°F (about 121°C) for 8 hours and calcined at 1150°F
07 (about 621°C) for 1 hour at 1 SCFH dry air. The
08 extrudates were then subjected to a sequence of 4 NH_4NO_3
09 ion-exchanges in a 1M solution, each for 2 hours at
10 100°C.
11

12 The bound exchanged zeolite was impregnated with 0.325
13 wt% platinum from platinum tetraaminonitrate as follows:
14 A platinum solution was prepared by combining 6.44 grams
15 $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ with 337 grams water and 48.2 grams of
16 dilute NH_4OH (1/100 volume dilution of concentration NH_4OH
17 containing 28.5% NH_3). A slurry was also prepared by
18 combining 100 grams zeolite (volatiles-free basis) with
19 1048 grams deionized water and 201 grams of 1/100 diluted
20 NH_4OH . The zeolite slurry was contacted with the platinum
21 solution for 24 hours. The zeolite slurry was then
22 filtered, washed by reslurrying twice with a 10/1 weight
23 ration of deionized water, air dried for at 30 minutes,
24 and dried at 250°F (about 121°C) for 4 hours in forced
25 air. The zeolite was then calcined at 250°F (about
26 121°C) for 2 hours and then heated at 100°F/hr (about
27 56°C/hr) to 550°F (about 288°C), and held at 550°F (about
28 288°C) for 3 hours in 1 SCFH dry air.
29

30 Before testing the catalyst with heavy waxy oil feeds, it
31 was reduced in flowing hydrogen at 400°F (about 204°C)
32 and 2300 psig pressure for 4 hours in order to
33 equilibrate activity.
34

!This Sheet Has Been Replaced



EXAMPLE 2

01
02
03 The SSZ-32 zeolite of Example 1 was tested with a slack
04 wax having the following properties:
05

06	Gravity, °API	21.2
07	Sulfur, ppm	30
08	Nitrogen, ppm	<1
09	Pour Point, °C	63
10	Cloud Point, °C	77
11	Viscosity, cSt @ 100°C	8.473
12	Oil Content, wt% (ASTM D-721)	30
13	Simulated Distillation (ASTM D-2887)	
14	10% overhead	886°F (about 474°C)
15	50% overhead	963°F (about 517°C)
16	90% overhead	1028°F (about 553°C)
17	N-paraffin content of deoiled wax, wt%	30

18
19 The reaction conditions and product properties from the
20 reaction test were as follows:
21

22	Number		Test
23		1	2
24	Reaction Conditions		
25	Temperature, °F (°C)	670 (354)	580
26	(304)		
27	WHSV	0.49	0.47
28	Gas Rate, SCFB	7070	7242
29	Inlet H ₂ Pressure, psia	2242	392
30	Product Properties		
31	Viscosity, cSt (corrected to 500°F flash point)		
32	@ 40°C	52.92	56.50
33	Viscosity Index	133	132
34	Pour Point, °C	-27	-18
35	Cloud Point, °C	-7	-7
36	Refractive Index		
37	@ 20°C	1.4666	1.4684
38	Yield, wt%	63.3	68.6

This Sheet Has Been Replaced



EXAMPLE 3

The SSZ-32 zeolite of Example 1 was tested with a microcrystalline wax having the following properties:

Gravity, °API	32.1
Sulfur, ppm	6
Nitrogen, ppm	0.62
Pour Point, °C	81
Cloud Point, °C	
Viscosity, cSt @ 100°C	21.13
Oil Content, wt% (ASTM D-721)	6.7
Simulated Distillation (ASTM D-2887)	
10% overhead	1052°F (567°C)
50% overhead	1160°F (627°C)
95% overhead	1238°F (670°C)
N-paraffin content (estimated), wt%	25

The reaction conditions and product properties from the reaction test were as follows:

Number	Test
3	4
Reaction Conditions	
Temperature, °F (°C)	680(360)
600(316)	
WHSV	0.40 0.41
Gas Rate, SCFB	7953 7833
Inlet H ₂ Pressure, psia	2272 405
Product Properties	
Viscosity, cSt (corrected to 500°F flash point)	
@ 40°C	134.1 166.6
Viscosity Index	127 120
Pour Point, °C	-39 -42
Cloud Point, °C	-5 4
Refractive Index	
@ 20°C	1.4655 1.4704
Yield, wt%	25.1 31.4

This Sheet Has Been Replaced



EXAMPLE 4

01
02
03 The SSZ-32 zeolite of Example 1 was tested with a heavy
04 hydrocracked oil having the following properties:
05

06 Gravity, °API	29.6
07 Sulfur, ppm	10
Nitrogen, ppm	4.36
08 Pour Point, °C	54
Cloud Point, °C	60
Viscosity, cSt @ 70°C	25.98
10 Viscosity, cSt @ 100°C	11.05
Wax Content, wt%	18.0
N-paraffin content of wax, wt%	29
12 Simulated Distillation (by ASTM D-2887)	
13 10% overhead	866°F (463°C)
50% overhead	953°F (512°C)
14 95% overhead	1025°F (552°C)

15
16 The reaction conditions and product properties from the
17 reaction test were as follows:
18

19		Test
20	Number	
	5	6
21	Reaction Conditions	
22	Temperature, °F (°C)	660(349)
23	WHSV	2.16
24	Gas Rate, SCFB	4991
25	Inlet H ₂ Pressure, psia	2227
26	Product Properties	
27	Viscosity, cSt (corrected to 500°F flash point)	
28	@ 40°C	102.5
29	Viscosity Index	100
30	Pour Point, °C	-21
31	Cloud Point, °C	-7
32	Refractive Index	
33	@ 20°C	1.4781
34	Yield, wt%	89.1

35
36 The examples above show the high yield and excellent
37 viscosity index possible when dewaxing heavy waxy oils
38 with SSZ-32.





01 WHAT IS CLAIMED IS:

02 *amended*,

03 1. A process for producing a lubricating oil base stock
04 from a heavy oil which contains wax, said process
05 comprising contacting said heavy oil under mild
06 cracking and isomerization conditions with a
07 catalyst comprising

08

09 (a) a zeolite having a mole ratio of silicon oxide
10 to aluminum oxide greater than about 20:1 to
11 less than 40:1, and having the X-ray
12 diffraction lines of Table 1; and

13

14 (b) at least one Group VIII metal,

15

16 wherein said ~~wax~~ *heavy oil contains* is a naphthenic wax, and wherein
17 the pour point of said lubricating oil base stock is
18 reduced relative to the pour point of said heavy
19 oil.

20

21 2. The process according to Claim 1 wherein the heavy
22 oil contains at least 5 weight percent wax.

23

24 3. The process according to Claim 2 wherein the heavy
25 oil contains at least 10 weight percent wax.

26

27 4. The process according to Claim 1 wherein the
28 naphthenic wax contains less than about 50 weight
29 percent normal alkanes.

30

31 5. The process according to Claim 4 wherein the
32 naphthenic wax contains less than about 40 weight
33 percent normal alkanes.

34

This Sheet Has Been Replaced





- 01 6. The process according to Claim 1 wherein at least
02 about 80 volume percent of the heavy oil boils at a
03 temperature greater than about 800°F at atmospheric
04 pressure.
05
- 06 7. The process according to Claim 1 wherein the heavy
07 oil is a heavy gas oil.
08
- 09 8. The process according to Claim 1 wherein said heavy
10 oil is a hydrocracked stock.
11
- 12 9. The process according to Claim 1 wherein said heavy
13 oil is a solvent refined stock.
14
- 15 10. The process according to Claim 1 wherein at least
16 about 80 volume percent of the heavy oil boils at a
17 temperature greater than about 1000°F at atmospheric
18 pressure.
19
- 20 11. The process according to Claim 10 wherein the heavy
21 oil is bright stock.
22
- 23 12. The process according to Claim 11 wherein the bright
24 stock contains at least about 5% by weight of wax.
25
- 26 13. The process according to Claim 1 wherein said
27 contacting is carried out at a temperature of from
28 about 400°F to about 850°F, a reaction pressure of
29 from about 15 psig to about 3000 psig and a liquid
30 hourly space velocity from about 0.1 to about 20
31 hr⁻¹.
32
- 33 14. The process according to Claim 13 wherein said
34 pressure is from about 100 to about 2500 psig.

This Sheet Has Been Replaced





- 01 15. The process according to Claim 13 wherein the liquid
02 hourly space velocity is from about 0.1 to about 5.
03
- 04 16. The process according to Claim 1 wherein said
05 contacting is carried out in the presence of between
06 about 400 to about 8000 standard cubic feet of
07 hydrogen per barrel of feedstock.
08
- 09 17. The process according to Claim 1 further comprising
10 hydrofinishing the dewaxed lube oil.
11
- 12 18. The process according to Claim 17 wherein
13 hydrofinishing is carried out at a temperature of
14 from about 190°C to about 340°C and a pressure of
15 from about 400 psig to about 3000 psig.
16
- 17 19. The process according to Claim 17 wherein
18 hydrofinishing is carried out in the presence of a
19 metallic hydrogenation catalyst.
20
- 21 20. The process according to Claim 1 wherein said heavy
22 oil is one or a mixture of materials selected from
23 the group consisting of crude oils, gas oils,
24 lubricating oil stocks, foots oils, slack waxes,
25 deoiled waxes, waxy bright stock and
26 microcrystalline waxes.
27
- 28 21. The process according to Claim 20 wherein the heavy
29 oil contains greater than about 70 weight percent
30 wax.
31
- 32 22. The process according to Claim 21 wherein the heavy
33 oil contains greater than about 80 weight percent
34 wax.

This Sheet Has Been Replaced





- 01 23. The process according to Claim 21 wherein the wax
02 contains less than about 50 weight percent normal
03 alkanes.
04
05 24. The process according to Claim 23 wherein the wax
06 contains less than about 40 weight percent normal
07 alkanes.
08
09 25. The process according to Claim 20 wherein the wax is
10 a slack wax from a heavy gas oil.
11
12 26. The process according to Claim 20 wherein the wax is
13 a heavy microcrystalline wax from a bright stock.
14
15 27. The process according to Claim 1 wherein the
16 Group VIII metal is platinum, palladium, or mixtures
17 thereof.
18
19 28. The process according to Claim 1 wherein the
20 Group VIII metal is present in the range from about
21 0.1 to about 5% by weight.
22
23 29. The process according to Claim 1 wherein the zeolite
24 has a crystallite size of less than about 0.5
25 microns.
26
27 30. The process according to Claim 01 wherein the
28 zeolite has a constraint index of greater than 12.
29
30
31
32
33
34

This Sheet Has Been Replaced

