

[54] LUBE OIL HYDROCRACKING WITH ZSM-5
ZEOLITE

[75] Inventor: Bernard A. Orkin, Cherry Hill, N.J.

[73] Assignee: Mobil Oil Corporation, New York,
N.Y.

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[51] Int. Cl. C10g 13/02, C10g 37/02

[58] Field of Search 208/111, 18

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UNITED STATES PATENTS

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3,650,945 3/1972 Bertolacini et al. 208/111

Primary Examiner—Delbert E. Gantz

Assistant Examiner—G. E. Schmitkons

Attorney—Oswald G. Hayes and Andrew L. Gaboriault

[57]

ABSTRACT

A process for preparing lube oils characterized by possessing low pour points is set forth. The process involves subjecting a lube stock to a hydrocracking operation utilizing a catalyst mixture comprising hydrogenation components, a conventional cracking catalyst which can be either crystalline or amorphous and a crystalline aluminosilicate of the ZSM-5 type.

9 Claims, No Drawings

LUBE OIL HYDROCRACKING WITH ZSM-5 ZEOLITE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the production of lube oils of high VI and low pour points by a completely catalytic process so that solvent dewaxing can be eliminated. The above is accomplished by using a hydrocracking catalyst which contains a mixture of at least two acidic components — one acidic component being a conventional cracking catalyst, e.g. silica-alumina, or a large pore zeolite such as X or Y or mixtures thereof and the other acidic component being a crystalline aluminosilicate zeolite of the ZSM-5 type. A hydrogenation/dehydrogenation component is also present either as separate discrete particles or associated with either or both of the acidic components by conventional techniques such as base exchange or impregnation.

2. Description of the prior Art

It is well known in the art to form various lubricating oils commonly referred to as lubes from hydrocarbon fractions derived from petroleum crudes. A heretofore practiced common procedure known in the art is to extract these hydrocarbon fractions with various selective solvents for aromatic compounds so as to obtain a raffinate of a desired high viscosity index, such material being resistant to changes in viscosity with changes in temperature and thus being useful under various operating conditions. Moreover, it is particularly desired that the lube oil have a low pour point so that it can be effectively used at low temperature conditions since formation of wax crystals at low temperatures clogs strainers and inhibits circulation of the lubricant. This has generally been accomplished by solvent dewaxing at low temperature with solvent mixtures such as ketone plus benzene. The heretofore practiced conventional solvent extraction processes plus solvent dewaxing, although accepted commercially, nevertheless, suffer from the disadvantage that the combination is relatively expensive to operate.

It has been shown that high VI lube stocks can be prepared from raw distillates and residual oils by a mild hydrocracking adequate to open aromatic ring structures without excessive conversion to naphtha and light gaseous hydrocarbons. The resultant products often have VI higher than solvent refined oils from the same source, but still require dewaxing for acceptable pour point. Solvent dewaxing is the accepted operation, since it will remove both paraffin wax and microcrystalline wax.

Recently proposals have been made to accomplish dewaxing in a catalytic operation by contact with a shape selective cracking of hydrocracking catalyst. Such materials as zeolite A and erionite will not accept the slightly branched chain compounds of microcrystalline wax. Due to their great size, paraffin wax (straight chains of 20-24 carbon atoms) are admitted slowly, if at all. Mordenite tends to coke up and become inoperative during relatively short time on stream.

In an attempt to overcome the inherent difficulties when employing a crystalline aluminosilicate having a pore size of five Angstrom units for catalytic dewaxing, the prior art resorted to so-called combination processes wherein dewaxing was carried out utilizing both solvent techniques and catalytic conversion. In pro-

cesses of this type, a conventional feed or a portion thereof was subjected to solvent extraction and solvent dewaxing followed by conversion with a crystalline aluminosilicate having a pore size of about 5 Angstrom units. Clearly, a process of this type involves the use of separate reactors which adds to its overall cost of operation and detracts from the overall economy.

In copending application Ser. No. 56,652, filed July 20, 1970, now abandoned, a process is disclosed for the production of lube stocks utilizing a catalyst of the ZSM-5 type. In said copending application, a lube stock is first subjected to mild solvent dewaxing followed by catalytic conversion over a ZSM-5 type catalyst. Although the process disclosed in this application represents a significant advance over the heretofore practiced processes with respect to the quality of wax which is produced and the yields which are obtained, nevertheless, it is still necessary to use both solvent dewaxing and catalytic conversion thereby suffering the disadvantage of the use of multiple reactors.

DESCRIPTION OF THE INVENTION

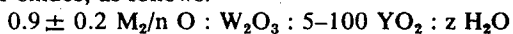
It has now been found that improved results can be obtained in the catalytic hydrocracking of lube stocks to produce lube oils having high viscosity indexes and low pour points by contacting said lube stock in the presence of hydrogen with a catalyst mixture which comprises a hydrogenation component and at least two separate acidic cracking catalysts, one being a conventional cracking catalyst of the large pore type and the other being a crystalline aluminosilicate of the ZSM-5 type. As is more fully set forth in copending application Ser. No. 56,652 the ZSM-5 type zeolites which are used in combination with the large pore cracking catalysts can generally be started to possess a pore size which will allow entry into their internal pore structure of normal aliphatic compounds and slightly branched aliphatic compounds, particularly monomethyl-substituted compounds, yet substantially exclude all compounds containing at least a quaternary carbon atom or compounds having a molecular dimension equal to or substantially greater than a quaternary carbon atom. Thus, ZSM-5 type crystalline aluminosilicates have pore sizes which are larger than the conventional 5 Angstrom type aluminosilicates and yet smaller than the large pore size aluminosilicates such as those of the faujasite family.

The second acidic component employed in the novel catalyst mixtures of this invention is a conventional large pore cracking catalyst such as silica-alumina, silica-titania, silica-zirconia, silica-boria, clay, or a large pore aluminosilicate of the X and Y type of any mixtures thereof. These materials, as is generally known in the art, have pore sizes such that they will allow entry of essentially all the components present in a lube stock.

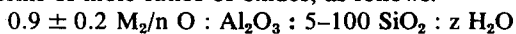
While not wishing to be bound by any theory of operation, nevertheless, it appears that conventional acidic component of the hydrocracking catalyst hydrogenates and opens ring compounds which have low VI whereas the ZSM-5 type catalyst preferentially hydrocracks the constituents which impart high pour point. It would also appear likely that there is a synergistic effect due to a mutual coaction of each acidic component not only with each other but also with the feed material. In any event, irrespective of any theoretical consideration as to why the catalyst system operates, it has been

found that such a catalyst system results in the production of acceptable lubes from raw distillates and residuals by a completely catalytic process without necessitating solvent dewaxing.

The ZSM-5 type zeolite utilized in the novel process of this invention has the characteristic x-ray diffraction pattern set forth in Table I, hereinbelow. ZSM-5 compositions can also be identified, in terms of mole ratios of oxides, as follows:



wherein M is a cation, n is the valence of said cation, W is selected from the group consisting of aluminum and gallium, Y is selected from the group consisting of silicon and germanium, and z is from 0 to 40. In a preferred synthesized form, the zeolite has a formula, in terms of mole ratios of oxides, as follows:



and M is selected from the group consisting of a mixture of alkali metal cations, especially sodium, and tetraalkylammonium cations, the alkyl groups of which preferably contain to carbon atoms.

In a preferred embodiment of ZSM-5, W is aluminum, Y is silicon and the silica/alumina mole ratio is at least 10 and ranges up to about 60.

Members of the family of ZSM-5 zeolites possess a definite distinguishing crystalline structure whose x-ray diffraction pattern shows the following significant lines:

TABLE I

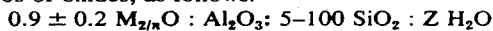
Interplanar Spacing d(A)	Relative Intensity
11.1 \pm 0.2	S
11.0 \pm 0.2	S
7.4 \pm 0.15	W
7.1 \pm 0.15	W
6.3 \pm 0.1	W
6.04 \pm 0.1	W
5.97 \pm 0.1	W
5.56 \pm 0.1	W
5.01 \pm 0.1	W
4.60 \pm 0.08	W
4.25 \pm 0.08	W
3.85 \pm 0.07	VS
3.71 \pm 0.05	S
3.64 \pm 0.05	M
3.04 \pm 0.03	W
2.99 \pm 0.02	W
2.94 \pm 0.02	W

These values as well as all other x-ray data were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak heights, I , and the positions as a function of two times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these the relative intensities, $100 I/I$, where I is the intensity of the strongest line or peak, and $d(obs)$, the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table I the relative intensities are given in terms of the symbols S = strong, M = medium, MS = medium strong, MW = medium weak and VS = very strong. It should be understood that this x-ray diffraction pattern is characteristic of all the species of ZSM-5 compositions. Ion exchange of the sodium ion with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample, as well as if it has been subjected to thermal treatment.

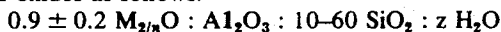
ZSM-5 is disclosed and claimed in copending application Ser. No. 865,472, filed Oct. 10, 1969.

Another operable zeolite falling within the above class is zeolite ZSM-8 which is described and claimed in Ser. No. 865,418, filed October 10, 1969.

ZSM-8 can also be identified, in terms of the mole ratios of oxides, as follows:



wherein M is at least one cation, n is the valence thereof and z is from 0 to 40. In a preferred synthesized form, the zeolite has a formula, in terms of mole ratios of oxides as follows:



and M is selected from the group consisting of a mixture of alkali metal cations, especially sodium, and tetraethylammonium cations.

The ZSM-5 type zeolites used in the instant invention usually have the original cations associated therewith replaced by a wide variety of other cations according to techniques well known in the art. Typical replacing cations would include hydrogen, ammonium and metal cations including mixtures of the same. Of the replacing metallic cations, particular preference is given to cations of ammonium, hydrogen, rare earth, Mg^{++} , Zn^{++} , Mn^{++} , Al^{+++} , Ca^{++} , and mixtures thereof.

Typical ion exchange techniques would be to contact the particular zeolite with a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.

Representative ion exchange techniques are disclosed in a wide variety of patents including U.S. Pat Nos. 3,140,249; 3,140,251; and 3,140,253.

Following contact with the salt solution of the desired replacing cation, the zeolites may be washed with water and dried at a temperature ranging from 150°F to about 600°F and thereafter heated in air or other inert gas at temperatures ranging from about 500°F to 1500°F for periods of time ranging from 0.1 to 48 hours or more.

As had heretofore been pointed out in one embodiment, the novel catalyst composites of this invention comprise a physical mixture of at least two different cracking components, a ZSM-5 type zeolite and a conventional large pore cracking catalyst. In one embodiment, a mixture of catalyst particles is used in which each particle contains only one of the two types of cracking components. Thus, for example, a mixture of particles of ZSM-5 type crystals and particles comprising silica-alumina may be composited in a hydrocracking catalyst. A hydrogenation/dehydrogenation component is present in both cracking components. Alternatively, the catalyst components may be pelleted, cast, molded, spray-dried, or otherwise formed into pieces of desired size and shape such as rods, spheres, pellets, etc.

The large pore size conventional cracking catalyst includes inorganic oxides. Of these, inorganic oxides such as clay, chemically treated clay, silica, silica-alumina, etc. are particularly preferred because of their superior porosity, and stability under a reaction conditions, especially those reaction conditions encountered in the hydrocracking of lube stocks.

The compositing of the ZSM-5 type zeolite with an inorganic oxide cracking catalyst can be achieved by several methods wherein the aluminosilicates are reduced to a particle size less than 40 microns, preferably less than 10 microns, and intimately admixed with an inorganic oxide while the latter is in a hydrous state such as in the form of hydrosol, hydrogel, wet gelati-

nous precipitate, or in a dried state, or a mixture thereof. Thus, finely divided ZSM-5 type aluminosilicates can be mixed directly with a siliceous gel formed by hydrolyzing a basic solution of alkali metal silicate with an acid such as hydrochloric, sulfuric, acetic, etc. The mixing of the three components can be accomplished in any desired manner, such as in ball mill or other types of mills. The aluminosilicates also may be dispersed in a hydrosol obtained by reacting an alkali metal silicate with an acid or alkaline coagulant. The hydrosol is then permitted to set in mass to a hydrogel which is thereafter dried and broken into pieces of desired shape or dried by conventional spray drying techniques or dispersed through a nozzle into a bath of oil or other water-immiscible suspending medium to obtain spheroidally shaped "bead" particles of catalyst such as described in U.S. Pat. No. 2,384,946. The aluminosilicate siliceous gel thus obtained is washed free of soluble salts and thereafter dried and/or calcined as desired.

The catalytically inorganic oxide cracking component may also consist of a plural gel comprising a predominant amount of silica with one or more metals or oxides thereof selected from Groups IB, II, III, IV, V, VI, VII and VIII of the Periodic Table. Particular preference is given to plural gels or silica with metal oxides of Groups IIA, III and IVa of the Periodic Table, especially wherein the metal oxide is rare earth oxide, magnesia, alumina, zirconia, titania, beryllia, thoria, or combinations thereof. The preparation of plural gels is well known and generally involves either separate precipitation or coprecipitation techniques, in which a suitable salt of the metal oxide is added to an alkali metal silicate and an acid or base, as required, is added to precipitate the corresponding oxide. The silica content of the siliceous gel matrix contemplated herein is generally within the range of 55 to 100 weight percent with the metal oxide content ranging from 0 to 45 percent.

The inorganic oxide may also consist of raw clay or a clay mineral which has been treated with an acid medium to render it active. The aluminosilicate can be incorporated into the clay simply by blending the two and fashioning the mixture into desired shapes. Suitable clays include attapulgite, kaolin, sepiolite, polygarskite, kaolinite, halloysite, plastic ball clays, bentonite, montmorillonite, illite, chlorite, etc.

The catalyst product can be heated in steam or in other atmospheres, e.g., air, near the temperature contemplated for conversion but may be heated to operating temperatures initially during use in the conversion process. Generally, the catalyst is dried between 150°F and 600°F and thereafter may be calcined in air, steam, nitrogen, helium, flue gas, hydrogen or other gases not harmful to the catalyst product at temperatures ranging from about 500°F to 1,600°F for periods of time ranging from 1 to 48 hours or more. It is to be understood that the ZSM-5 aluminosilicate can also be calcined prior to incorporation into the inorganic oxide gel cracking catalyst. It is also to be understood that the ZSM-5 need not be ion exchanged prior to incorporation in the inorganic oxide but can be so treated during or after said incorporation.

The catalyst can be subjected to a mild stream treatment at elevated temperatures of 800°F to 1,600°F and preferably at temperatures of about 1,000°F to 1,500°F such is desired. The treatment may be accomplished in an atmosphere of 100 percent steam or in an atmo-

sphere consisting of steam and air or a gas which is not harmful to the aluminosilicates or to the hydrogenation component. The steam treatment can be conducted before, after, or in place of the calcination treatment.

The particle size of each type of cracking component making up the catalyst system is not narrowly critical but should be less than 100 microns and particle sizes within the range of from less than 0.1 to 10 microns are preferred. It is also to be noted that each individual component in the catalyst system need not be of the same particle size.

The particular proportion of one component to the other in the catalyst is also not narrowly critical and can vary over an extremely wide range. However, it has been found that for most purposes the weight ratio of the ZSM-5 type aluminosilicate to the large pore cracking catalyst can range from 1:10 to 2:1 and preferably from 1:5 up to 2:1 and still more preferably 1:4 to 1:1.

The ZSM-5 type crystalline aluminosilicates and the large pore conventional cracking catalyst may be added to a hydrocracking unit as a mixture of crystallites within the same particles of catalyst composite, whether the particles are beads, extrudates, or spray-dried microspheres. Alternately, a mixture of particles may be added to the hydrocracking unit, some particles containing only the ZSM-5 type aluminosilicate crystallites and hydrogenation component and the other particles containing only the large pore cracking catalyst and hydrogenation component. In either case, the ratio of ZSM-5 type aluminosilicates to large pore cracking catalyst should be within the range of 1:10 to 2:1.

The amount of the hydrogenation/dehydrogenation component employed is not narrowly critical and can range from about 0.01 to about 30 weight percent based on the entire catalyst. A variety of hydrogenation components may be combined with either or both of the cracking components in any feasible manner which affords intimate contact of the components, employing well known techniques such as impregnation, coprecipitation, cogellation, mechanical admixture of one component with the other exchange and the like. The hydrogenation component can include metals, oxides, and sulfides of metals of the Periodic Table which fall in Group VIB including chromium, molybdenum, tungsten, and the like; Group IIB including zinc cadmium; and Group VIII including cobalt, nickel, platinum, palladium, rhenium, rhodium and the like and combinations of metals, sulfides and oxides of metals of Group VIB and VIII, such as nickel-tungsten-sulfide, cobalt oxide-molybdenum oxide and the like.

The pre-treatment before use varies depending on the hydrogenation component present. For example, with components such as nickel-tungsten and cobalt molybdenum, the catalyst is sulfur activated. But with metals like platinum or palladium, a hydrogenation step is employed. These techniques are well known in the art and are accomplished in a conventional manner.

Although the conventional large pore cracking component has been described with specific reference to amorphous type cracking components, nevertheless, it is to be understood that it is within the scope of this invention to employ a large pore crystalline aluminosilicate as the cracking component. These large pore crystalline aluminosilicates are, indeed, well known in the art and particular preference is given to faujasites,

both natural and synthetic, such as zeolites X and Y. Thus, one embodiment of this invention then includes a mixture of a ZSM-5 type catalyst together with zeolite X or Y wherein either or both of the aluminosilicates have a hydrogenation component associated therewith. When employing zeolites such as X and Y as the cracking component, it is preferred to base exchange said materials with cations in order to reduce the sodium content thereof. Compositions of this type include techniques with their base exchange are well known in the art and are set forth in U.S. Pat Nos. 3,140,249; 3,140,251; 3,140,252; and 3,140,253.

Still another embodiment of this invention resides in the use of a matrix material in conjunction with the large pore size aluminosilicate and the ZSM-5 type zeolite. Thus, by way of illustration, the process of this invention can be carried out with a ZSM-5 type zeolite which is dispersed in a matrix such as silica-alumina into which is added a large pore crystalline aluminosilicate such as zeolite X which is also dispersed in a matrix such as silica alumina. The hydrogenation component can be present in either or both of the crystalline aluminosilicates and/or either or both of the matrices.

The novel process of this invention is carried out at temperatures of below about 650° to about 1,000°F, a pressure between 100 and 5000 psig, but preferably between 1250-3000 psig. The liquid hourly space velocity is generally between 0.1 and 100 and preferably between 0.5 to 20. The hydrogen to hydrocarbon mole ratio is generally between 1 to 80 and preferably between 4 and 40.

The feed stocks which can be treated according to the novel process of this invention are waxy raw distillates and residual stocks boiling above 650°F and particularly boiling between about 650°F to about 1150°F.

In each of the examples (except 14) below, there is used a catalyst composite of ZSM-5 with a silica-zirconia-clay composite which had been impregnated with nickel and tungsten to prepare a hydrocracking catalyst. That material was prepared by adding 1,350 g. kaolin-clay (moisture free basis) to 34,800 g. water with stirring. This slurry was added 2,037 g. silica (SiO₂) as sodium silicate solution and then 31.8 g. kaolin-clay (moisture free basis). A solution was made up by adding 49 g. sodium zirconium silicate powder (contains 224 g. ZrO₂ and 114 g. SiO₂) to 4,880 g. water and then adding 418 g. H₂SO₄ (as 93.2% wt. H₂SO₄

a pore volume by water titration of 0.48 cc/g, and loss-on-ignition at 1,400°F of 9 percent wt. Its composition is 77.8 percent SiO₂, 16.2 percent Al₂O₃, 5.5 percent ZrO₂ and 0.56 percent Na.

5 An impregnation solution was prepared by dissolving 128.6 g of ammonium metatungstate (72.3 percent wt W) and 184.4 g nickel nitrate Ni(NO₃)₂ · 6H₂O in 200 cc water. This was diluted with water to 330 cc. The solution was then mixed with 880 g of the silica-zirconia-clay powder (91.0 percent solids). After addition of 10 150 cc water to make the material extrudable, it was extruded twice through 1/16 inch hole with roller type California Pellet Mill. The extrudate was dried 16 hours at 250°F and calcined in flowing air for 3 hours at 1,000°F. The product had a packed density of 0.87 g/cc and crush strength averaged 15 pounds for 25 pellets. Analysis showed 4 percent of nickel and 10 percent of tungsten, by weight.

The following examples will illustrate the best mode contemplated for carrying out this invention.

EXAMPLES 1-7

In Examples 1-7, a catalyst mixture comprising 80 cubic centimeters of the above described nickel-tungsten impregnated silica-zirconia-clay and 40 cubic centimeters of ZSM-5 which had been base exchanged with zinc and ammonium cations (ZnH/ZSM-5) were used to hydrocrack a lube stock in order to produce lubes.

30 The lube stock employed as a feed material in each of these examples had the following characteristics:

Gravity, °API	29.3
Pour Point, °F	+80
Sulfur, Wt. %	0.47
Hydrogen, Wt. %	13.04
K.V. at 210°F, cs	4.31
Wax, Wt. %	16.3
Vacuum Assay, °F	
IBP	652
5% 10%	686 700
30% 50%	733 767
70% 90%	804 844
95%	852

45 The procedure employed involved contacting the catalyst mixture with the charge stock at a hydrogen circulation of 8,000 SCF/bbl. Additional operating conditions, as well as the results obtained, are shown in the following table.

Example	Pressure (p.s.i.g.)	Temp., °F	LHSV	650° F.+, wt. percent	Pour point, °F	KV at 100°	KV at 210°	VI
1-----	2,500	760	1.0	49.3	0	20.27	3.96	100
2-----	2,500	760	1.5	58.4	20	24.77	4.46	99
3-----	2,500	740	1.0	66.7	10	24.76	4.40	93
4-----	1,500	740	1.0	71.3	-5	28.55	4.65	80
5-----	1,500	760	1.0	70.4	-10	25.80	4.46	87
6-----	1,500	760	1.5	72.1	+20	27.84	4.59	80
7-----	1,500	760	0.5	43.4	-25	21.65	4.06	92

solution). The above solution was added to slurry of 60 clay in water plus sodium silicate. Then was added 35 percent H₂SO₄ till pH was 4-4.5. The acidified slurry was spray dried and the product was exchanged with (NH₄)₂SO₄ solution, then with NH₄OH solution. The exchanged material was washed with water and flash 65 dried.

The product is a powder with average particle size of about 64 microns. It has a packed density of 0.56 g/cc,

EXAMPLES 8-14

The procedure of Examples 1-7 was repeated with the exception that the ratio of cracking components was changed. In Examples 8-13, the catalyst mixture contained 100 cubic centimeters of the nickel-tungsten-silica-zirconia-clay and 20 cubic centimeters of ZnH/ZSM-5.

In Example 14 no conventional cracking component was present in the catalyst so that the catalyst was

solely ZnH/ZSM-5. This example serves a control so as to show the improved results obtained by the composite catalyst. Note the unacceptably low Viscosity Index (VI).

Additional operating conditions and results are shown below:

Example	Pressure (p.s.i.g.)	Temp., ° F.	LHSV	650° F., wt. percent	Pour point, ° F.	KV at 100°	KV at 210°	VI
8.....	2,500	760	1 {	49	+20	17.14	3.70	112
9.....	2,500	740	1	57	+25	19.36	3.86	100
10.....	1,500	740	1	61	+30	20.96	4.16	111
11.....	1,500	760	1	68	+20	22.17	4.13	93
12.....	1,500	760	0.5	52	0	21.80	4.14	100
13.....	1,500	740	0.5	40	-30	17.01	3.57	99
14.....	1,500	740	0.5	49	-10	22.69	4.20	95
14.....	500	700	16	73	-15	34.18	4.98	66

EXAMPLES 25 - 28

These examples, taken with Examples 29-31 illustrate the effect of varied proportions of the two components of the catalyst when processing stocks of very high pour point (high wax content). It should be borne

EXAMPLES 15 - 19

The procedure of Examples 1-7 was repeated with the exception that a charge stock was used which had the following characteristics:

Gravity, °API	23.2
Pour Point, °F	+90
Sulfur, Wt. %	2.07
Wax, Wt. %	9.0
K.V. 100°F, cs	66.72
K. V. 210°F, cs	7.16
Vacuum Assay, °F	
IBP	721
5%	778
10%	805
30%	834
50%	846
70%	871
90%	893
95%	916
Aniline point, %	180.5

Additional operating conditions and results are shown below:

Example	Pressure (p.s.i.g.)	Temp., ° F.	LHSV	650° F., wt. percent	Pour point, ° F.	KV at 100° F.	KV at 210° F.	VI
15.....	2,500	760	1.0	62.8	0	30.13	4.94	95
16.....	2,500	740	1.0	73.7	15	39.85	5.66	85
17.....	1,500	740	1.0	80.8	10	46.18	6.02	76
18.....	1,500	760	1.0	70.5	5	40.15	5.70	86
19.....	1,500	760	1.5	48.5	-10	27.69	4.71	95

EXAMPLES 20-24

The procedure of Examples 15-19 was repeated with the exception that the ratio of cracking components was changed. In Examples 20-24, the catalyst mixture contained 100 cubic centimeters of the nickel-tungsten-silica-zirconia-clay and 20 cubic centimeters of ZnH/ZSM-5.

Additional operating conditions and results are shown below:

Example	Pressure (p.s.i.g.)	Temp., ° F.	LHSV	650° F., wt. percent	Pour point, ° F.	KV at 100° F.	KV at 210° F.	VI
20.....	2,500	760	1	55	10	28.33	4.89	97
21.....	2,500	740	1	70	40	33.10	5.30	101
22.....	1,500	760	1	65	20	31.44	5.08	96+
23.....	1,500	740	1	78	40	37.95	5.55	89
24.....	1,500	760	0.5	39	-10	28.12	4.33	104

20 in mind that hydrocracking with conventional catalyst gives a net production of wax by opening rings to high boiling straight or slightly branched aliphatic compounds. For examples 25-28, the catalyst contained 100 parts of nickel-tungsten-silica-zirconia-clay and 20 parts of ZnH/ZSM-5. The charge stock had the following properties:

Gravity, °API	23.8
Pour Point, °F.	>120
Sulfur, wt. %	0.53
KV at 210°F, cs.	16.7
Wax., wt. %	16.2

Vacuum Assay (10 mm), °F

IBP	859
5%	911
10%	922
30%	940
50%	957
70%	973
90%	1002
95%	1020

After solvent dewaxing, the stock had these characteristics:

Pour Point, °F.	0
KV ₂₁₀ , cs	20.25, 20.32
KV ₁₀₀ , cs	362.9, 364.3
VI	65
Sulfur, wt. %	0.67

Processing conditions with 8,000 SCF/B of hydrogen and results of processing are shown in the following Table:

Example	Pressure (p.s.i.g.)	Temp., ° F.	LHSV	650° F.+, wt. percent	Wax, wt. percent	Pour pt., ° F.	KV at 100° F.	KV at 210° F.	VI
25.....	2,500	760	1.0	85.3	5.3	70	134.1	12.31	88
						*0	160.8	13.56	85
26.....	2,500	760	0.5	70.0	5.3	60	90.39	10.23	103
						*0	93.69	10.28	99
27.....	1,500	760	0.5	72.0	5.0	50	120.8	11.74	92
						*-5	127.9	11.89	88
28.....	1,500	760	1.0	87.6	-----	70	169.2	13.77	81

* Hydrocracked product solvent dewaxed to pour point indicated.

Example 25 was run at 2,500 psig, 760°F, 1.0 LHSV, 8,000 SCF/B hydrogen. The 650°F+ product was obtained in 85.3 percent yield with 88 VI. Removal of 5.3 percent wax brought the pour point down to 0°F. This demonstrates that the combination operation removed at least 11 percent wax (hydrocracking produces wax) and raised the VI by 20 units (the raw, dewaxed charge has a 65 VI). Similarly at 0.5 LHSV, the raw 650°F+ product was obtained in 70 percent yield with a +60°F pour point (and 5 percent wax). After dewaxing, the hydrocracked oil had a 99 VI.

Examples 27 and 28 show that the operation is also feasible at 1,500 psig — where the yields are higher and the VI's are lower.

EXAMPLES 29-31

Using the same charge stock as shown for Examples 25-28, runs were made with a catalyst composite of 80 parts nickel-tungsten-silica-zirconia-clay at 8,000 SCF/B hydrogen. Further processing conditions and results obtained are shown in the following table:

Example	Pressure (p.s.i.g.)	Temp., ° F.	LHSV	650° F.+, wt. percent	Wax, wt. percent	Pour pt., ° F.	KV at 100° F.	KV at 210° F.	VI
29.....	1,500	760	0.5	81.0	-----	40	124.5	11.72	89
30.....	1,500	760	1.0	83.0	-----	50	154.4	12.86	80
31.....	2,500	760	0.5	77.7	-----	50	113.6	11.28	93

What is claimed is:

1. A process for preparing low pour point lube oils which comprises contacting a petroleum charge stock having a boiling point above 650° F. and a low Viscosity Index under hydrocracking conditions to produce lubricant of substantially higher Viscosity Index with a catalyst composition comprising a mixture of

a. a crystalline aluminosilicate of the ZSM-5 type having a composition in terms of mole ratios of oxides as follows:

$0.9 \pm 0.2 M_{2/n}O : Al_2O_3 : Y SiO_2 : z H_2O$ wherein M is at least one cation having a valence n , Y is at least 5 and z is between 0 and 40, said aluminosilicate having the x-ray diffraction lines as set forth in Table 1 of the specification,

b. a large pore cracking catalyst, and

c. a hydrogenation/dehydrogenation component in association with at least one of catalysts (a) or (b) whereby the Viscosity Index and the Pour Point of the oil are simultaneously enhanced.

2. The process of claim 1 wherein the large pore size aluminosilicate is synthetic faujasite.

3. The process of claim 1 wherein the ZSM-5 type catalyst is ZSM-8.

4. The process of claim 1 wherein the ZSM-5 type catalyst has been base exchanged with hydrogen ions, ammonium ions, and mixtures thereof.

5. The process of claim 1 wherein the large pore cracking catalyst is an inorganic oxide.

6. The process of claim 5 wherein the inorganic oxide comprises silica.

7. The process of claim 1 wherein the large pore cracking catalyst is a crystalline aluminosilicate having a pore size from 6 to 15 Angstrom units.

8. The process for preparing low pour point lube oils which comprises contacting a petroleum feed stock

having a boiling point above 650° F. under hydrocracking conditions with a catalyst composition comprising

a. A ZSM-5 type zeolite having a composition in terms of mole ratios of oxides as follows:

$0.9 \pm 0.2 M_{2/n}O : Al_2O_3 : Y SiO_2 : z H_2O$ wherein M is at least one cation having a valence n , Y is at least 5 and z is between 0 and 40, said aluminosilicate having the x-ray diffraction lines as set forth in Table 1 of the specification, and

b. a nickel-tungsten-silica-zirconia-clay cracking catalyst.

9. The process of claim 8 wherein M is a mixture of ammonium and zinc cations.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,755,145 Dated August 28, 1973

Inventor(s) BERNARD A. ORKIN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 64, "catalystic" should be catalytic--.
Column 2, line 53, "of" should be --or--. Column 3, line 21, "to" should be -- 2-5 --.

Column 4, line 58, "under a reaction" should be --under reaction--.; column 4, line 61, "compositng" should be --compositing--.

Column 5, line 19, "an" should be --and--.; column 5, line 63, "stream" should be --steam--.; column 5, line 65, "1500°F" should be --1500°F if--.

Column 6, line 1, "stream" should be --steam--.; column 6, line 17, "1:10 to 2:1" should be --1:10 up to 2:1--.

Column 7, lines 9-10, Delete "Compositions of this type include techniques with"; column 7, line 31 "to" should be --and--.

Signed and sealed this 5th day of February 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patent