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(54) **Catalytic dewaxing process using ZSM-11 zeolite.**

(57) Waxy oil, either a lubricating oil base stock or a fuel oil, is catalytically dewaxed using a catalyst comprising ZSM-11. The ZSM-11 may contain hydrogenation/dehydrogenation component such as Pt or Ni Mo. Dewaxing proceeds by wax cracking and wax isomerization.

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CATALYTIC DEWAXING PROCESS USING ZSM-11 ZEOLITE

Modern petroleum refining is heavily dependent on catalytic processes which chemically change the naturally occurring constituents of petroleum. Such processes include hydrocracking, catalytic cracking, reforming and hydrotreating.

The porous inorganic solids that were originally found useful for catalytic processes included certain clays, aluminas, silica-aluminas and other silicas coprecipitated with magnesia, for example, and such solids are still extensively used in the industry. In general, all of these solids had pores that were not of uniform size, and most of the pore volume was in pores having diameters larger than about 30 Angstroms, with some of the pores as large or larger than 100 Angstroms.

Zeolite molecular sieves have been found to be highly effective as hydrocarbon conversion catalysts. The conversion of gas oil to gasoline and distillate by catalytic cracking, the alkylation of benzene to ethylbenzene, the isomerization of xylenes and the disproportionation of toluene all involve molecules which are smaller in critical diameter than 1,3,5-triethylbenzene, and such molecules are occluded and acted upon by zeolite molecular sieves having an effective pore diameter of about 10 Angstroms. A particularly interesting catalytic transformation which requires a molecular sieve catalyst is the reduction of the pour point of waxy distillates and residual hydrocarbon fractions. Effective pour point reduction depends on the selective conversion of normal, high melting point paraffin molecules that have an effective critical diameter of about 5 Angstroms to substances of lower molecular weight that are easily separated from the low-pour product. Effective catalytic dewaxing depends at least in part on the regularity of the pore size of the crystalline zeolites, which allows selective conversion of unwanted constituents.

The dewaxing of oils by shape selective cracking and hydrocracking over ZSM-5 zeolites is discussed in Re 28,398 to Chen et al. U. S. Patent 3,956,102 discloses dewaxing a petroleum distillate with a ZSM-5 catalyst. Catalytic dewaxing of petroleum stocks with mordenite is described in the Oil and Gas Journal, January 6, 1975 issue at pages 69-73. See also U. S. Patent 3,668,113.

Crystalline zeolite ZSM-11 is disclosed in U.S. Patent 3,709,979. Example 9 of this patent taught fluid catalytic cracking at 875°F of a gas oil having a pour point of 100°F. High yields of olefins were obtained. The pour point of the product was reduced.

Later patents relating to improvements in the catalytic dewaxing process taught that the use of shape selective zeolites for catalytic dewaxing was preferred. These references taught that any shape selective zeolite with a Constraint Index of 1 to 12, as hereafter defined, could be used but that ZSM-5 and ZSM-11 were especially preferred. The only work reported was done on ZSM-5 catalyst.

Typical of these patents is U.S. 4,181,598 which taught making lube base stock oil of lower pour point from a waxy crude oil fraction by solvent refining, catalytic dewaxing over an intermediate pore size zeolite, e.g., ZSM-5, followed by hydrotreating.

U.S. 4,332,670 taught catalytic dewaxing of middle distillates to produce a low pour fuel oil by using an intermediate pore size zeolite. There are no examples showing use of ZSM-11.

We also wanted a catalyst that would achieve effective dewaxing, but minimize loss of valuable liquids, which invariably occurred using typical shape selective dewaxing catalysts. The only way to remove wax using one of these zeolites was to crack it down to small fragments.

We discovered that ZSM-11, which has been ignored experimentally by all prior workers in the lube oil and fuel oil area, is better for catalytic dewaxing than ZSM-5.

Accordingly, the present invention provides a process for catalytically dewaxing a wax containing hydrocarbon feedstock to produce a dewaxed oil which comprises contacting said stock at a temperature of 230 to 450°C, at a pressure of atmospheric to 14,000 kPa, and in the presence of hydrogen in a reaction zone with a catalyst comprising ZSM-11.

In another embodiment, the present invention provides a process for producing lubricating oil base stock with high viscosity index comprising contacting a lubricating oil base feedstock containing waxy components with a dewaxing catalyst comprising 10 to 95 wt % ZSM-11 catalyst and 90 to 5 wt % refractory inorganic oxide binder in a catalytic dewaxing zone operated at 230 to 400°C, a pressure of atmospheric to 14,000 kPa, liquid hourly space velocity of 0.1 to 20 and wherein hydrogen is present and the ratio of hydrogen to hydrocarbon is 50 to 1,000 volumes of H_2 at standard conditions per volume of liquid oil at standard conditions to produce a lubricating oil base stock with reduced wax content.

In a more limited embodiment, the present invention provides a process for catalytic dewaxing of a wax containing oil comprising contacting said oil in the presence of hydrogen at a temperature of 230 to 450°C, a hydrogen partial pressure of atmospheric to 14,000 kPa with a fixed bed of catalyst comprising ZSM-11 and a platinum group metal component to produce a catalytically dewaxed oil.

ZSM-11

Details of preparation of ZSM-11 are given in U.S. Patent 3,709,979. A number of properties of ZSM-11 zeolites are discussed hereafter.

SILICA/ALUMINA RATIO

The silica to alumina mole ratio of ZSM-11, and other zeolites, may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with silica to alumina mole ratios of at least 10 are useful, it is preferred to use zeolites having higher ratios than about 12, preferably about 15 to 200. In addition, zeolites as otherwise characterized herein but which are substantially free of aluminum, that is zeolites having silica to alumina mole ratios of up to infinity, are found to be useful and even preferable in some instances. Such "high silica" or "highly siliceous" zeolites tend to be hydrophobic and are intended to be included within this description. Also included within this definition are substantially pure silica analogues of the useful zeolites described herein, that is to say those zeolites having no measurable amount of aluminum (silica to alumina mole ratio of infinity) but which otherwise embody the characteristics disclosed.

In general, higher aluminum contents in the zeolite framework give more acid activity to the catalyst. The acid activity may be adjusted by crystallizing the ZSM-11 with only a little, or a lot, of aluminum, steaming the ZSM-11, acid extracting, or any other means conventionally used to adjust acid activity.

ALPHA ACTIVITY

One method of measuring acid activity is to measure the cracking activity of a catalyst to obtain an alpha value or alpha activity. A method of determining alpha activity is described in U.S. Patent 4,016,218. The alpha test is a good measure of cracking activity, but not a measure of hydroisomerization activity. Our ZSM-11 dewaxing process is believed to proceed by both cracking and hydroisomerization, so alpha activity provides some information about only one of the several reactions believed to occur during dewaxing. An activated large pore zeolite, e.g., RENaX, might have an alpha activity of over 10,000 and be a good FCC catalyst but do little or no dewaxing. A good dewaxing catalyst, e.g., Ni-ZSM-5, partially deactivated by coking, might have a low alpha activity and still do a good dewaxing job, so long as reactor temperatures were raised somewhat to adjust for the low alpha activity.

CONSTRAINT INDEX

The "Constraint Index" may be determined by passing continuously a mixture of an equal weight of normal hexane and 3-methylpentane over a sample of zeolite at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 538°C for at least 15 minutes. The zeolite is then flushed with helium and the temperature is adjusted between 275 and 510°C to give an overall conversion of between 10% and 60%. The mixture of hydrocarbons is passed at 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of zeolite per hour) over the zeolite with a helium dilution to give a helium to (total) hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

It may be necessary to use more severe conditions for samples of very low activity, such as those having an exceptionally high silica to alumina mole ratio.

The "Constraint Index" is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10}\ (\text{fraction of hexane remaining})}{\log_{10}\ (\text{fraction of 3-methylpentane remaining})}$$

The Constraint Index approximates the ratio of the cracking rate constants for the two hydrocarbons. Constraint Index (CI) values for ZSM-5 is about 8.3, while for ZSM-11 it is 8.7. Both values can vary, depending on test conditions

CATALYTIC DEWAXING OF LUBRICATING OILS

Refining suitable petroleum crude oils to obtain a variety of lubricating oils which function effectively in diverse environments has become a highly developed and complex art.

Although the broad principles involved in refining are qualitatively understood, the art is encumbered by quantitative uncertainties which require considerable resort to empiricism in practical refining. Underlying these quantitative uncertainties is the complexity of the molecular constitution of lubricating oils. Because lubricating oils for the most part are based on petroleum fractions boiling over 225°C, the molecular weight of the hydrocarbon constituents is high and these constituents display almost all conceivable structures and structure types.

Usually in lubricant refining, a crude oil that contains a suitable fraction of lubricant stock, as judged by experience or assay, is selected for processing. The process of refining to isolate that lubricant stock consists of a set of subtractive unit operations which removes the unwanted components. The most important of these unit operations include distillation, solvent refining, and dewaxing, which basically are physical separation processes in the sense that if all the separated fractions were recombined one would reconstitute the crude oil.

A refined lubricant stock may be used as such as a lubricant, or it may be blended with another refined lubricant stock having somewhat different properties. Or, the refined lubricant stock, prior to use as a lubricant, may be compounded with one or more additives which function, for example, as antioxidants, extreme pressure additives, and V.I. improvers. As used herein, the term "stock", regardless whether or not the term is further qualified, will refer only to a hydrocarbon oil without additives. The term "raw stock" will be used herein to refer to a viscous distillate fraction of crude petroleum oil isolated by vacuum distillation of a reduced crude from atmospheric distillation, and before further processing, or its equivalent. The term "raffinate" will refer to an oil that has been solvent refined, for example with furfural.

The term "dewaxed stock" or "dewaxed raffinate" will refer to an oil which has been treated by any method to remove or otherwise convert the wax contained therein and thereby reduce its pour point. The term "waxy", as used herein will refer to an oil of sufficient wax content to result in a pour point greater than 0°C. The term "stock", when unqualified, will be used herein generically to refer to the viscous fraction in any stage of refining, but in all cases free of additives.

The current practice is to vacuum distill an atmospheric tower residuum from an appropriate crude oil as the first step. This provides one or more raw stocks within the boiling range of 230 - 565°C. Raw stock is then extracted with a solvent, e.g., furfural, phenol, or chlorex, selective for aromatic hydrocarbons, and which removes undesirable components. The raffinate from solvent refining is then dewaxed, for example, by admixing with a solvent such as a blend of methyl ethyl ketone and toluene. The mixture is chilled to induce crystallization of the paraffin waxes which are then separated from the dewaxed dissolved raffinate in quantity sufficient to provide the desired pour point for the subsequently recovered raffinate. The catalytic dewaxing process of the present invention, discussed in more detail hereafter, is used instead of solvent dewaxing. Hydrotreating or hydrofinishing may be used in conjunction with catalytic dewaxing. Hydrofinishing or clay percolation may be used if needed to reduce the nitrogen and sulfur content or improve the color of the lubricating oil stock, and to improve oxidation resistance.

Hydrotreating may be used instead of, or in conjunction with, solvent refining to prepare the feedstock for the present invention.

The advantage of hydrotreating before catalytic dewaxing is that many catalyst poisons will be converted catalytically in the hydrotreater or deposited on the hydrotreating catalyst. This results in superior operation in the catalytic dewaxing unit, and in a longer operational life.

Conventional hydrotreating processes use a catalyst containing a hydrogenation component on a support, preferably a non-acidic support, e.g., Co-Mo or Ni-Mo on alumina.

The hydrotreater usually operates at relatively low temperatures, typically 200 - 450°C, preferably at 300 - 425°C.

The hydrotreating catalyst may be disposed as a fixed, fluidized, or moving bed of catalyst, though down flow, fixed bed operation is preferred because of its simplicity. When the hydrotreating catalyst is disposed as a fixed bed of catalyst, the liquid hourly space velocity, or volume per hour of liquid feed measured at standard conditions volume of catalyst will usually be 0.1 to 10, preferably about 1 to 5. Typical hydrogen partial pressures are 1 to 100 atmospheres, absolute. Hydrogen can be added to the feed on a once through basis, or recycled by conventional means.

Suitable hydrotreating/hydrogenation components include one or more of the metals, or compounds thereof, selected from Groups II, III, IV, V, VIB, VIIB, VIII and mixtures thereof of the Periodic Table of the Elements. Preferred metals include molybdenum, tungsten, vanadium, chromium,-cobalt, titanium, iron, nickel and mixtures thereof.

Usually the hydrotreating metal component will be present in an amount equal to 0.1 to 20 wt % of the support, with operation with 0.1 to 10 wt % hydrogenation metal, on an elemental basis, giving good results.

The hydrogenation components are usually disposed on a support, preferably an amorphous support such as silica, alumina, silica-alumina, etc. Any other conventional support material may also be used. It is also possible to include on the support an acid acting component, such as an acid exchanged clay or a zeolite.

Preferably the support does not have much acidity, it is the intent of the present invention to primarily conduct hydrotreating in the hydrotreating zone and minimize cracking or other reactions therein. Preferably, the support has a low enough acid acting activity that the pour point of the lube oil stock passing through the hydrotreating zone is not changed at all, or is changed less than 5 - 6°C by hydrotreating.

Viscosity index (V.I.) is a quality parameter of considerable importance for distillate lubricating oils to be used in automotive engines and aircraft engines. This Index is a series of numbers ranging from 0 to 100 or higher which indicate the rate of change of viscosity with temperature. A viscosity index of 100 indicates an oil that does not tend to become viscous at low temperature or become thin at high temperatures. Measurement of the Saybolt Universal Viscosity of an oil at 38 and 99°C (100 and 210°F) and referral to correlations, provides a measure of the V.I. of the oil. V.I. is defined in the Viscosity Index tabulation of the ASTM (D567), published by ASTM, 1916 Race Street, Philadelphia , Pa.

To prepare high V.I. automotive and aircraft oils the refiner usually selects a crude oil relatively rich in paraffinic hydrocarbons, since experience has shown that crudes poor in paraffins, such as those commonly termed "naphthene-base" crudes yield little or no refined stock having a V.I. above about 40. (See Nelson, supra, pages 80-81 for classifications of crude oils). Suitable stocks for high V.I. oils usually contain substantial quantities of waxes which result in solvent-refined lubricating oil stocks of high pour point.

Raw distillate lubricating oil stocks usually do not have a particularly high V.I. However, solvent-refining, as with furfural for example, in addition to removing unstable and sludge-forming components from the crude distillate, also removes components which adversely affect the V.I. Thus, a solvent refined stock prior to dewaxing usually has a V.I. in excess of specifications.

In general, the catalyst hydrodewaxing process of the present invention operates at about 230 to 400°C, pressures of atmospheric to 14,000 kPa, liquid hourly space velocities of 0.1 to 20, preferably 0.5 to 4, and hydrogen to hydrocarbon ratios of 90 to 1,000 volumes of hydrogen at standard conditions per volume of liquid oil at standard conditions. Any conventional catalytic dewaxing conditions may be used.

Catalytic dewaxing may be conducted by passing the feed over a fixed, fluidized or moving bed of catalyst comprising ZSM-11.

The ZSM-11 catalyst may be used neat, although it is preferably incorporated in a binder such as alumina, or silica/alumina.

Merely substituting ZSM-11, wherever ZSM-5 was used before for catalytic dewaxing, gives surprisingly better results.

HYDROGENATION/DEHYDROGENATION COMPONENT OF DEWAXING CATALYST

It is within the scope of the present invention to add a hydrogenation/dehydrogenation component, either a base metal or a platinum group metal component into the dewaxing catalyst.

The hydrogenation/dehydrogenation component is believed to promote hydroisomerization activity in addition to the shape selective cracking that occurs with ZSM-11. This combination of activities gives higher activity, better selectivity and lower pour point product than can be achieved with ZSM-5 catalysts.

The hydrogenation/dehydrogenation component may be added by ion exchange or impregnation, or any other method known to the art of incorporating hydrogenation/dehydrogenation components in a support, the support in this instance being either ZSM-11 alone or in admixture with a refractory inorganic oxide binder. Suitable hydrogenation/ dehydrogenation components may be selected from one or more of the metals, or compounds thereof, selected from Groups II, III, IV, V, VIB, VIIB, VIII and mixtures thereof of the Periodic Table of the Elements.

Preferred base metals include molybdenum, tungsten, vanadium, chromium, cobalt, titanium, iron, nickel and mixtures thereof, e.g., Co-Mo or Ni-Mo.

Preferred platinum group metals are platinum, irridium and palladium, with platinum giving especially good results.

The platinum group component will usually be added as a soluble, decomposable compound of the platinum group metal. After incorporation of this metal onto the ZSM-11 catalyst or binder or both, the resulting composite will usually be calcined to fix the metal components firmly to the catalyst.

The metal component may be incorporated into the catalyst by impregnation, by ion exchange or by other means by contacting either the catalyst or a component thereof with a solution of a compound of the metal in an appropriate amount necessary to provide the desired concentration within the scope of the invention. The metal component may be incorporated either in any step during preparation of the catalyst or after the finished catalyst has been prepared. A preferred manner of incorporation is to ion-exchange a crystalline aluminosilicate and then compositing the ion-exchanged product with a porous matrix. Also useful is the ion-exchanging or impregnation of siliceous solids or clays. Suitable metal compounds include the metal halides, preferably chlorides, nitrates, ammine halides, oxides, sulfates, phosphates and other water-soluble inorganic salts; and also the metal carboxylates of from 1 to 5 carbon atoms, alcoholates. Specific examples include palladium chloride, chloroplatinic acid, ruthenium penta-ammine chloride, osmium chloride perrhenic acid, dioxobis (ethylenediamine) rhenium (V) chloride, rhodium chloride and the like. Alternatively, an oil-soluble or oil-dispersable compound of the metal may be added in suitable amount of a hydrocarbon feedstock, such as a gas oil charge stock, for incorporation in the catalyst as the charge is cracked. Such compounds include metal diketonates, carbonyls, metallocenes, olefin complexes of 2 to 20 carbons, acetylene complexes, alkyl or aryl phosphine complexes and carboxylates of 1 to 20 carbons.

Specific examples of these are platinum acetylacetonate, tris (acetylacetonato) rhodium (III), triiodoiridium (III) tricarbonyl, -cyclopentadienylrhenium (I) tricarbonyl, ruthenocene, -cyclopentadienylosmium (I) dicarbonyl dimer, dichloro (ethylene) palladium (II) dimer (-cyclopentadienyl) (ethylene) rhodium (I), diphenylacetylenebis (triphenyl- phosphino) platinum (0), bromomethylbis (triethylphosphino) palladium (II), tetrakis (triphenylphosphino)palladium (0), chlorocarbonylbis(triphenylphosphino) iridium (I), palladium acetate, and palladium naphthenate.

The hydrogenation/dehydrogenation component will also, to a certain extent, serve as a hydrogenation/dehydrogenation promoter but that is not the primary purpose of adding this component.

There will be a small amount of hydrotreating, i.e., removal of any sulfur and nitrogen compounds present, due to the presence of the e.g., platinum group component and this is a beneficial, though unintended result.

The hydrogenation/dehydrogenation component is believed to promote hydroisomerization of long chain normal or slightly branched paraffins to more highly branched paraffins. This hydroisomerization converts the waxy long chain paraffins into materials which are compatible with the fuel oil product, permitting increased yields of fuel oil when using the process of the present invention. It is much more beneficial, from a liquid yield standpoint, to hydroisomerize long chain paraffins to other liquid products than it is to simply hydrocrack these materials.

The amount of the hydrogenation/dehydrogenation component added to the catalytic dewaxing catalyst is not narrowly critical and may range from about 0.01 to 30 wt %, calculated as the elemental metal based upon the weight of the entire catalyst.

Operation with 0.05 to 5 wt %, calculated as the elemental metal of a Pt group component gives good results, with the preferred amount of Pt group metal component being equal to 0.1 to 2.0 wt %.

DISTILLATE DEWAXING TO IMPROVE POUR POINT

Catalytic dewaxing of oils to reduce pour point is another application of catalytic dewaxing. For pour point reduction, the feed will usually not be given the solvent refining given lube oil stocks.

The catalytic dewaxing conditions used for pour point reduction of fuel oils are usually somewhat more severe than conditions used for lube oil dewaxing, usually 260 to 430°C, and a LHSV of 0.1 to 10.

Catalytic dewaxing of fuels may be conducted using the same equipment used for dewaxing lube oils, e.g., passing the feed over a fixed, fluidized or moving bed of catalyst comprising ZSM-11, which may be used neat, although it is preferably incorporated in a binder such as alumina, or silica/alumina.

Suitable fuels or distillates include waxy hydrocarbon oils boiling within the range of 175 to 550°C. Gas oils, kerosenes, vacuum gas oils, whole crudes and oils derived from tar sands, shale and coal are contemplated for use herein.

EXAMPLES

Example 1 (Prior Art) Lube Oil Dewaxing - ZSM-5

This is Example 3 of U.S. 4,181,598 and illustrates the preparation of a heavy automotive neutral oil by solvent extraction, catalytic dewaxing over an unsteamed ZSM-5 catalyst, and hydrotreating.

A commercially-prepared, nominal 450 SUS at 38°C (100°F) distillate from Arabian Light crude was furfural extracted at 99°C (210°F) and 160% volume furfural. The furfural raffinate which had a 41°C (+105°F) pour point, was catalytically dewaxed/hydrotreated in a two reactor system with effluent from reactor #1 passing directly to reactor #2. The ZSM-5 had a $SiO_2:Al_2O_3$ ratio of 70:1. The extrudate had an alpha activity of 200. Reactor #1 contained NiZSM-5 (1 wt % Ni by exchange) catalyst for dewaxing, reactor #2 contained a commercial hydrotreating catalyst (2.8 wt %

CoO/9.4 wt % MoO_3/Al_2O_3). Both reactors were run at 1.0 LHSV, 2,900 kPa (400 psig) 450 volumes H_2 at standard conditions, volume of liquid oil at standard conditions (2500 SCF H_2/bbl); the initial temperature in reactor #1 was 288°C (550°F) and the hydrotreating reactor was at 246°C (475°F).

Properties of the dewaxed/hydrotreated oil were:

Pour Point, °F/°C	+20/-7
Viscosity Index (VI)	92
Bromine No.	0.9
343°C (650°F+) LV%	81.9

Bromine number is an indication of unsaturation and must be low to obtain good stability. The dewaxed/hydrotreated oil passed the standard, 240 hour Caterpillar 1-H engine test, indicating its acceptable quality for premium automotive use.

Example 2 (Prior Art) Lube Oil Dewaxing - ZSM-5

This illustrates the dewaxing stage in a commercial process with conventional catalyst, a steamed 0.9% Ni - 65% ZSM-5/35% Al_2O_3 (Ni by exchange). The ZSM-5 had a SiO_2:Al_2O_3 ratio of about 70:1.

Commercially-prepared, extruded catalyst was laboratory steamed 6 hours at 482°C (900°F). The steamed catalyst was used to hydrodewax a commercial, solvent-extracted heavy neutral lube stock having a pour point of 41°C (+105°F) in a 1-liter, batch shaker-bomb reactor at 3,500 kPa (500 psig) H_2, 130 minutes, and 5 oil-to-catalyst by weight; runs were at 274, 288, and 316°C (525, 550, and 600°F) with fresh catalyst for each. The product was topped at 343°C (650°F). The bottoms had the following properties:

	650°F+ Bottoms		
Temperature, °F/°C	525/274	550/288	600/316
Pour Point, °F/°C	+50/10	+20/-7	-35/-37
Viscosity Index° (VI)	99	93	81
Bromine No.	1.5	1.4	2.3

Example 3 (Prior Art) Lube Oil Dewaxing - ZSM-5

This illustrates the use of unsteamed catalyst in the dewaxing stage.

The same commercial catalyst that was steamed in Example 2 was used without steaming for dewaxing, as in Example 2. The results were as follows:

	Bottoms	
Temperature, °F/°C	525/274	550/288
Pour Point, °F/°C	+40/4	0/-18
Viscosity Index (VI)	97	89
Bromine No.	1.1	1.8

These results show that unsteamed catalyst is more active than steamed catalyst for dewaxing to the target -70°C (+20°F) pour point. At 274°C (525°F) the pour point achieved using unsteamed ZSM-5 is 6°C (10°F) lower than can be achieved with steamed ZSM-5.

Example 4 (Invention) Lube Oil Dewaxing - ZSM-11

This illustrates the use of unsteamed ZSM-11 catalyst in the dewaxing stage.

A catalyst was prepared by extruding a mix of 65 wt % ZSM-11 (as crystallized) and 35 wt % Al_2O_3, precalcining at 538°C (1000°F), exchanging to low sodium with NH_4NO_3, exchanging with $Ni(NO_3)_2$ and calcining at 538°C (1000°F). The Ni level was 0.6 wt %. The ZSM-11 used in this and subsequent experiments had a SiO_2:Al_2O_3 ratio of 78:1. The extrudate had an alpha activity of 113.

The catalyst was used for dewaxing (as in Example 2) with the following results:

		Bottoms	
Temperature, °F/°C	500/260	525/274	550/288
Pour Point, °F/°C	+70/21	+25/-4	-35/-37
Viscosity Index (VI)	100	93	80

The results show the unsteamed ZSM-11 catalyst is much more active than the steamed or unsteamed ZSM-5 catalysts of Examples 2 and 3. Regardless of reactor temperature, a lower pour point is achieved with the unsteamed ZSM-11 catalyst.

Example 5 (Invention) Lube Oil Dewaxing - ZSM-11

A portion of the ZSM-11 catalyst of Example 4 was laboratory steamed 6 hours at 402°C (900°F) (as in Example 2). The steamed catalyst was used for dewaxing (as in Example 2) with these results:

	Bottoms
Temperature, °F/°C	550/288
Pour Point, °F/°C	-5/-21
Viscosity Index (VI)	88

The steamed ZSM-11 catalyst is much more active than steamed ZSM-5 catalyst of Example 2.

Example 6 (Invention) Lube Oil Dewaxing - ZSM-11

The catalysts of Examples 2-5 contained about 1.0 wt % Ni or slightly less by exchange. The catalyst of Example 6 contained no exchanged nickel and comprised 65% HZSM-11/35% Al_2O_3. The unsteamed catalyst was used for dewaxing as in Example 2 with these results:

	Bottoms
Temperature, °F/°C	525/274
Pour Point, °F/°C	+10/-12
Viscosity Index (VI)	91

The results indicate little difference in activity between nickel and non-nickel exchanged catalysts.

Example 7 (Invention) Lube Oil Dewaxing - ZSM-11

This illustrates the use of NiMo impregnated, unsteamed 0.6 wt % Ni-(65% ZSM-11/35% Al_2O_3) catalyst in the dewaxing stage.

The catalyst of Example 4 was impregnated to 3.5 wt % MoO_3 and 1.2 wt % NiO and calcined at 538°C (1000°F). The catalyst was used for dewaxing as in Example 2 with these results for the bottoms product:

Reactor Temp, °F/°C	500/260	515/268	530/277
Pour Point, °F/°C	25/-4	0/-18	-40/-40
Viscosity Index (VI)	95	90	84

Example 8 (Invention)

A NiMo catalyst was prepared like the catalyst of Example 7, but on a support that had not been previously exchanged with nickel. The catalyst was used for dewaxing as in Example 2 but only at 263°C (505°F). The bottoms product had these properties:

Reactor Temp, °F/ C	505/263
Pour Point, °F/ C	+15/ -9
Viscosity Index (VI)	94

These results are similar to those of Example 7. Thus, the nickel exchange (Example 7) is not necessary to realize the benefits of impregnating with nickel and molybdenum.

Discussion Of Lube Oil Dewaxing With Base Metal ZSM-1

The catalyst of the invention, Example 7, produces a much lower product pour point than the commercial dewaxing catalyst of Example 2. At the target pour point of -7 C°(+20°F) the activity advantage is 26°C (46°F).

The catalyst of Example 7 yields a bottoms product of higher VI than the commercial-dewaxing catalyst of Example 2. At the target pour point, the advantage is over 1.0 VI.

The ZSM-5 catalyst was steamed. Unsteamed ZSM-5 would enjoy an initial activity advantage over steamed ZSM-5, however, unsteamed ZSM-5 deactivates rapidly in gas oil dewaxing, so commercially steamed ZSM-5 is used in this service.

Yields are not usually calculated or reported for shaker bomb tests. This batch test is valid for screening but it does not correspond exactly to commercial processing, which is usually continuous, with a fixed bed of catalyst. This batch test method does not lend itself to precise yield calculations. We believe that the yields of dewaxed oil from ZSM-11 are as good as, or better than the yields obtainable by dewaxing to the same pour point with ZSM-5.

Example 9 - Lube Oil Dewaxing - (Pt-Ni-ZSM-11)

Another portion of the ZSM-11 catalyst of Example 4 was impregnated with chloroplatinic acid. The Ni-ZSM-11 catalyst was used as a starting material because it happened to be readily available when we ran the test.

We weighed 9.6 grams of H_2PtCl_6 solution, containing 3.15 wt % Pt, and diluted this to 39 ml. This solution was added to 50 grams of the nickel ZSM-11/Al_2O_3 catalyst of Example 4 in a rotary impregnator. CO_2 was added to the rotary impregnator, then the vessel was evacuated, and vacuum broken with more CO_2, and this was repeated several times to ensure a CO_2 atmosphere. Rotary impregnation continued for 60 minutes, followed by drying at 121°C (250°F) and calcining in an air flow for 3 hours at 482°C (900°)F. Temperatures were increased at the rate of 2-3°C (3-5°F) per minute. The Pt-NiZSM-11/Al_2O_3 catalyst had a packed density of 0.542 g/cc. Finished catalyst, weighing 49.95g, was recovered.

This material was tested for lubricant dewaxing, as in Example 2. Although platinum was present on the catalyst, there was no sulfiding pretreatment of the catalyst prior to use. Experimental results were as follows:

	Bottoms
Temperature, °F/°C	550/288
Pour Point, °F/°C	-20/-29
Viscosity Index (VI)	84

These results, with the Pt-Ni-ZSM-11 catalyst, were inconclusive. They may show that when Pt is used, it should be reduced to the elemental metal form prior to use.

The Pt-Ni-ZSM-11 was not steamed prior to use, and should be compared to Example 4, unsteamed Ni-ZSM-11.

Examples 10 (Pt-ZSM-11) and Example 11 (Pt-ZSM-5)

Platinum catalysts were prepared on bases containing ZSM-11 and ZSM-5 by the procedure used in Example 9; these contained no nickel. the Pt-ZSM-11 is identified as Example 10 and the Pt-ZSM-5 as Example 11.

Example 12 (Fixed Bed Testing With Light Neutral Stock)

Examples 2-9 were shaker bomb tests which are useful in screening catalysts. Although more time is involved, fixed bed, pilot plant testing is preferred because it resembles commercial practice more.

The catalysts of Examples 10 and 11 were loaded into fixed-bed units, reduced with hydrogen at 2900 kPa (400 psig), 482°C (900°F) for one hour and tested with light neutral stock at the following conditions:

Pressure	400 psig 2,900 kPa
Space Velocity	1 LHSV
Hydrogen Circulation	(2500 SCF/Bbl)
Volume H_2 at Std.Cond./ Volume liquid feed, Std.Cond.	4500 VIV

The results are reported in Table 1.

They are the basis for the following comparison to obtain 343°C (650°F$^+$) lube of -9°C (15°F) pour point after 3 days on stream:

Catalyst of Example No.	10	11	Delta
Temperature Required, °F/°C	540/282	556/291	-16/9
Viscosity Index	95.2	94.4	+0.8
Lube Yield, wt %	81.9	80.5	+1.4

These results show the Pt ZSM-11 catalyst has advantage in activity, VI and yield over Pt ZSM-5 for dewaxing light neutral stock to -9°C (+15°F) pour point.

Table 1

0.5 wt % Pt on (65% Zeolite/35% Al_2O_3) Catalysts
Dewaxing of Light Neutral Stock

Catalyst of Example	Charge Stock	10 (ZSM-11)		11 (ZSM-5)	
Time on Stream, Days		3.5	5.5	3.0	5.0
Temperature, °F/°C	--	540/282	540/282	565/296	550/288
Yields, wt %					
C_1-C_3		2.6	2.5	4.6	4.0
C_4	2.8	2.7	5.4	5.0	
C_5	2.4	2.6	1.5	3.1	
C_6 343°C(650°F)		10.3	9.2	8.8	7.7
343°C (650°F+) Lube	100	81.9	83.0	80.7	80.3
Lube Properties					
Pour Point, °F/°C		15/9	35/2	5/-15	30/-1
Viscosity Index		95.2	98.7	91.5	98.1
ASTM Color	0.5	0.5	0.5	0.5	
Sulfur, wt % 0.76	0.84	0.83	0.91	0.83	
Hydrogen, wt %	13.70	13.79	13.80	13.56	13.76
Basic Nitrogen, ppm	45	43	40	42	40
Viscosity					
KV @ 100°F, cs		46.93	45.03	50.42	45.72
KV @ 210°F, cs		6.465	6.375	6.673	6.423
KV @ 40°C, cs		42.32	40.67	45.35	41.27
KV @ 100°C, cs	5.341	6.31	6.223	6.505	6.265
SUS @ 100°F(38°C)		218	210	234	213
SUS @ 210°F(99°C)		47.4	47.1	48.1	47.2

Example 13 (Test with Bright Stock)

The catalysts of Examples 10 and 11 were also tested in the fixed bed unit with bright stock at the following conditions:

Pressure	400 psig 2,900 kPa
Space Velocity	0.75 LHSV
Hydrogen Circulation	2500 SCF/Bbl 450 VIV

The results are reported in Table 2.

Table 2

0.5 wt % Pt on (65% Zeolite/35% Al_2O_3) Catalysts
Dewaxing of Light Neutral Stock

Catalyst of Example	Charge Stock	10 (ZSM-11)		11 (ZSM-5)
Time on Stream, Days		7.5	10.5	3
Temperature, °F/°C	--	555/291	585/307	600/316
Yields, wt %				
C_1-C_3		2.9	3.9	9.4
C_4		3.8	2.1	2.8
C_5	2.3	2.7	0.3	
C_6 343°C(650°F)		4.1	3.8	1.9
343°C(650°F+) Lube	100	86.9	87.5	84.8
Lube Properties				
Pour Point, °F/°C	120/49	0/-18	-5/-21	-5/-21
Viscosity Index		93.2	92.3	91.5
ASTM Color		3	3	8
Sulfur, wt %	1.13	1.24	1.23	1.26
Hydrogen, wt %		13.39	13.41	13.17
Basic Nitrogen, ppm	130	118	122	112
Viscosity				
KV @ 100°F, cs		583.3	597.4	563.6
KV @ 210°F, cs		32.78	33.0	31.6
KV @ 40°C, cs		502.5	514.2	485.4
KV @ 100°C, cs	29.06	31.64	31.85	30.5
SUS @ 100°F(38°C)		2702	2767	2611
SUS @ 210°F(99°C)		155	156	149.7

It is evident from these results that the catalyst of Example 10 (Pt ZSM-11) is some 22°C (40°F+) more active than that of Example 11 (Pt ZSM-5). At -21°C (-5°F) pour point, it also yields an incremental 2.7 wt % lube stock, which has higher VI by 0.8 numbers.

Example 14 (Prior Art) Fuel Oil Dewaxing - ZSM-5

This illustrates the dewaxing of distillate using a conventional catalyst, a steamed 0.9% Ni - 65% ZSM-5/35% Al_2O_3 (Ni by exchange). The ZSM-5 had a SiO_2:Al_2O_3 ratio of about 70.

Commercially-prepared, extruded catalyst was laboratory steamed 6 hours at 482°C (900°F). The steamed catalyst was used to hydrodewax feed having the properties shown in Table 3.

Table 3

	Gas Oil A	Gas Oil B	Gas Oil C
Density g/cc	0.845	0.905	0.885
Gravity, °API	35.9	24.8	28.0
Pour Point, °F/°C	75/24	65/18	85/29
Cloud Point, °F/°C	100/38	88/31	
KV @ 40°C, cs	7.07	21.64	23.77
KV @ 100°C, cs	2.186	4.169	4.423
Sulfur, wt %	0.09	2.25	0.84
Nitrogen, ppm	180	460	560
Hydrogen, wt %	13.65	12.60	13.18
Bromine No.	0.8	4.3	2.1
Carbon Residue by MCRT, %	0.02	0.01	0.01

Vacuum Distillation - D1160

	°F	°C	°F	°C	°F	°C
IBP	482	250	660	349	597	314
5 Vol % Distillated	531	277	703	373	693	367
10	551	288	714	379	726	386
20	585	307	724	384	755	402
30	615	324	736	391	771	411
40	641	338	749	398	782	417
50	668	353	763	406	794	423
60	693	367	776	413	802	428
70	721	383	789	421	811	433
80	744	396	803	428	823	439
90	791	422	824	440	836	447
95	831	444	837	447	847	453
End Point	875	468	837	447	870	466

The catalyst was disposed as a fixed bed of catalyst in a reactor.

Reaction conditions and product properties are reported in Table 4, after Example 15.

Example 15 (Invention) Fuel Oil Dewaxing - ZSM-11

The catalyst used in this study was prepared by flushing unsteamed HZSM-11, 65 wt % ZSM-11 (with a silica to alumina ratio, on a molar basis, of about 70) and 35 wt % alumina in particular size of approximately 0.60 to 1.2 mm (14-25 mesh), with CO_2 for a few minutes, followed by chloroplatinic acid-impregnation to 0.5% platinum by weight. The platinum ZSM-11 catalyst was loaded into the same fixed bed reactor used in Ex. 14 and reduced in situ at 2,900 kPa (400 psig) of hydrogen and 482°C (900°F) for one hour. Light neutral stock was then pumped into the reactor along with hydrogen after the reactor temperature was lowered to the desired setting. After five days on stream with light neutral stock, the feed was switched to bright stock. These runs were made at 282-307°C (540-585°F), 2,900 kPa (400 psig) of H_2, 450 V/V H_2 (2500 SCF/bbl), and 0.75-1.0 LHSV. After five days, the feed was changed to Gas Oil A.

The test conditions and properties of dewaxed distillate products processed with the Pt/ZSM-11 catalyst (invention) are compared to Ni-ZSM-5 (prior art), in Table 4.

Table 4

Property Comparison of Dewaxed Distillate

Catalyst	Steamed Ni-ZSM-5 (Ex. 14)	Unsteamed Pt-ZSM-11 (Ex. 15)	
Reactor Temp., °F/ C	700/371	700/371	744/396
Pressure, psig/kPa	400/2,900	400/2,900	400/2,900
LHSV	1	1	1
H_2 Circ.,(SCF/bbl)/VIV	2000/14,000	2000/14,000	2000/14,000
Days on Stream	15	13	14
Pour Point, °F/°C	20/-7	LT -65/-54	LT -65/-54
Product Selectivity, wt %			
C_1-C_2	0.2	1.1	1.1
C_3	5.3	12.7	11.6
C_4	9.3	7.1	6.4
C_5 166°C (330°F)	29.2	20.2	22.3
166°C (330°F$^+$)	56.0	58.9	58.6

At 371°C (700°F) reactor temperature, the product from ZSM-11 has a pour point lower than -54°C (-65°F) while that from Ni-ZSM-5 has a -7°C (20°F) pour, indicating that Pt-ZSM-11 is more active than Ni-ZSM-5 for distillate dewaxing.

Both catalysts gave the almost same distillate yields as shown in the table. In distillate dewaxing, removal of waxy components to reduce pour point usually results in removal of product, and lower yields. Consequently, the distillate yield with Pt-ZSM-11 would be much higher than 60 wt % if the reactor temperature was dropped to give a pour point of -7°C (20°F). Pt-ZSM-11 is far more selective than ZSM-5.

Example 3 (Invention) Fuel Oil Dewaxing - ZSM-11

The catalyst of Example 15 was used for dewaxing Gas Oil B. Results are reported in Table 5. The reactor pressure, LHSV and hydrogen circulation were identical to those reported in Table 4.

Table 5

Property Comparison of Dewaxed Distillate

	Steamed Ni-ZSM-5	Unsteamed Pt-ZSM-11
Reactor Temp. °F/°C	700/371	625/329
Pour Point, °F/°C	5/-15	5/-15
Product Selectivity, wt %		
C_4^-	4.0	4.0
C_5 166°C (330°F)	9.0	8.7
166°C+ (330°F+)	87.0	87.3

For Gas Oil B, the Pt/ZSM-11 catalyst is 42°C (75°F) more active than steamed Ni-ZSM-5 while the selectivities are comparable.

Example 17 (Invention) Fuel Oil Dewaxing - ZSM-11

The catalyst of Example 15 was used for dewaxing Gas Oil C. Reactor pressure, LHSV, H_2 circulation remained the same as in Table 4. The results are shown in Table 6:

Table 6

Property Comparison of Dewaxed Distillate

	Steamed Ni-ZSM-5	Unsteamed Pt-ZSM-11
Reactor Temp. °F/°C	710/377	655/346
Pour Point, °F/°C	0/-18	0/-18
Product Selectivity, wt %		
C_4^-	6.6	5.7
C_5-166 C (330°F)	11.4	9.8
166 C^+ (330°F^+)	82.0	84.5

For Gas Oil C, the Pt/ZSM-11 catalyst offers a catalyst activity advantage of 31°C (55°F) over steamed Ni-ZSM-5. In addition, Pt/ZSM-11 improves the 166°C^+ (330°F^+ selectivity by 2.5%.

If we were building a catalytic dewaxing unit to produce lube oil base stock today, we would use a catalyst comprising 65 wt % ZSM-11 and 35 wt % alumina, with about 1 wt % nickel and about 3 wt % molybdenum added by exchange or impregnation.

Some work has been done adding platinum to the ZSM-11 catalyst. The benefits of adding Pt may justify the added cost of this component.

For lube oil dewaxing, we prefer that the catalyst would be disposed as a fixed bed in a reactor operated at 260-360°C under hydrogen pressure of 1,500-3,500 kPa with hydrogen circulation of 100-500 VIV, at 0.5-2.0 LHSV. The effluent of the catalytic dewaxing would be cascaded into a hydrotreater containing, as catalyst, a hydrogenation component on a non-acidic support such as cobalt molybdate or nickel molybdate on alumina.

We would give the catalyst a steaming treatment prior to use if necessary. For some feeds, steaming reduces the catalyst activity at the start, but the catalyst lasts longer.

For fuel oil dewaxing we would use the same basic catalyst, but containing as a hydrogenation component about 0.5 wt % Pt, added by impregnation.

The ZSM-11 used would have a $SiO_2:Al_2O_3$ ratio of about 70 and would not be steamed. The Pt would be calcined to fix it on the support, then reduced with hydrogen to the elemental state.

The catalyst would be disposed as a fixed bed in a reactor operated at 260-450°C under hydrogen pressure of 1,500-3,500 kPa and with hydrogen circulation of 100-500 VIV, at 0.5-2.0 LHSV.

In general the use of ZSM-11 zeolite as a dewaxing catalyst will result in at least twice as much hydroisomerization of waxy components as can be achieved using conventional shape selective zeolites. It is possible to achieve five to ten times as much hydroisomerization with ZSM-11 as compared to, e.g., dewaxing with ZSM-5.

Preferably a majority of the waxy components, such as the normal and singly branched paraffins are converted to less waxy components. We prefer to obtain as much isomerization as possible, and for every 100 moles of waxy components converted, we try to produce at least 5 to 10 more moles of hydroisomerized product, which is a valuable liquid product.

WHAT IS CLAIMED IS

1. In a process for catalytically dewaxing a wax containing hydrocarbon feedstock to produce a dewaxed oil by contacting said stock at catalytic dewaxing conditions in a reaction zone with a shape selective wax cracking catalyst with a Constraint Index of 1-12 to crack wax to lighter boiling range components, the improvement characterized by using a crystalline catalyst with the crystal structure of ZSM-11 to remove wax by both cracking and isomerization.

2. The process of claim 1 wherein catalytic dewaxing conditions include a hydrogen pressure of atmospheric to 14,000 kPa, a ratio of hydrogen to hydrocarbon of 90 to 900 volumes of H_2 per volume of feedstock, a liquid hourly space velocity of 0.5 to 5.

3. The process of claim 1 or 2 wherein the catalyst comprises ZSM-11 and a refractory inorganic oxide binder.

4. The process of claim 3 wherein the binder is alumina, silica or silica alumina.

5. The process of any of claims 1 to 4 wherein the catalyst comprises 10 to 95 wt % ZSM-11 and 90 to 5 wt % alumina.

6. The process of any of claims 1 to 5 wherein the ZSM-11 has a silica:alumina ratio greater than 12:1.

7. The process of claim 1 wherein the ZSM-11 has a silica:alumina ratio of about 15:1 to 200:1.

8. The process of any of claims 1 to 7 wherein the catalyst contains a hydrogenation/dehydrogenation component.

9. The process of claim 8 wherein the catalyst contains 0.01 to 30 wt %, on an elemental basis, of a hydrogenation component selected from Groups II, III, IV, V, VII and VIII and mixtures thereof.

10. The process of claim 8 wherein the catalyst contains 0.01 to 1 wt %, on an elemental metal basis, platinum group metal.

11. The process of any of claims 1 to 10 wherein the feedstock is a lubricating oil base stock.

12. The process of any of claims 1 to 10 wherein the feedstock is a fuel oil.

13. The process of any of claims 1 to 12 wherein a majority of the wax in the feedstock is converted.

14. The process of any of claims 1 to 13 wherein for every 100 moles of wax converted, at least 5 moles are converted by hydroisomerization.

15. The process of claim 14 wherein at least 10 moles are converted by hydroisomerization.