United States Patent Office 3,539,498 Patented Nov. 10, 1970

3,539,498

CATALYTIC DEWAXING WITH THE USE OF A CRYSTALLINE ALUMINO ZEOLITE OF THE MORDENITE TYPE IN THE PRESENCE OF HYDROGEN

Herbert C. Morris and Paul P. Bozeman, Jr., Groves, Howard T. Horton, Jr., Beaumont, and Billy H. Cummins, Nederland, Tex., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed June 20, 1966, Ser. No. 558,569
Int. Cl. C10g 37/02
U.S. Cl. 208—111 6 Claims

ABSTRACT OF THE DISCLOSURE

A process for selective conversion of waxy hydrocarbons, i.e. higher melting point paraffinic hydrocarbons, in a lubricating oil stock to lower boiling hydrocarbons which may be removed from the non-waxy hydrocarbons by distillation to give a product of improved pour point. In this process, wax-containing feedstock is contacted with a mordenite-type crystalline alumino-silicate zeolite in hydrogen form having a silica to alumina ratio of at least 6, preferably containing 0.1 to 5 weight percent added Group VIII metal, at a temperature in the range of 450 to 950° F. and a pressure in the range of 100 to 1500 p.s.i.g. in the presence of hydrogen in an amount within the range of 300 to 10,000 standard cubic feet per barrel of oil at a space velocity in the range of 0.2 to 5 volumes of oil per volume of catalyst per hour. The process is useful for dewaxing lubricating oil stocks to a product having improved haze temperature, improved pour point, or both.

This invention relates to a process for selective conversion of wax-like hydrocarbons to non-waxy products. In one of its more specific aspects, the present invention relates to a process for the treatment of a petroleum fraction to reduce its pour point. The process of this invention is particularly useful for dewaxing lubricating oil base stocks from petroleum distillate fractions and for the selective elimination of wax-like materials from fuel oil fractions of petroleum distillates.

In accordance with the present invention, a petroleum fraction containing wax-like hydrocarbons is contacted with a mordenite type zeolite in hydrogen form at a temperature effective for conversion of at least part of the higher melting point, wax-like hydrocarbons to non-waxy products. Usually the wax-like hydrocarbons are in admixture with non-waxy paraffins, and usually mixed also with hydrocarbons of other types, for example, naphthenes, aromatics, olefins, and asphaltic materials. In a preferred method of operation, hydrocarbon feed stock containing wax-like hydrocarbons is passed in the presence of hydrogen into contact with a zeolite of the mordenite type under relatively mild hydroconversion reaction conditions. A catalytic material, suitably a Group VIII metal, preferably a platinum group metal, is preferably associated with the zeolite.

It has been proposed heretofore to contact petroleum fractions with molecular sieves, i.e., zeolites capable of preferentially adsorbing one hydrocarbon type, for example, straight chain normal paraffins or aromatic hydrocarbons, from a mixture containing several hydrocarbon types. In particular, molecular sieves having mean pore diameters of about 5 A. have been used for selectively removing straight chain paraffins from hydrocarbon mixtures. It has also been proposed to contact a petroleum distillate fraction in admixture with hydrogen with a molecular sieve having a pore diameter of about 5 A.

under suitable operating conditions of temperature, pressure, and space velocity to cause cracking of the normal paraffin hydrocarbons to lower boiling straight chain hydrocarbons which can be removed from the feed stock by distillation.

We have found, that while some reduction in pour point of a hydrocarbon mixture, such as a lubricating oil fraction, can be effected by selective cracking in the presence of 5 A. molecular sieves in accordance with teachings of the prior art, the effective catalyst life is relatively short. Generally the catalyst loses its activity or fails to produce the desired removal of high molecular weight paraffins after only a few hours of operation.

In contrast, we have developed a process for continuously selectively converting high melting point hydrocarbons, particularly paraffin hydrocarbons, to products having lower melting points. Our process is capable of effecting substantial reduction in pour point of hydrocarbon fractions. The catalyst remains active for long periods of time, for example, up to several months without the necessity for regeneration. Our process is capable of effecting complete wax removal from a hydrocarbon containing wax-like hydrocarbons.

We have found that decationized mordenite type zeolite structures, which have pore sizes sufficient to admit not only the straight chain hydrocarbons but also cyclic hydrocarbons as well, have a greater capacity for selective conversion of paraffin hydrocarbons to lower molecular weight products than do the 5 A. molecular sieves which selectively admit only the paraffin hydrocarbons into their unit cell structures.

We have discovered that when mixed hydrocarbon distillate fractions are contacted with the decationized form of mordenite for example, calcined synthetic mordenite product sold commercially under the trade name Zeolon H by the Norton Company, such material shows exceptionally high activity and selectivity for the selective conversion of higher melting point hydrocarbons in the mixture to lower melting point hydrocarbons and other non-waxy products. The activity of the zeolite catalyst is enhanced and its useful life extended by the addition of Group VIII metals to the zeolite either by impregnation or by ion exchange techniques. For example, a —60° F. pour point product can be produced from a 50° F. pour point feedstock by contacting the feedstock in the presence of hydrogen at 600° F. (850 p.s.i.g. and 8000 s.c.f./bbl. and 0.5 LHSV) with a decationized mordenite bearing a catalytic addition of 0.5% palladium. A 0° F. pour point product can be produced from said feedstock at 550° F. or from a 95° F. pour point, furfural refined paraffin base distillate at 680° F. using 8000 s.c.f. of hydrogen per barrel of charge stock at 0.5 LHSV and 850 p.s.i.g. Details of these and other examples of the effectiveness of the present process are set forth hereinafter. The principal products of the selective reaction of waxy hydrocarbons by the process of our invention are gaseous hydrocarbons.

Mordenite structures are characterized by parallel sorption channels of uniform cross-section. The sorption channels are parallel to the C-axis of the crystal and are elliptical in cross-section. The sorption channels dimensions of sodium mordenite, based on crystallographic studies, have been reported as having a minor diameter of 5.8–5.9 A. and a major diameter of 7.0–7.1 A. and a free diameter of 6.6 A.; the hydrogen form of mordenite is believed to have somewhat larger pore openings with a minor diameter of not less than about 5.8 A. and a major diameter less than 8 A.

The effective working pore diameter of hydrogen mordenite (Zeolon H) prepared by acid treating synthetic sodium mordenite appears to be in the range of 8 A. to 10 A. as indicated by adsorption of aromatic hydrocarbons.

Mordenite does not selectively absorb paraffin hydrocarbons and will not function as a molecular sieve for the separation of paraffins from aromatics by adsorption. On the other hand, zeolite structures of the type represented by faujasite, a natural zeolite, and Type A, Type X, Type Y, and Type L synthetic zeolites, hereinafter for the sake of simplicity referred to as molecular sieves, are capable of selectively adsorbing particular hydrocarbon types from one another. For example, when a mixture of n-heptane and benzene, is contacted with a 5 A. molecular sieve at room temperature, n-heptane is selectively adsorbed. The 4–5 A. sieves quantitatively remove the straight chain paraffns from cyclic or aromatic components of the mixture. Some of the molecular sieves will also selectively separate normal from branched chain hydrocarbons.

With 5 A. molecular sieves, some reduction in pour point of waxy feedstocks may be obtained by percolating the feedstock over the molecular sieve. Reduction in pour point is obtained for a relatively short period of time during which the pores of the zeolite apparently become saturated with the waxy components. In contrast, no reduction in pour point is exhibited when the waxy stocks are percolated over hydrogen mordenite (Zeolon H) at temperatures below the temperatures required to crack the wax, e.g. below 200° F. It is necessary to raise the temperature to a temperature effective for reaction, i.e. above about 450° F., in order to obtain any significant dewaxing or pour point reduction of the feedstock. In addition, we have found that the sodium form of mordenite is not effective for wax conversion regardless of whether or not the temperature is within the cracking region and regardless of catalytic additions.

It appears that the effectiveness of the mordenite type zeolite catalyst structures for selective cracking of high molecular weight paraffins is not solely dependent upon the size of the pore opening. The synthetic mordenites have pore sizes as determined by crystallographic measurements, somewhere between those of Type A molecular sieves on the one hand, which are capable of admitting no hydrocarbons larger than normal paraffins into the unit cells, and the Types X and Y synthetic zeolites and faujasite, on the other hand, which admit also the larger molecules. Attempts to use modified Types A, X, and Y molecular sieves having pore diameters larger than conventional Type A and smaller than the conventional Types X and Y as substitutes for mordenite in our process have proved unsuccessful.

Mordenite has a chain type zeolite structure in which a number of chains are linked together into a structural pattern with parallel sorption channels similar to a bundle of parallel tubes. In contrast, the Type A and Types X and Y synthetic zeolites and faujasite have three dimensional crystalline cage structures having 4 to 6 windows or pore openings per unit cell through which access may be had to the inner cavity or unit cell of the zeolite. These three dimensional molecular sieves are important catalysts for use in a number of hydrocarbon reactions. We have found, however, that they are relatively ineffective for selective conversion of paraffin waxes or other high melting point hydrocarbons to lower molecular weight products as compared with the synthetic mordenite zeolitic structures.

Regardless of the particular reaction mechanism involved in our process, we have found that the hydrogen form of synthetic mordenite (Zeolon H) having a sodium content of less than 5 weight percent, is exceptionally effective for selectively converting wax-like hydrocarbons to non-waxy hydrocarbons.

In addition to the crystal structure characteristics of mordenite which distinguish it from the three dimensional lattices characteristic of molecular sieve zeolites, mordenites are characterized by relatively high silica contents; the sodium form has a silica to alumina mol ratio of 10 and generally contains more than 80 mol perecnt

silica, less than 10 percent alumina, and less than 10 percent soda (dehydrated basis). In contrast, the faujasites contain 55–72 percent silica, and 14–23 percent of each alumina and soda, while Type A zeolite contains about 50 percent silica and 25 percent each of alumina and soda.

It is characteristic of the catalysts used in the present invention that they are not seriously effected by nitrogen or sulfur compounds contained in the feedstock and therefore may be used for a reduction of wax content of shale oils, high nitrogen crude oils, or high sulfur oils which normally are difficult to process catalytically. Since platinum is usually readily poisoned by sulfur compounds, this result is quite unexpected.

An object of this invention is to provide an improved process for selective conversion of high molecular weight paraffin hydrocarbons to lower molecular weight hydrocarbons.

Another object of the present invention is to provide an improved process for the dewaxing of fuel and lubricating oil base stocks by catalytic treatment with a chain type zeolite.

It is still another object of this invention to provide an improved process for the selective conversion of petroleum wax to normally liquid and/or normally gaseous hydrocarbons of lower molecular weight.

A still further object of this invention is to provide an improved process for reducing the haze temperatures of low temperature refrigerator oils.

A further object of this invention is to provide a process for reducing the pour point of hydrocarbon distillates in the middle distillate range to improve the low temperature flow properties of the hydrocarbon fractions as fuel oils.

It is a still further object of this invention to provide a process for reducing the viscosity of heavy fuel, heavy crude oils, shale oils and the like.

These and other objects of the present invention are effected by bringing a hydrocarbon feedstock containing high molecular weight paraffin components in admixture with other types of hydrocarbons into contact with a decationized synthetic zeolite of the mordenite type in the presence of added hydrogen at hydrocarbon conversion temperature.

Synthetic mordenite is usually produced in the sodium form, i.e., as a sodium alumino silicate. Sodium mordenite is inactive for the selective cracking or hydrocracking of waxy hydrocarbons. The hydrogen form, or decationized form, however, which may be produced by ion exchange of sodium in the mordenite with ammonium ions followed by heating, or calcining, to drive off ammonia, or by acid treatment of sodium mordenite, is an extremely effective catalyst as illustrated in the specific examples which appear hereinafter. Acid treatment may also remove some of the alumina from the mordenite zeolite structure and thereby increase the relative proportions of silica to alumina in the zeolite. The weight ratio of silica to alumina is about 6 in natural or synthetic sodium mordenite. Acid treatment suitably is effected with dilute hydrochloric acid. Mordenite structures are acid stable. In contrast, the structures of Type A, of faujasite, Type X and Type Y zeolites are readily destroyed by acid. Up to 70 percent of the sodium cations in the mordenite can be replaced with hydrogen by acid treatment, e.g., by treatment with dilute aqueous hydrochloric acid. Hydrogen mordenite prepared by treating synthetic sodium mordenite with hydrochloric acid, e.g. warm 3 N to 6 N hydrochloric acid, is a preferred catalyst. It is desirable to calcine the mordenite, with or without metal additions, by heating in air to a temperature above 500° F., preferably to 1000° F.

Decationized mordenite, or calcined hydrogen mordenite (Zeolon H), alone is an effective catalyst for selective conversion of wax-like hydrocarbons to non-waxy products, i.e. an effective dewaxing catalyst to improve the haze temperatures or pour points, or both, of fuel oils and

lubricating oil base stocks. Hydrogen mordenite exhibits extremely long catalyst life in comparison with the three dimensional zeolite structures of the 5 A. type. Hydrogen, though not necessary for the selective catalytic activity of mordenite for the waxy hydrocarbons, is desirable in that hydrogen extends the life of the catalyst. Hydrogen apparently removes unsaturated or polymeric materials from the mordenite and prevents fouling of the pore openings with carbon and polymeric materials. It is also desirable to precondition the catalyst by heating to a temperature in the range of 450 to 1000° F. in hydrogen.

Catalytic additions are also generally desirable, particularly when treating charge stocks containing relatively large percentages of high melting point hydrocarbons, e.g. high melting point paraffins or petroleum waxes. Group VIII metals, particularly nickel, palladium, platinum, and rhodium have been found especially useful catalytic additions to hydrogen mordenite zeolitic base structures. The catalytic metal may be incorporated in or on the zeolite base either by ion exchange or by impregnation techniques already well known in the art of catalyst manufacture. Hydrogen mordenite containing from 0.1 to 5 percent platinum or palladium by weight, preferably 0.5 to 2.5 percent of either platinum or palladium are effective catalysts for use in the process of this invention. Synthetic mordenite in hydrogen form having 2 to 2.5 percent by weight palladium incorporated thereon by impregnation has proven to be a very active and very rugged catalyst. This last mentioned catalyst is highly resistant to high temperatures, permitting regeneration of the catalyst by either oxidation techniques or high temperature hydrogen treatment.

Regeneration of catalysts by oxidation involves controlled burning of contaminants from the surface of the catalyst structure with air, or a mixture of inert gas with air or oxygen. Regeneration may also be effected by treatment of the catalyst with hydrogen at temperatures generally well above the usual conversion reaction temperature. We have found that palladium or mordenite catalyst structures will withstand high temperatures, e.g. temperatures above 1200° F. and possibly as high as 1500° F., without evidence of damage to the catalyst or deleterious effect on the activity of the catalyst for selective dewaxing.

Mordenite base catalysts comprising 1 to 10 weight percent nickel, cobalt, or iron, preferably from 1 to 5 percent by weight of an iron group metal, also are very rugged catalysts in that they are capable of operating for hundreds of hours in a hydrogen atmosphere without appreciable deactivation and are capable of withstanding high regeneration temperature.

The amount of Group VIII catalytic metal added to the mordenite base affects to some extent at least the activity and resistance of catalysts to deactivation. For example, a catalyst comprising 2 percent by weight of palladium on mordenite is more resistant to deactivation than a corresponding catalyst containing 0.5 weight percent palladium. In addition, the 2 percent palladium catalyst has an activity, as indicated by product tests, at temperatures in the wax conversion range comparable to that of the 0.5 percent palladium catalyst at approximately a 50° F. higher conversion temperature. Since operating temperature affects the life of a catalyst, it is generally advantageous to employ more active catalyst at lower initial operating temperatures, i.e. to employ catalysts having the higher catalytic metal contents.

As the catalyst ages, its activity for the desired reaction tends to slowly diminish. The catalyst can be maintained at or periodically brought back to approximately its initial level of activity by increasing the operating temperature as the catalyst ages. In general, we have found that an increase in temperature of about 12° F. effects about 1 percent increase in the amount of wax cracked, i.e. converted to lower boiling products.

The terms "wax," "waxy" and "wax-like," as used herein, have their usual meaning in the art, i.e. those high melting point hydrocarbons which can be removed from hydrocarbon mixtures by solvent dewaxing procedures involving dilution and chilling of the mixture followed by removal of solidified hydrocarbons from the solution. The amounts of wax removed catalytically by conversion to low boiling hydrocarbons which are subsequently separated from the feedstock by distillation, i.e. the extent of wax removal from a feedstock, is expressed herein in the same terms and has the same meaning as though used in connection with conventional dewaxing processes. The process is referred to for convenience as a catalytic dewaxing process. In reporting liquid yields in this description of the process, the catalytically treated hydrocarbon is stripped of lighter materials than the initial boiling point components of the charge stock and the remainder is reported as the liquid yield.

In general, preferred operating conditions for continuous catalytic dewaxing, i.e. selective conversion of high melting point hydrocarbons to lower molecular weight lower boiling hydrocarbons, are: hydrogen feed rates in the range 0–20,000 s.c.f./bbl., preferably 500–10,000 s.c.f./bbl.; space velocities in the range of about 0.1 to 10 liquid volumes per hour per volume of catalyst, preferably, 0.25 to 5.0 LHSV, temperatures in the range of about 450 to 950° F., preferably 500 to 850° F., and pressures within the range of atmospheric to 5000 p.s.i.g., preferably in the range of 200 to 1500 p.s.i.g.

The catalyst may be in the form of granules, e.g. 10–25 mesh Tyler Standard Screen Scale, and preferably is in the form of pellets or extrusions having a diameter of about ⅛ inch. The reaction suitably is carried out over a fixed bed of catalyst with the hydrogen and feedstock passing downwardly through the catalyst bed. Unreacted hydrogen may be separated from the effluent stream from the catalyst bed and recycled to the process.

In addition to the Group VIII metals which are desirable components of the catalyst and which include iron, nickel, cobalt, platinum, palladium, it may be desirable to include metals of Group VI–B of the Periodic Table. For example, molybdenum and tungsten and in particular, combinations of cobalt and molybdenum, nickel and molybdenum, and nickel and tungsten are desirable in the catalyst.

An advantageous plant process for dewaxing lubricating oil charge stocks, particularly those containing relatively large amounts of paraffin waxes, such as a vacuum distillate suitable for the production of SAE 20 lubricating oil, comprises subjecting the feedstock first to a conventional solvent dewaxing operation, e.g. propane dewaxing, designed only to remove a part of the wax and produce a relatively high pour point oil, and then subjecting the partially dewaxed charge stock to catalytic dewaxing in accordance with the process of the present invention. Part of the paraffin wax is recovered for use as a commercial product, the solvent dewaxing system is operated with relatively low ratios of solvent to oil and relatively small amounts of refrigeration, and the final, low pour point product is obtained by selective catalytic conversion of wax from partially dewaxed charge stock.

As a basis for comparison, a typical solvent dewaxing operation required to produce a 10° F. pour point oil from Wax Distillate 20 usually employs a solvent: oil ratio of about 2.5:1 and requires chilling of the mixture to a temperature of about 0° F. In a combination operation, the solvent-oil mixture need be chilled, for example, only to about 40° F. to remove approximately 50% of the wax obtainable by solvent dewaxing at 0° F. and produce an oil having a pour point of about 50° F. The partially dewaxed or 50° F. pour point feedstock is then passed under typical operating conditions of about 550° F. and 500 p.s.i.g. with 8000 s.c.f. of hydrogen per barrel of feedstock over catalyst containing 2.5% palladium on Zeolon H at a space velocity of about 1.0 volume of

liquid per volume of catalyst per hour to produce a finished product having a 10° F. pour point. In an alternate method of operation, part of the lubricating oil charge stock is subjected to solvent dewaxing and part to catalytic dewaxing and the resulting products blended to produce the desired refined dewaxed lubricating oil base. For example, a light fraction may be solvent dewaxed, a heaxy fraction catalytically dewaxed, and the resulting products blended.

For the production of lubricating oils it is desirable to remove the aromatic components from the lubricating oil feedstock, for example, by furfural refining, a well known commercial operation. The lubricating oil feedstock processed by the catalytic dewaxing process of the present invention may be subjected to furfural refining either before or after the catalytic treatment. In order to reduce the throughput on the furfural refining facilities, and to increase yield and viscosity index of the dewaxed oil, it is desirable to furfural refine the lubricating oil base stock after the catalytic dewaxing operation. In the following specific examples, reference to refined distillates means charge stocks which have been previously furfural refined.

Operating temperature and catalyst activity are correlated with space velocity to give reasonably rapid processing of the feedstock at catalyst deactivation rates which insure maximum on-stream time of the catalyst between periods of regeneration. On-stream time between periods of regeneration usually range from two months to two years.

Hydrogen consumption usually depends primarily upon the severity of the operating conditions and the content of high melting point paraffin hydrocarbons contained in the charge stock. For example, in the catalytic treatment of refrigerator oils for haze temperature reduction hydrogen consumption generally is less than 100 standard cubic feet per barrel, whereas dewaxing of conventional motor oil base stocks normally results in consumption of 150 to 600 standard cubic feet per barrel.

We have found that the process of this invention is very effective for the removal of small amounts of wax from distillate stocks to produce very low pour point and low haze temperature oils suitable for refrigerator oils.

The following runs illustrate improvements in haze and floc properties (indicative of wax contents) of Edeleanu treated (ET) and furfural refined (R) vacuum distillate (pale oil) charge stocks having Saybolt Universal viscosities of approximately 80, 300 and 500 seconds at 100° F.

TABLE I

Example No.	1	2	3
Catalyst	2.5% Pd on Zeolon H		
Age, hrs	492	480	372
Feed stock	ET 80	R 300	R 500
Gravity, ° API	27.3	24.4	22.5
Viscosity SUS at 100° F	83	309	522
Viscosity SUS at 210° F	37	48	55
Pour point, ° F	−60	−30	−30
Freon haze, ° F	−45		−10
Freon floc, ° F	−60	−20	−20
Pressure, p.s.i.g.	300	300	300
Temperature, ° F	625	625	625
Space velocity, v./hr./v.	4.5	4.6	4.6
H_2 rate s.c.f./bbl	600	660	580
Product:			
Yield, vol. percent of charge	97	97	98.5
Viscosity, SUS at 100° F	84.8	313	564
Freon haze, ° F	−75	−60	−60
Freon floc, ° F	<−100	−85	−85

Viscosities, as reported herein were determined by ASTM Test Method D445 of determining kinematic viscosities (ASTM Standards on Petroleum Products and Lubricants, published by American Society for Testing and Materials, Philadelphia, Pa.) and converted by ASTM Test Method D446 to equivalent Saybolt Universal seconds. Freon haze, as reported herein, is the temperature at which the first evidence of haziness is discernible in a mixture of one part oil and nine parts dichlorodifluoromethane in an acetone-solid carbon dioxide bath; Freon floc is the temperature at which initial agglomerates or flocs are observed.

Activities of various mordenite catalysts for selective conversion of paraffin wax in paraffin base light lubricating oil distillate feedstocks, typically boiling in the range of 600° F. to 750° F., are illustrated in Table II. The following distillate feedstocks are conventionally solvent dewaxed (propane dewaxing) and hydrofinished (mild hydrogenation) to produce light lubricating oils. All of the catalysts in the following table were hydrogen mordenite (Zeolon H) impregnated with catalytic metals in the amounts indicated in Examples 5 to 8 and without any added catalyst in Example 4.

TABLE II

Example No.	4	5	6	7	8
Catalyst	Zeolon H	+2% Pd	+.5% Pt	+3% Ni	+1.0% Rh
Age, hrs	23	41	56	15	40
Feed stock:					
Viscosity, SUS at 100° F.	65.5	65.5	70	69.7	65.8
Pour point, ° F	50	50	55	55	50
Pressure, p.s.i.g.	850	850	850	850	850
Temperature, ° F	750	500	660	760	625
Space velocity, v./hr./v.	0.43	0.75	0.27	0.47	0.50
H_2 rate, s.c.f./bbl	5,000	8,200	8,000	8,000	9,200
Product:					
Yield, vol. percent of charge	66	86.6	68.0	82.0	88.0
Viscosity, SUS at 100° F.	65.2	72	80	87.5	83.5
Pour point, ° F	0	−30	−10	−35	−40

It will be noted from the above examples that palladium, platinum, and rhodium, and, to a lesser extent nickel, are particularly effective catalyst metals when combined with H-mordenite (Zeolon H).

The effect of increasing amounts of catalytic metal on activity of hydrogen mordenite (Zeolon H) catalyst for wax conversion, as indicated by pour point reduction, is shown in Table III. As in Table II, feedstocks are paraffin base light lubricating oil feedstocks.

TABLE III

Example No.	9	10	11
Catalyst, Zeolon H	+0.5% Pd	+2.0% Pd	+2.5% Pd
Age, hrs.	14	29	8
Feed stock:			
Viscosity, SUS at 100° F.	69.7	65.5	68.8
Pour point, ° F.	55	50	50
Pressure, p.s.i.g.	850	850	850
Temperature, ° F.	550	500	550
Space velocity, v./hr./v.	.51	0.50	0.46
H_2 rate, s.c.f./bbl.	8,000	9,000	8,300
Product:			
Yield, vol. percent of charge.	79.6	78.4	70
Viscosity, SUS at 100° F.	82.8	73.7	91.0
Pour point, ° F.	5	−25	−30

The relative ineffectiveness of the sodium form of mordenite (Zeolon Na) with and without the addition of a Group VIII metal catalyst, and of Type X (Linde 10X) and Type Y (Linde SK110) for selective dewaxing is illustrated in Table IV. Feedstocks are the same as in Table II. Comparison may be made with Example 4.

TABLE IV

Example No.	12	13	14	15
Catalyst	(1)	(2)	(3)	(4)
Age, hrs.	45	45	23	41
Feed stock:				
Viscosity, SUS at 100° F.	69	70	70	70
Pour point, ° F.	50	55	55	55
Pressure, p.s.i.g.	850	850	850	850
Temperature, ° F.	850	822	808	540
Space velocity, v./hr./v.	0.48	0.08	0.08	0.61
H_2 rate, s.c.f./bbl.	9,400	14,700	24,000	5,000
Product:				
Yield, vol. percent of charge	20.0	62.1	32.0	47.5
Voscosity, SUS at 100° F.	105			
Pour point, ° F.	65	50	50	55

[1] Zeolon Na. [2] Zeolon Na+3% Ni. [3] Linde 10X+3% Ni. [4] Linde SK110.

The effectiveness of our process for dewaxing heavy oil charge stocks is illustrated in Table V. Example 16 shows data for waxy distillate which has previously been furfural refined (RWD); Example 17 for a corresponding untreated waxy distillate (WD). Example 18 shows data for a wide boiling range lubricating oil fraction (LDS) from a semi-naphthenic (mixed paraffinic and naphthenic) base crude oil; and Example 19 for a reduced crude (RC).

TABLE V

Example No.	16	17	18	19
Catalyst, Zeolon H	+2.5% Pd	+2% Pd	+2.5% Pd	+2% Pd
Age, hrs.	636*	74	928*	344*
Feed stock	RWD	WD	LDS	RC
Viscosity, SUS at 100° F.	271	405	601	245
Pour point, ° F.	95	100	30	60
Pressure, p.s.i.g.	850	850	850	1,500
Temperature, ° F.	725	775	725	900
Space velocity, v./hr./v.	0.50	0.71	0.48	1.02
H_2 rate, s.c.f./bbl.	9,000	9,000	8,800	7,000
Product:				
Yield vol. percent of charge	79	97	95	72
Viscosity, SUS at 100° F.	370	466	578	54.4
Pour point, ° F.	10	−20	−15	−50

*Previously used on other stocks, without regeneration.

The process of this invention is also effective for reducing the pour point of atmospheric gas oil and similar fuel products. This is particularly important for product improvement of fuel oil fractions in areas where atmospheric temperatures are likely to fall below the pour point of the fuel and in areas where the characteristics of the crude oil are such that the fuel oil fractions have relatively high pour points. Example 20, Table VI, illustrates the effectiveness of the process for reducing the pour of a Port Arthur, Tex., atmospheric gas oil feedstock.

TABLE VI

Example No.	20
Catalyst (Zeolon H+0.5% Pd):	
Age, hrs.	[1] 228
Feed stock (atmos. gas oil):	
Viscosity, SUS at 100° F.	58.8
Pour point, ° F.	50
Pressure, p.s.i.g.	850
Temperature, ° F.	630
Space velocity, v./hr./v.	0.97
H_2 rate s.c.f./bbl.	8500
Product:	
Yield, vol. percent of charge	83.0
Viscosity, SUS at 100° F.	61.2
Pour point, ° F.	−70

[1] Previously used with other charge stocks, without regeneration.

The extraordinary long life of the H-mordenite, palladium impregnated catalysts for selective catalytic dewaxing is illustrated in Table VII. The catalyst was used on various feedstocks during the life test and was not regenerated. The feedstocks for Examples 21 and 22 correspond with those of Tables II and III, while the feedstocks of Examples 23 and 24 contain considerably more wax and correspond to the feedstock of Example 16 (Examples 16 and 23 are identical).

TABLE VII

Example No.	21	22	23	24
Catalyst	Zeolon H+2.5% palladium			
Age, hrs.	8	1,092	636	1,316
Feed stock:				
Viscosity, SUS at 100° F.	68.8	68.8	271	271
Pour point, ° F.	50	50	95	95
Pressure, p.s.i.g.	850	850	850	850
Temperature, ° F.	550	700	725	750
Space velocity, v./hr./v.	0.46	1.01	0.50	0.49
H_2 rate, s.c.f./bbl.	8,300	8,010	9,000	9,050
Product:				
Yield, vol. percent of charge	70	67.7	79	79.5
Viscosity, SUS at 100° F.	91.0	97.8	370	328
Pour point, ° F.	−30	−30	10	10

The following examples (Table VIII) illustrate the effectiveness of combinations of Group VI–B metals with Group VIII metals as catalytic additions to hydrogen mordenite (Zeolon H) for dewaxing operations. The charge stocks (RWD) are furfural refined wax distillates similar to the charge stocks of Examples 16 and 21–24. The catalyst of Example 25 contains 1.0% Pd, 1.0% Ni and 1.0% W. The catalyst of Example 26 contains 0.4% Pd, 0.4% NiO and 1.2% MoO_3. The catalyst of Example 27 contains 0.5% Pd, 0.4% CoO, and 1.2% MoO_3.

TABLE VIII

Example No.	25	26	27
Catalyst	(1)	(2)	(3)
Age, hrs.	19	26	96
Feed stock	RWD	RWD	RWD
Viscosity, SUS at 100° F.	264	264	264
Pour point, ° F.	100	100	100
Pressure, p.s.i.g.	850	850	850
Temperature, ° F.	750	750	800
Space velocity, v./hr./v.	1.0	0.50	0.51
H_2 rate, s.c.f./bbl.	6,900	8,000	8,600
Product:			
Yield vol. percent of charge	60	62	81
Viscosity, SUS at 100° F.	479	508	244
Pour point, ° F.	−30	−15	−10

[1] Pd, Ni, W.
[2] Pd, NiO, MoO_3.
[3] Pd, CoO, MoO_3.

In the preparation of all catalysts for the foregoing examples, the catalysts were air dried, heated in air at 300° F. for 12–16 hours and 500° F. for 1 hour, after which the temperature is increased in 100° F. per hour increments to 1000° F. and held at 1000° F. for 2 hours.

Prior to contact with hydrocarbon feedstocks the catalysts were preconditioned by heating in a stream of hydrogen at a flow rate of 6000 standard cubic feet of hydrogen per 42 gallon barrel of catalyst per hour at 280° F. for 2 hours; 500° F., 1 hour; 850° F., 1 hour; and 1000° F. for 2 hours. Preconditioning of the catalyst is desirable but not essential to operation of the process.

We claim:

1. A process for selective conversion of wax-like hydrocarbons in a lubricating oil base stock which comprises contacting said base stock at a temperature in the range of 450 to 950° F. and at elevated pressure in the presence of hydrogen with a catalyst consisting essentially of a crystalline alumino-silicate of the mordenite type in hydrogen form having uniform pore openings with a minor pore diameter as determined by crystallography of not less than 5.8 and a major pore diameter less than 8 A. and recovering a product having reduced wax content.

2. A process for dewaxing a wax-containing lubricating oil base stock which comprises contacting said oil

base stock at a temperature in the range of 450 to 950° F. and an elevated pressure in the presence of hydrogen with a catalyst consisting essentially of a hydrogen form crystalline alumino-silicate zeolite of the mordenite type having parallel sorption channels with a silica to alumina weight ratio of at least 6 and recovering a product having reduced wax content.

3. A process according to claim 2 wherein said alumino-silicate zeolite is acid treated mordenite.

4. A process according to claim 3 wherein said mordenite prior to acid treatment is synthetic sodium mordenite.

5. A process as defined in claim 1 wherein said wax-like hydrocarbons are contained in refrigerator oil stocks and said conversion effects a reduction in haze temperature of the stock.

6. A process for dewaxing a wax-containing hydrocarbon lubricating oil base stock which comprises contacting said oil base stock with a catalyst consisting essentially of hydrogen form mordenite-type crystalline alumino-silicate zeolite at a temperature in the range of 450 to 950° F. in the presence of hydrogen in the range of 300 to 10,000 standard cubic feet per barrel of oil at a space velocity in the range of 0.2 to 5 liquid volumes of said oil per volume of catalyst per hour and at a pressure in the range of 100 to 1500 p.s.i.g., and recovering a product having reduced wax content.

References Cited

UNITED STATES PATENTS

3,258,417	6/1966	Hess et al.	
3,259,564	7/1966	Kimberlin	208—111
3,268,436	8/1966	Arey et al.	208—59

DELBERT E. GANTZ, Primary Examiner

A. RIMENS, Assistant Examiner

U.S. Cl. X.R.

208—26