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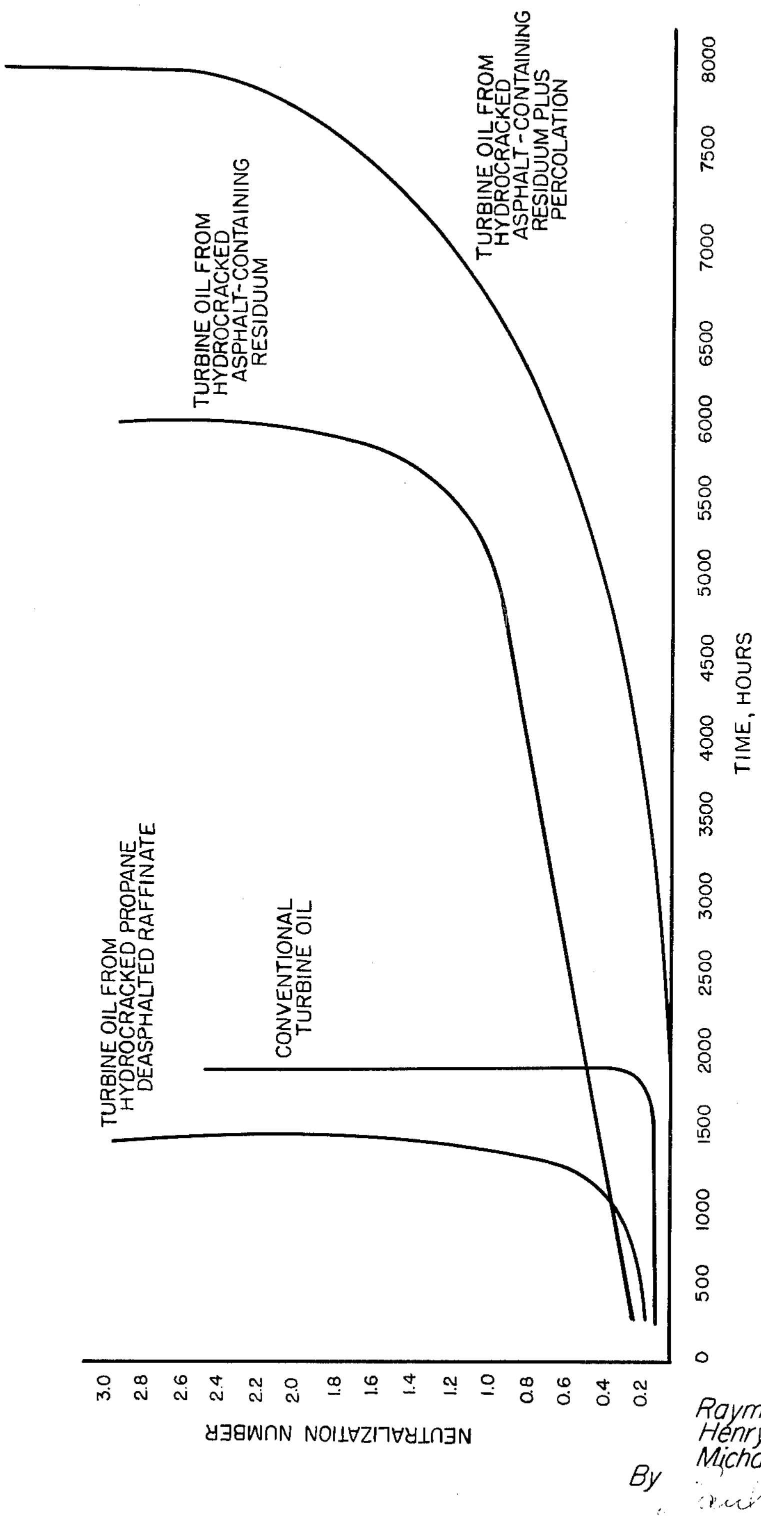

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PROCESS OF OBTAINING LUBRICATING OILS FROM THE HYDROCRACKING OF ASPHALTIC HYDROCARBON OILS

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This application is a continuation-in-part of application Ser. No. 159,340, filed December 14, 1961, now abandoned, and application Ser. No. 237,163, filed November 13, 1962, now abandoned.

This invention relates to the production of improved lubricating oils. In one aspect, this invention relates to a method for preparing improved lubricating oils suitable for use in engines, turbines and as automatic transmission fluid base stocks. In other aspects, this invention relates to improved lubricating oils composed of the combination of a mixture of specific hydrocracked hydrocarbons and at least one lubricating oil additive suitable for enhancing the properties of said hydrocracked hydrocarbons to provide improved engine oils, turbine oils and automatic transmission fluids.

The desirable characteristics of satisfactory lubricating oils and specific types of lubricating oils are known in the art. For instance, a satisfactory turbine oil should possess properties such as a high flash test, a low viscosity, the ability to maintain its body and efficiency under high temperatures, low moisture-absorptive capacity, oxidation stability and the like. Of the above-identified properties, the oxidation stability of a turbine oil is of extreme importance. Satisfactory automatic transmission fluid base oils should possess not only most of the properties described above for turbine oils but in addition, a low wax content and a high viscosity index so as to provide lubrication over a wide temperature range. To provide lubricating oils which can be used for specific purposes and have acceptable physical characteristics, the refining processes, which are known, generally require a careful selection of the crude base stock, which may involve a pretreatment step, and an expensive combination of refining steps such as acid treatment, solvent refining, and the like to produce desirable lubricating oils under exacting and careful conditions. Although these procedures provide lubricating oils which can be satisfactorily used, these known processes are expensive, time consuming, and the yields of the lubricating oil product are generally low since the impurities must be removed from the hydrocarbon charge stocks in the refining operation. It would be highly desirable to utilize a refining process which uses a minimum number of refining steps, converts impurities which are generally removed and obtain improved lubricating oils in higher yields over the known processes. It is the purpose of this invention to provide these improvements.

Accordingly, one or more of the following objects will be achieved by the practice of the invention. It is an object of this invention to provide an economical and commercially feasible process to produce improved lubricating oils in high yields. It is a further object of this invention to provide a process wherein any type of asphalt-containing hydrocarbon boiling above about 650° F. is hydrocracked to provide improved lubricating oils in high yields. It is another object of the invention to provide improved turbine oils which have superior characteristics of improved oxidation resistance, improved durability, and possess other satisfactory properties required of acceptable turbine oils. An additional object of this invention is to provide improved automatic transmission fluid

base stocks which have superior characteristics of improved oxidation resistance, improved shear stability, high viscosity indices and possess other satisfactory properties of acceptable automatic transmission fluid base stocks. It is also an object of the invention to provide improved lubricating oils composed of the combination of a mixture of specific hydrocracked hydrocarbons and at least one lubricating oil additive suitable for enhancing the properties of turbine oils, automatic transmission fluids and engine oils. It is a further object of this invention to provide a process wherein any type of asphalt-containing hydrocarbon boiling above 650° F. is hydrocracked and subsequently subjected to a percolating process over adsorbent materials to produce improved oxidation resistant turbine oils. Numerous other objects will become apparent to those skilled in the art from a consideration of the disclosure and appended claims.

In accordance with the present invention, improved lubricating oils such as engine oils, turbine oils, and automatic transmission fluid base stocks are produced by the treatment of an asphalt-containing petroleum hydrocarbon oil having a boiling point in excess of about 650° F. with hydrogen in the presence of a catalyst having hydrogenation and cracking properties utilizing conventional hydrocracking conditions and separating the lubricating oils from the hydrocracked product. The starting material which can be utilized in the process of this invention can be any asphalt-containing petroleum hydrocarbon boiling in excess of 650° F. These petroleum hydrocarbons can be obtained by vacuum distillation or like distillation of asphalt-containing crude oils, such as, Mid-Continent, North African, Gulf Coast, West Texas, Kuwait among others. For purposes of this invention in producing lubricating oils such as turbine oils, it is essential that the hydrocarbon charge stock used in the hydrocracking process contain asphalt in amounts ranging from about 2 to about 70 volume percent preferably in the range from about 5 to about 40 volume percent of the charge stock. In producing automatic transmission fluid base stocks, it is essential that the hydrocarbon charge stock used contain asphalt in amounts ranging from about 2 to about 50 volume percent, preferably in the range from about 2 to about 40 volume percent of the charge stock. The term "asphalt" as used herein is defined as the amount of asphalt tar which can be removed from the asphalt-containing hydrocarbon charge stock by a propane deasphalting procedure. It is an additional requirement of the petroleum hydrocarbon charge stock that this material is sufficiently fluid so that is will flow and has the ability to be pumped. If the starting material is not sufficiently fluid, a hydrocarbon diluent can be added so as to provide the desired flowable viscosity.

In a particular aspect of the present invention wherein turbine oils having good oxidation stability are produced, an asphalt-containing petroleum hydrocarbon oil having a boiling point in excess of about 650° F. and containing asphalt in an amount in the range of from about 2 to about 70 volume percent is hydrocracked in the manner described below. The turbine oil is separated from the hydrocracked product and is percolated over an adsorbent material such as activated clay and activated charcoal including bauxite, porocel, fuller's earth and the like.

The reaction conditions necessary in the hydrocracking process for the production of the improved lubricating oils of this invention include a temperature range from about 700° F. to about 870° F., preferably in the range from about 725° F. to about 850° F. The pressures which are employed include those ranging from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge, preferably in the range from about 2000 to about 3500 pounds per square inch gauge. The liquid hourly space velocity which can be used ranges from about 0.1 to about 2.0, preferably in the range from about 0.2 to about 1.0. The hydrocracking reaction conditions of this process to produce improved turbine oils are maintained so as to provide a conversion in the range from about 15 to about 70 volume percent preferably in the range from about 25 to about 45 volume percent of the asphalt-containing hydrocarbon. The hydrocracking reaction conditions required to produce automatic transmission fluid base stocks are maintained so as to provide a conversion in the range from about 35 to about 70 volume percent preferably in the range from about 45 to about 55 volume percent of the asphalt-containing petroleum hydrocarbon. The term "conversion" as referred to herein is a generic term for the amount of products boiling below 650° F. obtained in the hydrocracking process. The conversion is expressed in terms of volume percent and determined as follows: 100-material in the product boiling about 650° F. expressed as volume percent of charge. It is a requirement of this process to utilize pressures in excess of 1700 pounds per square inch gauge in order to provide satisfactory percolated turbine oils having viscosity indices of at least about 100.

Although the above-described hydrocracking process provides an adequate once-through method to obtain the improved lubricating oils of this invention, a modification to this process will provide additional improvements. The presence of asphalt in the hydrocarbon charge stock tends to increase the aging properties of the catalyst utilized and requires frequent regeneration. It has been discovered that recycle of a specific product fraction of the hydrocracked hydrocarbon, i.e., the hydrocracked product boiling in the range from about 400 to about 700° F. does not only decrease aging of the catalyst and extend the operation time before regeneration is required but this process also produces a lubricating oil which is more viscous at the same conversion level than the once-through operation and produces a higher viscosity index oil product at the same viscosity level which would be a higher conversion level. The volumetric ratio of the recycle stock fraction obtained from the hydrocracked product to the hydrocarbon charge stock suitable to provide the improved process ranges from 0.1:1 respectively, to about 10:1 respectively, preferably in the range from about 1:1 respectively, to about 5:1 respectively.

The catalyst employed in the process of this invention can include any type of catalyst having hydrogenation and cracking properties. Such catalysts are known in the art, for instance, these catalysts can include oxides and sulfides of any metal of Group VI lefthand column of the Periodic system or mixture thereof, such as, chromium sulfide, molybdenum sulfide, tungsten sulfide and the like; oxides and sulfides of Group VIII of the Periodic Table or mixture thereof, such as, the sulfides of iron, cobalt, nickel, palladium, platinum, rhodium, osmium, iridium; mixtures of the above oxides and sulfides of the metals of Group VI lefthand column and Group VIII, such as, a mixture of nickel sulfide and tungsten sulfide, cobalt sulfide and molybdenum sulfide, nickel sulfide and molybdenum sulfide and the like. These metals can be deposited on absorbent carriers such as alumina, silica-alumina, silica-zirconia, among others. Preferred catalysts include those comprising at least one of the metals having atomic numbers 44, 45, 46, 76, 77 and 78 deposited on a composite-like oxide of at least 2 of the metals of Group IIA, IIB, IVA, and IVB of the Periodic Arrangement of the Elements particularly where such composite has an activity index in excess of 25. Additional preferred catalysts include a sulfided or unsulfided 1 to 8 weight percent cobalt oxide and 3 to 20 weight percent molybdenum trioxide on a silica-alumina or silica-zirconia base containing silica in amounts from about 5 to about 95 weight percent.

The catalyst after use in hydrocracking for a period of time such that its activity is detrimentally affected is subjected to regeneration. For such purpose, the spent cata-

lyst is contacted with an oxygen-containing atmosphere at an elevated temperature sufficient to burn carbonaceous deposits from the catalysts. Conditions for regenerating the hydrocracking catalysts include a temperature between about 600° F. and about 1000° F., a pressure of from atmospheric to about 500 pounds per square inch, a total gas flow rate of from about 1 to about 20 volumes per volume of catalyst and an oxygen concentration of from about 0.1 percent to 100 percent. The oxygen may be diluted with nitrogen or other inert gas.

Pure hydrogen can be used in this process. Hydrogen of low purity obtained by recycle or other hydrogenating process can be used, but it is recommended that the recycle hydrogen be subjected to a purification process to remove some of the undesirable impurities such as water, sulfur compounds, and the like. The hydrogen can be circulated at a rate in the range from about 1000 to about 10,000 s.c.f. per barrel of hydrocarbon charge preferably in the range from about 2000 to about 5000 s.c.f. per barrel of charge. It is essential, however, to obtain a hydrogen consumption of at least about 750 s.c.f. per barrel of hydrocarbon charge.

To obtain the improved turbine oils of this invention, the hydrocracked product of asphalt-containing petroleum hydrocarbon is separated so as to provide a fraction having a viscosity at 210° F. in the range from about 40 to about 70 S.S.U. and a flash point of about 390° F. to about 450° F. These fractions which can be obtained by distillation of the hydrocracked product can be used in its entirety as the improved turbine or several fractions can be blended to produce turbine oils in the form of a light, medium, or heavy oil product. In the embodiment of the present invention wherein the turbine oil fraction is to be passed over an adsorbent material percolation bed, a volume ratio of oil to adsorbent material of from about 0.1 to about 10 at a temperature of from about 50° F. to about 500° F. is employed. Preferably, the turbine oil is percolated at conditions wherein an oil to clay volume ratio of from about 2 to about 5 at a temperature of from about 120° F. to about 300° F. is employed.

To obtain the improved automatic transmission fluids base stocks of this invention, the hydrocracked product of asphalt-containing petroleum hydrocarbon is separated so as to provide a fraction having a viscosity at 210° F. in the range of about 40 to about 50 S.S.U., a flash-point of about 390° F. to about 425° F., and a viscosity index in excess of 115. These fractions which can be obtained by distillation of the hydrocracked product can be used in its entirety as the improved automatic transmission fluid base stock or several fractions can be blended to produce automatic transmission fluid base stocks to provide suitable properties required of said oil.

After separation of the lubricating oil or components thereof from the hydrocracked product, the desired oil may contain some wax products. Removal of wax, if present, is accomplished by any treatment conventionally used for dewaxing oils to give a pour point below about 20° F. specifically for turbine oils, preferably in the range from about 20 to about —25° F. Since the automatic transmission fluid base stocks require a low wax content, it is essential that these oils be dewaxed at temperatures to provide oils having pour points below about —10° F. Dewaxing to obtain exceptionally low pour points is essential for automatic transmission fluid base stocks so as to decrease the amount of pour depressant-viscosity index improvers which may be required to provide an oil which can be used in extreme cold weather climates without solidifying. The deep dewaxing operation generally decreases the viscosity index of the base oils 5 to 10 points and significantly demonstrates the requirement of the untreated base oil to have a viscosity index in excess of about 115. With this extreme dewaxing operation, therefore, the dewaxed base oils having viscosity indexes in excess of about 110 can be obtained which decreases the amount of a viscosity-index improver material necessary to obtain a high viscosity-index transmission fluid. Typical of a satisfactory dewaxing process is the method wherein the oil is dissolved in a solvent, such as, propane; methyl ethyl ketone and toluene; and the like, cooling and filtering. The dewaxing solvent can be removed by distillation.

The automatic transmission fluid base stocks obtained from the hydrocracked hydrocarbon may contain undesirable properties, such as, sludge-producing components or undesirable color characteristics. These properties can be improved, if desired, by percolating the automatic transmission fluid base stock, or the like in the presence of clay using conventional procedures.

The lubricating oils produced by the process of this invention can be further improved by the addition of conventional additives. The degree of improvement is equal to and in many cases greater than the improvement obtained by the addition of such conventional additives to other lubricating oils. Examples of additives which may be incorporated in the improved lubricating oils are the conventional and known viscosity-index improvers such as iso-butylene polymers, methacrylates and the like, detergents including those of the class of metal sulfonates, metal phenates, and metal naphthenates, and polymeric dispersants such as polyethylene glycol substituted polymethacrylates, and the like. Additional additives which can be used include antioxidants such as zinc dithiophosphates, alkylated phenols and the like and known rust inhibitors, if desired, such as those of the class of amine derived succinic anhydrides. Other additives known in the art may be added to obtain additional desired effects.

Examples of additives which may be incorporated in the improved automatic transmission fluid base stocks are the conventional and known viscosity index improvers including those of the class of methacrylate, iso-butylene polymers and the like. Other additives which can be included in the automatic transmission fluid base stocks include the conventional and known detergents of the class of metal sulfonates, metal phenates, and metal naphthenates and the like; antioxidants such as zinc dithiophosphates, alkylated phenols and the like; rust inhibitors such as those of the class of amine derived succinic anhydrides; and pour depressants such as polymethacrylates. Other additives known in the art may be added to obtain additional desired effects.

The hydrocracking process of this invention can be carried out in any equipment suitable for catalytic hydrocracking operations. The process may be operated batch-wise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the process can be adapted to operations using a fixed bed of catalyst. Also, the process can be operated using a moving bed of catalyst wherein the hydrocarbon flow can be concurrent or countercurrent to the catalyst flow. A fluid type of operation can also be employed.

Important advantages are apparent in using the processes of this invention over the conventional acid treatment and/or solvent refining procedures in producing lubricating oils. Of significant importance, higher yields are obtained in the process of this invention over the conventional refining procedures since the lubricating oil fraction of the charge stock is hydrocracked and converts the undesirable material into acceptable products thereby utilizing the entire crude charge stock to produce the improved lubricating oil. The acid treating and solvent refining procedure removes the undesirable material from the charge stock thereby decreasing the yield of the resulting product. Not only are higher yields obtained in the process of this invention, but lubricating oils are produced which have improved characteristics of maintaining its resistance to chemical breakdown during use, the ability to maintain its body and efficiency under high-temperatures (shear stability) and the ability to maintain its stability under oxidizing conditions among other advantages over the conventional lubricating oils.

Important advantages are also apparent in employing an additional percolation step after the hydrocracking step over the conventional acid treatment and/or solvent refining procedures in producing turbine oils. It should be noted that the turbine oil product, by the process of this invention, has significantly improved oxidation resistant characteristics over the turbine oil product by the hydrocracking process without the percolation step. The following examples will serve to illustrate the processes and improved products of the invention without limiting the same.

EXAMPLE 1

The properties of the charge stocks used in the hydrocracking process are listed in Table I.

Table I

Charge Stock	Mid-Continent propane deasphalted raffinate	Mid-Continent 10% Residuum	Pan Fullerton 15% Residuum
Gravity, °API	23.8	12.8	17.2
Vacuum Assay, ° F.:			
IBP	589	700	643
5% Vol	983	1,032	974
10% Vol	1,050		1,011
20% Vol	1,070		
Pour Point, ° F	>115	90	65
Viscosity, S.S.U. at 210° F	184	2,412	843
Asphalt-Tar, Volume percent		57	52

The catalysts utilized were prepared by separately impregnating cobalt oxide and molybdenum oxide on a silica-alumina (CMAS) or silica-zirconia (CMZS) base and sulfiding the catalyst composite. The resulting catalysts possessed the following compositions and properties:

	CMZS	CMAS
Al_2O_3, weight percent		74.2
SiO_2, weight percent	78.3	15.4
ZrO_2, weight percent	10.6	
MoO_3, weight percent	8.5	8.1
CoO, weight percent	2.6	2.3
Sulfur content, weight percent	6.7	3.8
Packed density, g./cc	0.93	0.98
Surface area, m.²/g	373	241
Pore volume, cc./g	0.27	0.38
Average pore diameter, A	29	64

The propane deasphalted Mid-Continent raffinate, the Mid-Continent 10% residuum and the Pan Fullerton 15% residuum were hydrocracked over the CMAS catalyst described above, using the following conditions:

Hydrocracking conditions:

Pressure, p.s.i.g	3,000	3,000	3,000
Temperature, ° F	779	820	800
Liquid hourly space velocity	0.2	0.2	0.2
H_2 Circ. s.c.f./b	10,000	10,000	10,000
Conversion, percent Volume	46	70	48

The hydrocracked products were distilled to separate from the total liquid product, fractions suitable for turbine oils having the properties described in Table II below.

An oxidation stability test was conducted on each of the hereinafter described turbine oil fractions. This test involved subjecting a 25 milliliter sample of the oil to 15 liters of air per hour for 40 hours in the presence of 15.6 square inches of iron wire, 0.78 square inch of copper wire, 0.87 square inch of aluminum wire and 0.167 square inch of lead surface. The temperature was maintained at 260° F. Results are given in Table II.

Table II

PROPERTIES OF TURBINE OIL FRACTIONS

Initial Viscosity	Deasphalted Mid-Continent		Mid-Continent 10% Residuum	Pan Fullerton 15% Residuum
S.S.U. at 210° F.	41.2	53.2	41.0	52.1
Kinematic viscosity at 210° F.	4.55	8.21	4.50	7.90
Viscosity Index	130	121	116	104
Neutralization number mg. KOH/gm.	0.06	0.08	0.05	0.1
OXIDIZED OIL TEST				
Kinematic viscosity at 210° F.	17.44	32.42	4.79	8.49
Kinematic viscosity increase, percent	283	295	6.5	7.47
Neutralization number mg. KOH/gm.	18.1	16.1	1.5	1.5
Lead Loss, mg.	155.3	214.4	0.8	0.9

The small changes in neutralization number and viscosity and the low lead loss of the fractions obtained from the asphalt-containing hydrocarbons demonstrates the superior oxidation stability of these turbine oils over those fractions of the deasphalted hydrocarbons. This advantage aids in eliminating or reducing antioxidant additives required of a turbine oil. The above comparison also shows the improved characteristics of the hydrocracked turbine oils obtained from the asphalt-containing hydrocarbons in that these oils maintained their low viscosity during use and significantly suppressed acid formation over the hydrocracked turbine oils obtained from the deasphalted residuum. As should be realized, the turbine oil fractions obtained from the hydrocracked asphalt-containing petroleum hydrocarbons are suitable for use as lubricating oils to which lubricating oil additives can be added if desired.

EXAMPLE 2

The turbine oils of this invention can be further improved by the addition of conventional or known turbine oil additives. The following hydrocarbon charge stocks were hydrocracked utilizing the hydrocracking conditions as described below using the CMZS catalyst described in Example 1.

	Mid-Continent 25% Residuum	Deasphalted Kuwait Residuum
Gravity, ° API	19.6	20.3
Pour Point, ° F.	75	100
Vacuum Assay, ° F.:		
5% Vol.	693	960
10% Vol.	755	986
50% Vol.	1,011	1,081
EP	[1] 1,087	[2] 1,114
Kinematic viscosity at 210° F., C.S.	32.9	36.1
S.S.U. at 210° F.	155	170
Asphalt, Volume percent	26	0
Hydrocracking Conditions:		
Pressure, p.s.i.g.	3,000	3,000
Temperature, ° F.	764	750
Space Velocity	0.2	0.2
H^2 Circ., s.c.f./b.	10,000	10,000
Conversion, Percent Volume	33	42

[1] At 67 percent.
[2] At 56 percent.

The hydrocracked products were distilled and dewaxed and a light turbine oil fraction from each hydrocarbon charge stock was obtained having the following properties:

	Mid-Continent 25% Residuum	Deasphalted Kuwait Residuum
Oil Gravity, ° API	29.8	35.9
Viscosity:		
S.S.U. at 210° F.	42.0	42.8
Kinematic viscosity at 210° F., C.S.	4.81	5.05
Viscosity Index	105	126
Pour Point, ° F.	20	20

For comparison purposes, a light turbine oil was obtained directly by the conventional refining of an East Texas Crude. This turbine oil without the benefit of hydrocracking had the following properties:

Gravity, ° API	32.1
Pour point, ° F.	20
Flash, ° F.	395
S.S.U. @ 100° F.	153
S.S.U. @ 210° F.	43.5
VI	102
Neutralization number, mg. KOH/g.	0.03

Each of the above-described turbine oil base stocks were mixed with conventional turbine oil additives in the following formulation:

	Weight percent
Turbine oil base stock	99.61
2,6-ditertiary butyl paracresol	0.25
Zinc dihexyl dithiophosphate	0.10
Oleic acid-triethylene tetramine-tetrapropenyl succinic anhydride reaction product	0.04

Each of the above-described formulations were subjected to a Test For Oxidation of Inhibited Steam Turbine Oils as described in the ASTM Manual under Specification No. D943–54. The following results of Table III were obtained.

Table III

[Time of test—hours]

		270	6009	1,000	1,450	1,790	3,500	5,000	5,700
Hydrocracked Turbine Oil obtained from a deasphalted residuum.	Neutralization number, mg. of KOH/g.	0.17	0.19	0.20	>2.0	>2.0	>2.0	>2.0	>2.0
Hydrocracked Turbine Oil obtained from an asphalt-containing residuum.	do	0.25	0.30	0.38	0.40	0.46	0.70	0.90	2.0
Conventional Turbine Oil (not hydrocracked).	do	0.10	0.10	0.10	0.10	2.0	>2.0	>2.0	>2.0

The results of the turbine oil stability test are plotted in the accompanying figure wherein the time of the test is plotted vs. the neutralization number, mg. KOH/g. of the formulated turbine oil. For turbine oils, the absolute tolerability of acidity is reached when the neutralization number reaches 2. The figure significantly demonstrates that the formulation of the turbine oil obtained from an asphalt-containing hydrocarbon is approximately 3 to 4 times more stable, i.e., for the formation of tolerable acid, than the turbine oil obtained from the hydrocracked deasphalted residuum and the turbine oil obtained directly from a typical crude oil. The improved formulations of this invention provide for a more stable turbine oil which maintains the desired property characteristics over an extended life period.

EXAMPLE 3

A portion of a 25% Mid-Continent residuum charge stock having the properties as described in Example 2 was hydrocracked over a sulfided catalyst composed of cobalt oxide and molybdenum oxide on a silica-zirconia base (properties described in Example 1) utilizing the following hydrocracking conditions:

Reaction temperature for 45% conversion, ° F.	778.
Pressure pounds per square inch gauge	3000.
Liquid hourly space velocity (fresh feed)	0.2.
Hydrogen circulation ratio, s.c.f. per barrel of fresh feed	10,000.
Operation	Single pass (once-through.)

To demonstrate the advantages of the recycle operation i.e., the hydrocracked product boiling in the range from about 400° F. to about 700° F. and products boiling above 850° F. were recycled to the hydrocracking reactor, a portion of the same 25% Mid-Continent residuum charge stock described in the single pass operation above was hydrocracked over a sulfided catalyst composed of cobalt oxide and molybdenum oxide on a silica-zirconia base (properties described in Example 1) utilizing the following hydrocracking conditions:

Reaction temperature for 45% conversion, ° F.	790
Pressure, pounds per square inch gauge	3000
Liquid hourly space velocity (fresh feed)	0.2
Hydrogen circulation ratio, s.c.f. per barrel of fresh feed	10,000
Operation	Liquid recycle

The following comparative results of the single pass and recycle operations were obtained as described in Table IV below:

Table IV

	Single Pass	Liquid Recycle	
Recycle stock boiling range, ° F.		400–700	850+ bottoms.
Ratio of Recycle Stock to Fresh feed, volume/volume.		1:1	1:1.
Catalyst aging rate, ° F. per day	0.8	Very low [1]	Very low.[1]
Viscosity of 650° F plus oil products at 45% conv. S.S.U. at 210° F.	59.0	63.7	51.5.
Viscosity Index ° F. 650° F. plus oil products having a viscosity at 210° F. of 42 S.S.U. and dewaxed to a pour point of 20° F.	130	139	119.

[1] Utilizing similar conditions as the single pass operation, the catalyst aging rate was so low that a number could not be determined and assigned.

The use of a recycle stock boiling below lubricating oil stocks (400 to 700° F.) in the hydrocracking operation significantly improves the catalyst aging rate over the rate of the single pass operation. This recycle operation will extend catalyst life and periods of operation before regeneration is necessary over the single pass operation. In addition to the improved catalyst aging characteristics, the recycle operation utilizing the hydrocracked product boiling in the range of about 400° F.–700° F. provides a higher viscosity of the lubricating oil products boiling above 650° F. and higher viscosity indices of a particular oil fraction than the single pass operation and the recycle operation utilizing a heavy hydrocracked cycle stock boiling in excess of 850° F. These results indicate that a specific hydrocracked cycle stock (400–700° F.) can be used to obtain additional advantages of extended catalyst life and improved product characteristics.

EXAMPLE 4

An automatic transmission fluid base stock was obtained by hydrocracking a portion of a 25% Mid-Continent residuum (properties described in Example 2) over a sulfided catalyst composed of cobalt oxide and molybdenum oxide on a silica-zirconia base (preparation and properties described in Example 2) at a temperature of 782° F., a conversion level of 51 volume percent (100-material in the product boiling above 650° F. expressed as volume percent of charge) a pressure of 3000 pounds per square inch gauge, a liquid hourly space velocity of 0.2, and a hydrogen circulation ratio of 10,000 s.c.f. per barrel of charge. The resulting hydrocracked product was distilled to obtain a fraction having a viscosity at 210° F. of 42 S.S.U. This fraction was dewaxed at −35° F. to obtain a pour point of −15° F. and viscosity index of 115. This fraction demonstrates the same resistance to the oxidation reactions as the hydrocracked turbine oil in Example 1.

A conventional automatic transmission fluid base stock was prepared by blending a solvent refined paraffinic neutral oil designated as A, and a solvent refined coastal distillate oil designated as B. These oils have the following properties:

	A	B
Gravity, ° API	33.0	28.4
Specific gravity	0.860	0.885
Pour, ° F	20	−20
Flash point, ° F	400	340
Viscosity:		
S.S.U. at 100° F	136	105
S.S.U. at 210° F	42.4	38.6
Viscosity Index	105	38
Color, ASTM (maximum)	2½	2

The following automatic transmission fluids were prepared by the formulation of the above-described stocks and additives:

	Hydrocracked	Conventional
Base stock, weight percent:		
Hydrocracked Base Stock	88.8	
Stock A		35.7
Stock B		53.5
Additives:		
Conventional Viscosity Index Improvers:		
Methacrylate polymer	3.0	3.0
Iso-butylene polymer	3.0	2.6
Conventional Detergents:		
Barium wax benzene-sulfonate-oleate	3.0	3.0
Barium phenate	1.0	1.0
Wax phenol sulfonate	1.0	1.0

PROPERTIES OF THE AUTOMATIC TRANSMISSION FLUIDS

Viscosity:		
S.S.U. at 210° F	51.5	51.5
S.S.U. at 100° F	183	205
S.S.U. at 0° F. (extrapolated)	4,100	6,000
Viscosity Index	150	1 39
Brookfield Viscosities:		
Cps. at 0° F	1,040	1,750
Cps. at −30° F	7,410	16,000
Flash point, ° F	425	380
Pour Point, ° F	<−35	<−35
Shear Stability, 10 minutes, Sonic Oscillator Final S.S.U. at 210° F	47.0	47.4
Foam ASTM D-892-46-T Sequence 1, Tendency, ml	Nil	Nil
Rubber Swell Ford 91-48 70 hours at 300° F. Percent Volume change	2.8	2.5

As is demonstrated in the above example, the hydrocracked automatic transmission fluid formulation using conventional additives is a less viscous oil at lower temperatures and has a higher viscosity index than a conventional automatic transmission fluid using the equivalent amounts of the same additives (see S.S.U. viscosities at 100° F. and 0° F.). The comparative data of the Brookfield viscosities at 0° F. and −30° F. indicates that the viscosity of the hydrocracked transmission fluid ranges from about 1.7 to 2 times less viscous than the conventional transmission fluid. Other physical properties of the hydrocracked transmission fluid are as good or better than the conventional transmission fluid. Obtaining a low viscositly at low temperatures is a specific requirement necessary of a transmission fluid when used for lubrication in extremely cold climates and avoiding soldification of said fluid.

EXAMPLE 5

The catalyst utilized in the hydrocracking process was prepared by separately impregnating cobalt oxide and molybdenum oxide on silica zirconia and sulfiding the catalyst composite. This catalyst will be designated as CMZS. The resulting catalyst possessed the following composition and properties:

	CMZS
Al_2O_3, weight percent	---
SiO_2, weight percent	78.3
ZrO_2, weight percent	10.6
MoO_3, weight percent	8.5
CoO, weight percent	2.6
Sulfur content, weight percent	6.7
Packed densiyt, g./cc.	0.93
Surface area, m.²/g.	373
Pore volume, cc./g.	0.27
Average pore diameter, A.	29

The following hydrocarbon charge stocks were hydrocracked utilizing the hydrocracking conditions as described below using the CMZS catalyst described above.

	Mid-Continent 25% Residuum	Deasphalted Kuwait Residuum
Gravity, ° API	19.6	20.3
Pour Point, ° F	75	100
Vacuum Assay, ° F.		
5% vol	693	960
10% vol	755	986
50% vol	1,011	1,081
EP	[1] 1,087	[2] 1,114
Kinematic viscosity at 210° F., C.S	32.9	36.1
S.S.U. at 210° F	155	170
Asphalt, Volume Percent	26	0

	Mid-Continent 25% Residuum A	Mid-Continent 25% Residuum B	Deasphalted Kuwait Residuum
Hydrocracking Conditions:			
Pressure, p.s.i.g	3,000	3,000	3,000
Temperature, ° F	764	794	750
Space Velocity	0.2	0.2	0.2
H_2 Circ., s.c.f./b	10,000	10,000	10,000
Conversion, Percent Volume	33	50	42

[1] At 67%.
[2] At 56%.

The hydrocracked products were distilled and dewaxed and a light turbine oil fraction from each hydrocarbon charge stock was obtained having the following properties:

	Mid-Continent 25% Residuum A	Mid-Continent 25% Residuum B	Deasphalted Kuwait Residuum
Oil Gravity, ° API	29.8	30	35.9
Viscosity:			
S.S.U. at 210° F	42.0	43.1	42.8
Kinematic Visocity at 210° F., C.S	4.81	5.14	5.05
Viscosity Index	105	116	126
Pour Point, ° F	20	20	20

Oil B designated above was contacted in a percolation bed of 30–60 mesh freshly burned fuller's earth which is an activated clay employing a 0.2 to 1 oil to clay ratio by volume at 80° F. Pentane was used as a diluent to remove the contacted oil from the clay.

For comparison purposes, a light turbine oil was obtained directly by the conventional refining of an East Texas crude. This turbine oil without the benefit of hydrocracking had the following properties:

Gravity, ° API	32.1
Pour point, ° F.	20
Flash, ° F.	395
S.S.U. @ 100° F.	153
S.S.U. @ 210° F.	43.5
VI	102
Neutralization number, mq. KOH/g.	0.03

Each of the above-described turbine oil base stocks were mixed with conventional turbine oil additives in the following formulation

	Weight percent
Turbine oil base stock	99.61
2,6-ditertiary butyl paracresol	0.25
Zinc dihexyl dithiophosphate	0.10
Oleic acid-triethylene tetramine-tetrapropenyl succinic anhydride reaction product	0.04

Each of the above-described formulations were subjected to a Test for Oxidation of Inhibited Steam Turbine Oils as described in the ASTM Manual under Specification No. D943-54. The following results of Table I were obtained.

Table V

[Time of test—hours]

		270	600	1,000	1,450	1,790	3,500	5,000	5,700	6,400	7,000	7,600
Hydrocracked Turbine Oil obtained from a deasphalted residuum.	Neutralization number, mg. of KOH/g.	0.17	0.19	0.20	>2.0	>2.0	>2.0	>2.0	>2.0	>2.0	>2.0	>2.0
Hydrocracked Turbine Oil obtained from an asphalt-containing residuum.	do	0.25	0.30	0.38	0.40	0.46	0.70	0.90	2.0	>2.0	>2.0	>2.0
Hydrocracked Turbine Oil obtained from an asphalt-containing residuum with Percolation treatment.	do	0	0	0	0	0.05	0.25	0.43	0.51	0.57	1.05	2.0
Conventional Turbine Oil (not hydrocracked).	do	0.10	0.10	0.10	0.10	2.0	>2.0	>2.0	>2.0	>2.0	>2.0	>2.0

The results of the turbine oil stability test are plotted in the accompanying figure wherein the time of the test is plotted vs. the neutralization number, mg. KOH/g. of the formulated turbine oil. For turbine oils, the absolute tolerability of acidity is reached when the neutralization number reaches 2. The figure significantly demonstrates that the formulation of the turbine oil obtained from the hydrocracking of an asphalt-containing hydrocarbon followed by percolation can be used 1900 hours longer than the unpercolated hydrocracked turbine oil obtained from an asphalt-containing hydrocarbon for the formation of tolerable acid in the test turbine oil. The figure further demonstrates that the formulation of the percolated turbine oil obtained by hydrocracking an asphalt-containing hydrocarbon is approximately 4 to 8 times more stable, i.e. for the formation of tolerable acid, than the turbine oil obtained from the hydrocracked reasphalted residuum and the turbine oil obtained directly from a typical crude oil. The improved formulations of this invention provide for a more stable turbine oil which maintains the desired property characteristics over an extended life period.

An additional advantage observed in the test for Oxidation of Inhibited Steam Turbine Oil relates to the formation of sludge in minor amounts at 300 hours for the unpercolated hydrocracked turbine oil obtained from the asphalt-containing hydrocarbon, whereas no evidence of sludge was observed in the percolated hydrocracked turbine oil obtained from the asphalt-containing hydrocarbon until after 2100 hours of the oxidation test.

It is to be understood that the foregoing description is merely illustrative of preferred embodiments of the invention of which many variations may be made by those skilled in the art within the scope of the following claims without departing from the spirit thereof.

We claim:

1. A process for producing an improved turbine oil which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge, at temperatures in the range from about 700 to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved turbine oil having a viscosity at 210° F. in the range from about 40 to about 70 S.S.U. and a flash point in the range from about 390° F. to about 450° F.

2. A process for producing improved automatic transmission fluid base stock which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 50 volume percent asphalt with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge, at temperatures in the range from about 700 to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved automatic transmission fluid base stock having a viscosity at 210° F. in the range from about 40 to about 50 S.S.U., a flash point of about 390° F. to about 425° F. and a viscosity index in excess of about 115 and dewaxing said base stock to a pour point of −10° F. or less.

3. A process for producing improved lubricating oils which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge, at temperatures in the range from about 700° F. to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved lubricating oil having a viscosity at 210° F. in the range from about 35 to about 125 S.S.U. and a flash point in the range from about 310° F. to about 510° F.

4. A process for producing an improved turbine oil which comprises contacting a petroleum hydrocarbon fraction boiling above 650° F. and containing about 2 to about 70 volume percent asphalt with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 2000 pounds per square inch gauge to about 3500 pounds per square inch gauge, at temperatures in the range from about 700° F. to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved turbine oil having a viscosity at 210° F. in the range from about 40 to about 70 S.S.U. and a flash point in the range from about 390° F. to about 450° F.

5. A process for producing an improved lubricating oil which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing from about 2 to about 70 volume percent asphalt with a recycle stock boiling in the range from about 400° F. to about 700° F. obtained from hydrocracking said asphalt-containing petroleum hydrocarbon fraction, in which the volumetric ratio of said recycle stock to said fraction ranges from about 0.1:1, respectively to about 10:1 respectively, with a sulfided catalyst composed of cobalt oxide and molybdenum oxide on a silica-zirconia base in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000

pounds per square inch gauge at temperatures in the range from about 700° F. to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved lubricating oil having a viscosity at 210° F. in the range from about 35 to about 125 S.S.U. and a flash point in the range from about 310° F. to about 510° F.

6. A process for producing an improved turbine oil which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt with a recycle stock boiling in the range from about 400° F. to about 700° F. obtained from hydrocracking said asphalt-containing petroleum hydrocarbon fraction, in which the volumetric ratio of said recycle stock to said fraction ranges from about 1:1 respectively, to about 5:1 respectively, with a sulfided catalyst composed of cobalt oxide and molybdenum oxide on a silica-alumina base in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge, at temperatures in the range from about 700 to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved turbine oil having a viscosity at 210° F. in the range from about 40 to about 70 S.S.U. and a flash point in the range from about 390° F. to about 450° F.

7. A process for producing improved automatic transmission fluid base stock which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 50 volume percent asphalt with a recycle stock boiling in the range from about 400° F. to about 700° F. obtained from hydrocracking said asphalt-containing petroleum hydrocarbon fraction, in which the volumetric ratio of said recycle stock to said fraction ranges from 1:1 respectively, to about 5:1 respectively, with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge, a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved automatic transmission fluid base stock having a viscosity at 210° F. in the range from about 40 to about 50 S.S.U., a flash point of about 390° F. to about 425° F. and a viscosity index in excess of about 115 and dewaxing said base stock to a pour point of −10° F. or less.

8. A process for producing an improved lubricating oil which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt with a recycle stock boiling in the range from about 400° F. to about 700° F. obtained from hydrocracking said asphalt-containing petroleum hydrocarbon fraction, in which the volumetric ratio of said fraction ranges from about 1:1 respectively, to about 5:1 respectively, with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge at temperatures in the range from about 725° F. to about 850° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked

hydrocarbon oil an improved lubricating oil having a viscosity at 210° F. in the range from about 35 to about 125 S.S.U. and a flash point in the range from about 310° F. to about 510° F.

9. A process for producing an improved turbine oil which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt with a recycle stock boiling in the range from about 400° F. to about 700° F. obtained from hydrocracking said asphalt-containing hydrocarbon fraction, in which the volumetric ratio of said recycle stock to said fraction ranges from about 1:1 respectively, to about 5:1 respectively, with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 2000 pounds per square inch gauge to about 3500 pounds per square inch gauge, at temperatures in the range from about 700° F. to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved lubricating oil having a viscosity at 210° F. in the range from about 40 to about 70 S.S.U. and a flash point in the range from about 390° F. to about 450° F.

10. A process for producing an improved lubricating oil which comprises contacting an asphalt-containing petroleum hydrocarbon fraction boiling above about 650° F. and containing from about 2 to about 70 volume percent asphalt with a recycle stock boiling in the range from about 400° F. to about 700° F. obtained from hydrocracking said asphalt-containing petroleum hydrocarbon fraction, in which the volumetric ratio of said recycle stock to said fraction ranges from about 1:1 respectively, to about 5:1 respectively, with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 1700 pounds per square inch gauge to about 4000 pounds per square inch gauge, at temperatures in the range from about 700 to about 870° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocarcked hydrocarbon oil and separating from said hydrocracked hydrocarbon oil an improved turbine oil having a viscosity at 210° F. in the range from about 40 to about 70 S.S.U. and a flash point in the range from about 390° F. to about 450° F.

11. The process of claim **3** wherein the hydrocracking temperature is within the range of 725° F. to 850° F. and at least one lubricating oil additive is added to the lubricating oil product.

12. The process of claim **1** wherein the turbine oil product is percolated through a bed of suitable adsorbent material employing a volume ratio of turbine oil to adsorbent material from about 0.1 to about 10 at a temperature in the range from about 50° F. to about 500° F.

13. The process of claim **12** wherein the absorbent is activated clay.

14. The process of claim **4** wherein the turbine oil product is percolated through a bed of suitable adsorbent material employing a volume ratio of turbine oil to adsorbent material from about 0.1 to about 10 at a temperature in the range from about 50° F. to about 500° F.

15. The process of claim **14** wherein the adsorbent is activated clay.

16. A process for producing an improved turbine oil which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt with a catalyst having hydrogenation and cracking properties in the presence of hydrogen at pressures in the range from about 2000 pounds per square inch gauge to about 3500 pounds per square inch gauge, at temperatures in the range from about 725° F. to about 850° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil; separating from said hydrocracked hydrocarbon oil a turbine oil having a viscosity at 210° F. in the range from about 40 to about 70 S.S.U. and a flash point in the range from about 390° F. to about 450° F.; and percolating said turbine oil product through a bed of suitable adsorbent material employing a volume ratio of turbine oil to adsorbent material from about 0.1 to about 10 at a temperature in the range from about 50° F. to about 500° F.

17. The process of claim **16** wherein the adsorbent is activated clay.

18. A process for producing an improved turbine oil which comprises contacting a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt with a sulfided catalyst composed of cobalt and molybdenum oxide on a silica-zirconia base in the presence of hydrogen at pressures in the range from about 2000 pounds per square inch gauge to about 3500 pounds per square inch gauge, at temperatures in the range from about 725° F. to about 850° F., a hydrogen circulation rate in the range from about 1000 to about 10,000 s.c.f. per barrel of charge, and a liquid hourly space velocity from about 0.1 to about 2.0 to obtain a hydrocracked hydrocarbon oil; separating from said hydrocracked hydrocarbon oil a turbine oil having a viscosity at 210° F. in the range from about 390° F. to about 450° F.; and percolating said turbine oil product through a bed of suitable adsorbent material employing a volume ratio of turbine oil to

adsorbent material from about 0.1 to about 10 at a temperature in the range from about 50° F. to about 500° F.

19. The process of claim **18** wherein the adsorbent is activated clay.

20. A process for producing an improved turbine oil which comprises catalytically hydrocracking a petroleum hydrocarbon fraction boiling above about 650° F. and containing about 2 to about 70 volume percent asphalt under conditions sufficient to limit conversion to hydrocarbon products boiling below about 650° F. within the range of from about 25% to about 45% and produce hydrocracked products boiling above 650° F.; separating from said hydrocracked products a turbine oil having a viscosity at 210° F. in the range of from about 40 to about 70 S.S.U. and a flash point in the range of from about 390° F. to about 450° F.; percolating said turbine oil product through a bed of adsorbent clay type material employing a volume ratio of turbine oil to adsorbent material of from about 0.1 to about 10 and adding suitable additives to the turbine oil recovered from said percolation step.

21. The process of claim **4** wherein a hydrocracking temperature of 725 to 850° F. is employed and an additive is added to the turbine oil.

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