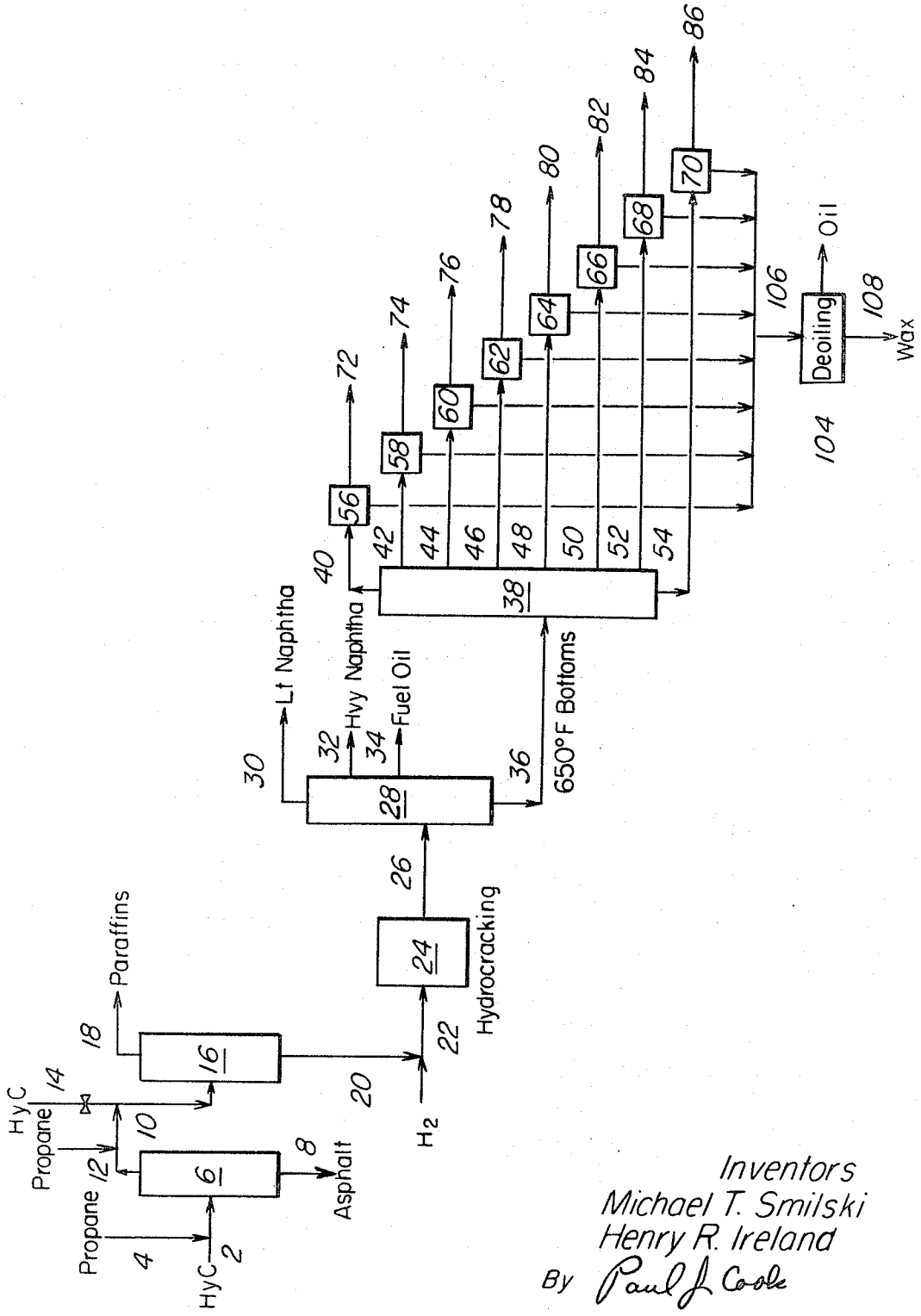
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PRODUCTION OF LUBRICATING OILS FROM RESIN EXTRACTS

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PRODUCTION OF LUBRICATING OILS FROM RESIN EXTRACTS

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9 Claims. (Cl. 208—87)

This application is a continuation-in-part of Ser. No. 285,331 filed June 4, 1963, now abandoned.

This invention relates to the preparation of lubricating oil and in a particular aspect relates to a process for the preparation of wide temperature range lubricating oils as well as multi-grade lubricating oils.

Mineral lubricating oils, known as multi-viscosity or multi-grade lubricating oils, are lubricating oils capable of meeting more than one, such as two or more viscosity grade specifications of the Society of Automotive Engineers (SAE). Such oils are desirable and essential when it is necessary to have a lubricant of sufficiently low viscosity at low temperatures to provide desired lubrication and of sufficiently high viscosity at considerably higher temperatures to also provide satisfactory lubrication at the higher temperatures.

However, lubricants particularly suitable for jet aircraft engines differ from multi-grade automotive lubricants in that they are required to lubricate and cool gears and bearings under relatively wide temperature conditions. Unlike piston engine lubes, gas turbine lubes employed in jet engines are contaminated substantially less with fuel and/or combustion deposits. However, they, on the other hand, are subjected to very high temperatures under oxidizing conditions and must also be useable at low temperatures. Generally speaking, jet engines operate at bulk oil temperatures of about 250° F. and bearing temperatures of the order of about 450–500° F. However, much higher operating temperatures are contemplated for the future. For example, bulk oil temperatures of about 500° F. are visualized for more advanced engine designs because of higher power output and increased aerodynamic heating effects.

At the present time wide temperature range lubricants for jet engines are being made by methods which include their preparation from chemical materials such as organic esters, glycols, silicons, polyolefins and halogenated hydrocarbons. These materials, however, are substantially more expensive than mineral oil base lubricants and have certain shortcomings in performance standards. Generally speaking, the synthetic lubricants are less satisfactory than petroleum lubricants in one or more of the following, including viscosity, temperature characteristics, volatility, flammability, oxidization stability, thermal stability, lubricating characteristics and costs.

Another method of obtaining multi-viscosity lube oils is by the addition of certain synthetic organic compounds known as viscosity index improvers to oils which are added in an amount sufficient to meet multi-grade specifications. However, these viscosity improver materials are objectionable because of costs and perhaps more importantly their instability during use. In addition to the above methods of preparation, lubricating oils have also been

prepared from relatively high boiling hydrocarbon fractions composed of paraffinic and naphthenic hydrocarbons containing isomeric molecules. These high boiling hydrocarbons, however, contain constituents which must be removed before the oil is suitable for lubricating purposes. Accordingly, in the prior art practice, a desired oil fraction is dewaxed by mixing with a suitable solvent such as a mixture of toluene, benzene and acetone, after which the mixture is cooled until the wax therein crystallizes. Filtering is employed to remove the precipitated wax and thereafter the solvent is separated and recovered from the oil. Heavy oils and particularly those boiling above about 900° F. and remaining after the removal of distillate boiling range material suitable for lubricating oils are known as cylinder stocks. The cylinder stock is thereafter subjected to a solvent dewaxing step and a step to remove resin therefrom to produce a deresined stock known as a Bright stock. The thus prepared Bright stock is used for blending with dewaxed lighter oils to form heavier grades of lubricating oils. In the treatment of cylinder stock for the preparation of Bright stock, resinous material and aromatic constituents are removed from the relatively high boiling petroleum fractions to produce a paraffinic Bright stock and there is recovered therefrom an extract phase or extract fraction known as the resin extract. Heretofore this resin extract fraction has been disposed of by burning as a fuel or disposed of by other suitable means.

It is an object of this invention to prepare wide temperature range lubricating oils from constituents of high boiling residual hydrocarbon fraction heretofore considered unsuitable for such purposes. Another object of this invention is directed to the method for upgrading a deasphalted residual oil extract phase to wide temperature range and multiple viscosity lubricating oils.

Still another object of this invention is directed to hydrocracking the resinous extract separated in the preparation of Bright stock to provide oil fractions which may be blended to desired lubricating oils.

In accordance with this invention, a relatively high molecular weight residual material comprising a resinous extract and aromatics either with or without waxy constituents are derived from a relatively high boiling hydrocarbon fraction, particularly an asphalt free or deasphalted petroleum residuum is passed with hydrogen to a hydrocracking zone maintained under relatively severe hydrocracking conditions. During the hydrocracking step, the resins, aromatics and any waxy constituents are upgraded to quality materials comprising lubricating oil, fuel oil and naphtha boiling range materials. The thus prepared lubricating oil boiling range material is thereafter separated by fractionating under vacuum conditions into desired viscosity boiling range product fractions and thereafter dewaxed to provide desired specific pour point lube oil or wide temperature range lubricants suitable for jet engines and hydraulic fluids.

It has been found quite unexpectedly that when a waxy bottom product having an initial boiling point of about 650° F. recovered from the total liquid product effluent of the hydrocracking step and further separated into a plurality of separate boiling range fractions that dewaxing conditions for removing wax from the individual fractions need not be as severe as normally required. That

is, subjecting the particular fractions thus obtained to 0° F. dewaxing conditions produced 0° F. pour point oil rather than a 20° F. pour point oil as would be normally expected. Generally speaking, and particularly when employing a feed material containing waxy constituents, it is preferred to employ lower product dewaxing temperature selected from within the range of from about minus 65° F. to about minus 80° F. to produce oils having a pour point of at least minus 25° F.

In a more particular aspect, it has been found that a resin extract either with or without waxy constituents and recovered from a cylinder stock in the prepartaion of Bright stock may be hydrocracked in the presence of hydrogen and a hydrocracking catalyst maintained at a temperature in the range of from about 720° F. to about 850° F.; a hydrogen partial pressure in the range of from about 800 p.s.i.g. to about 3,000 p.s.i.g.; a space velocity in the range of from about .05 to about 1.5 v./v./hour and preferably below .8 v./v./hour to useful upgraded products including a high boiling range material suitable for preparing lubricating oils, fuel oil, and light and heavy naphtha boiling range materials.

The resin extract feed which is employed in the process of this invention is derived from a petroleum residuum by a number of methods known in the art which involve solvent treatment of the residuum. Resin extract contains large proportions of petroleum resins which are hydrocarbons similar to asphaltenes except that they are not oxidized or combined with sulfur and therefore are soluble in petroleum ether. The resin extracts contemplated in the process of this invention have a viscosity at 210° F. of above about 700 SSU and can range as high as about 4100 SSU or higher and preferably in the range of between about 800 to 2000 SSU. Resin extract is commonly obtained by a multi step treatment of residuum with a low boiling paraffinic hydrocarbon, as for example, butane, propane or pentane. In this treatment, the asphalt portion of the residuum is first separated therefrom and thereafter the deasphalted oil is treated with solvent to obtain the resin extract and an oil which is both deasphalted and deresined.

Although a paraffin base crude is preferred as the starting material for use in the method of this invention, other feed stocks may be used including relatively high boiling deasphalted residual fractions from which a resin extract either with or without waxy material can be obtained. Accordingly, the starting petroleum charge stock can be any deasphalted petroleum residual fraction from which paraffinic and naphthenic constituents are removed having resinous and aromatic constituents therein and which may or may not have been subjected to partial or complete dewaxing at a temperature of about 0° F. This material either with or without wax constituents is the preferred hydrocarbon feed employed in the process of this invention. The wax constituents of the resin extract comprise essentially microcrystalline wax.

In a more particular aspect, destructive hydrogenation and/or hydrocracking conditions employed in the method of this invention are sufficient to convert a resin extract containing feed material and those conditions embody relatively severe carbon-carbon bond cleavage hydrocrack conditions in the presence of a gas exerting a hydrogen total pressure of at least about 1,500 p.s.i.g. and preferably about 2,500 p.s.i.g.; a temperature below about 810° F. and preferably about 770° F. while employing a hydrogen to hydrocarbon feed ratio of at least about 5 to 1 mole ratio and a space velocity below about .8 v./v./hour and preferably below about .3 v./v./hour. That is, a non-isomerizing hydrocracking catalyst of the type such as Co Mo Zr. Si may be employed or a hydrocracking catalyst exerting an isomerizing effect such as a Pt=Al catalyst promoted with from about 3–7 percent fluorine may be employed particularly when the resin extract contains appreciable wax.

The catalyst which may be employed in the hydrocracking step of this invention may be substantially any of the known catalysts which promote the hydrocracking reaction desired. It is preferred, however, to employ an acidic hydrocracking catalyst promoted with a Group VIII metal component. Other suitable hydrocracking catalysts include the oxides and sulfides of the metals of Group VI or mixtures thereof such as chromium sulfide, molybdenum sulfide, tungsten sulfide and the like; oxides and sulfides of Group VIII or mixtures thereof such as iron, cobalt, nickel, palladium, platinum, rhodium, osmium, iridium, or mixtures of one or more components selected from Groups VI and VIII of the Periodic Table. These materials and mixtures thereof may be deposited on a suitable carrier material, preferably, an acidic carrier material such as silica alumina, silica zirconium, and alumina promoted with boria and/or a halogen promoter such as bromine, chlorine, and fluorine.

The total liquid product obtained from the hydrocracking process herein described is separated under atmospheric distillation conditions to obtain a bottoms fraction having an initial boiling point of at least 600° F. and preferably about 650° F. which is thereafter separated under vacuum distillation conditions to obtain a plurality of separate boiling range fractions suitable for blending to desired lube oils. Depending on the producer, the overhead liquid hydrocracked product may be separated to recover a fuel oil from a light and heavy naphtha boiling range product.

EXAMPLE I

The following table shows the properties of typical resin extracts which can be employed in the process of this invention.

TABLE I

	A	B
Gravity ° API	23.4	22.2
Flash ° F. (COC)	630	680
Fine ° F. (COC)	725	745
Viscosity:		
SSU at 100° F	27,955	76,158
SSU at 210° F	842	1,674
Viscosity Index	109	112
Pour, ° F	20	35
Carbon Residue, Percent Wt	1.93	3.71
Sulfur, Percent Wt	0.16	----------
Aromatics, Percent Wt	67	----------
Molecular Wt	1,750	----------

Resin extract A of Table I was hydrocracked over a platinum on silica zirconia catalyst (87.7 wt. percent SiO_2, 11.8 wt. percent ZrO_2, 0.5 wt. percent Pt) under the following conditions.

TABLE II

Pressure	p.s.i.g.	3,000
Temperature	° F.	750
Space velocity	v./v./hr.	0.2
H_2 circulation	SCF/B	10,000

The reaction consumed hydrogen in an amount of 1215 SCG/B of charge. About 50 volume percent of the charge was converted to material boiling below 650° F. The product was distilled to obtain the following fractions.

TABLE III

Fraction	Boiling Range, ° F.	Percent Weight of Product
Light Naphtha	125–180	4.1
Heavy Naphtha	180–390	19.5
Gas Oil	390–600	23.6
Waxy Bottoms	600+	52.8

The waxy bottoms product having an initial boiling point of about 600° F. is vacuum retorted or separated into a plurality of separate boiling range fractions including a heavy bottoms fraction as shown in Table IV presented below and having the physical properties indicated.

TABLE IV

Cut No.	1	2	3	4	5	6	7	8
Boiling Range, ° F.	660–825	825–870	870–925	925–995	995–1,045	1,045–1,100	1,100–1,135	1,135+
Waxy Fractions: Pour Point, ° F.	20	30	35	50	60	70	65	5
Viscosity:								
KV at:								
100° F.	7.7	9.4	11.2		23.3	38.9	67.6	607
210° F.	2.2	2.6	2.9	3.6	4.7	6.7	9.6	44.5
SSU at:								
100° F.	51.1	56.9	63.3		112	181	313	2,813
210° F.	33.7	34.8	35.9	38.2	41.6	48.1	57.9	208
VI.	105	112	117		135	132	124	11

Flash Point: Cut 1, 340° F.; Cuts 2, 3, 4, 5, 6, 395° F. (SSU 39.3); Cuts 3, 4, 5, 6, 7, 410° F. (SSU 42.4).

Table V below identifies a plurality of lube oils prepared from blends of the oil fractions presented in Table IV. That is, Sample 1 of Table V was obtained by blending cuts 2 ot 8 of Table IV; Sample No. 2 of Table V is the same blend as Sample 1 but dewaxed at a temperature of minus 35° F.; Sample No. 3 of Table V is a blend of cuts 2 to 6 and then dewaxed at minus 35° F.; Sample No. 4 is a blend of cuts 3 to 7 of Table IV which was dewaxed at minus 35° F.; Sample No. 5 is a blend of cuts 3 to 8 of Table V; and Sample No. 6 is a blend of cuts 5 to 8 of Table IV.

TABLE V.—LUBE OIL BLENDS PREPARED FROM OIL FRACTION OF TABLE I

Sample No.	1	2	3	4	5	6
Dewaxing Temp. ° F.	0	−35	−35	−35	0	0
ASTM Pour, ° F.	0	−10	−25	−20	0	10
Viscosity:						
SSU at:						
100° F.	325	246	90	113	337	704
210° F.	60.8	53.7	39.2	41.7	61.8	89.1
KV at:						
100° F.	70.24	53.09	18.21	23.65	72.8	151.9
210° F.	10.43	8.37	3.94	4.71	10.7	17.8
−20° F.	10,000	7,200	1,350	1,800	13,000	36,000
−30° F.	22,000	15,000	2,500	3,300	28,000	75,000
−40° F.	45,000	35,000	5,000	7,500	60,000	180,000
−65° F.	460,000	370,000	47,000	65,000	700,000	2,000,000
Viscosity Index	131	131	130	134	130	124

Presented below in Table VI are specifications and characteristics of wide temperature range lube oils which may be prepared by blending and dewaxing the oil fractions of Table IV obtained by the method of this invention:

TABLE VI.—PHYSICAL SPECIFICATIONS OF ENGINE LUBRICANTS

Type	1	2	3	4
Speed in Mach	0.9–2.4	2.4–3.0	3.0–3.5	3.0–3.5
Temp. Range of Use, ° F. to	350	450	500	500
Physical Requirements:				
Viscosity:				
KV at:				
500° F.			>1.0	1.4
400° F.		>1.0		2.7
210° F.	>3.0	(3)	(5.6)	12.1
100° F.	>11.0	(12.4)	(34)	
−30° F.			<13,000	30,000
−65° F.	<13,000	<21,000		
Pour, ° F. (max.)	−75	−75	−40	−50
Flash, ° F.	400	425	500	505
Fire, ° F.				540
Spontaneous Ignition, ° F.		750	(1)	750
Volatility:				
Percent Evaporation at 400° F., 6½ hrs.	<35	<15		
Percent Evaporation at 500° F., 6½ hrs.			<10	6.7

[1] Report.

As a means of providing a better understanding of the method and sequence of process steps of this invention, a diagramatic flow arrangement of the process and method of operation is provided by way of example in the figure. In the drawing, an asphalt containing residual oil in conduit **2** is combined with a solvent material such as propane introduced by conduit **4** to form a mixture which is thereafter introduced into a propane deasphalting zone **6** maintained at a temperature in the range of from about 100 to about 105° F. for the purpose of separating relatively hard asphaltic material from the feed for removal from the bottom of zone **6** by conduit **8**. A deasphalted raffinate is recovered from the upper part of zone **6** by conduit **10**, combined with additional propane solvent introduced by conduit **12** and the mixture thus formed is passed to a second propane extraction treating zone **16** maintained at a temperature in the range of 100 to 140° F. wherein a separation is made between paraffin components and resin components combined with aromatic components. That is, normal paraffins and isoparaffins combined with naphthenic material in the feed will be removed overhead as a raffinate from zone **16** by conduit **18**. The resin extract containing aromatic either with or without waxy material is thereafter removed as an extract phase by conduit **20** for further treatment as hereinafter described.

In the event that a non-asphaltic crude oil is employed as feed material in the process or a residual fraction thereof, such as a cylinder stock obtained from a paraffinic Pennsylvania crude, provisions are made for bypassing deasphalting zone **6** by introducing the paraffinic feed stock such as a cylinder stock to the process by conduit **14** communicating with conduit **10**. If desired, however, dewaxing of the oil feed may be effected before or after the propane treating step accomplished in zone **16** of the process although as pointed out herein, it is not absolutely essential to dewax the feed and in some circumstances, it is preferred to employ a waxy feed material. When employing a waxy feed material, it is preferred to employ a catalyst promoting hydrocracking and hydroisomerization reactions such as a platinum-alumina catalyst promoted with a halogen promoter.

The use of propane for removal of resinous materials in the residual oil permits the sorting out, particularly from a high boiling asphaltic crude of the desirable constituents which go into making up a good residual oil boiling range material known as a Bright stock.

In accordance with this invention, an extract phase is recovered from zone **16** by conduit **20** comprising resinous material and aromatics either with or without waxy material which forms the particular and desired feed material of this invention. The resinous extract phase in conduit

20 is combined preferably with excess hydrogen rich gas introduced by conduit 22 and the thus formed mixture is passed to a hydrocracking zone 24. Hydrocracking zone 24 is controlled and maintained under sufficiently severe hydrocracking conditions to effect hydrocracking with or without hydroisomerization of the resin containing extract. In a specific embodiment, hydrocracking conditions include a temperature of about 750° F., a pressure of about 3,000 p.s.i.g., and a space velocity of about 0.2 v./v./hour. The total liquid product produced by and obtained from the above hydrocracking step is recovered and passed by conduit 26 to distillation zone 28 for initial separation therein, preferably under atmospheric conditions into a light naphtha fraction for withdrawal by conduit 30, a heavy naphtha fraction for withdrawal by conduit 32, a fuel oil fraction boiling in the range 375–650° F. for withdrawal by conduit 34 and a bottoms fraction having an initial boiling point of about 650° F. for withdrawal by conduit 36. The high boiling bottoms fraction boiling above the fuel oil boiling range material is withdrawn by conduit 36 and passed to zone 38 wherein it is subjected to vacuum distillation conditions sufficient to produce a plurality of separate boiling range fractions comprising in a specific example eight separate fractions similar to those identified by Table 1 above. The eight separate fractions have been diagrammatically shown as being withdrawn or recovered through conduits 40 to 54 respectively from zone 38. The separate cuts or fractions 1 to 8 identified in Table IV and withdrawn through conduits 40 to 54 respectively were each subjected to separate dewaxing steps in zones 56 to 70 respectively at dewaxing conditions in the range of from about 0° F. to about minus 80° F. It was found, however, quite unexpectedly that 0° F. dewaxing conditions could be employed to produce 0° F. pour point oil when employing a resin extract feed substantially free of waxy constituents.

It is contemplated employing, however, particularly when converting waxy feed materials, lower temperature dewaxing conditions, as low as minus 80° F., in any one or all of the dewaxing zones 56 to 70 shown so that desired pour point oil fractions may be recovered through conduits 72 to 86 respectively. In the method of this invention and particularly when employing dewaxing temperatures of the order of about minus 65° F. and lower, the waxy material separated therein and recovered from the plurality of dewaxing zones 56 to 70 by conduits 88 to 100 is passed by conduit 102 to a common deoiling zone 104 wherein, for example, a 20° F. pour point high VI oil may be separated from the waxy constituents previously separated at temperatures below minus 65° F. Generally, the deoiling step will be accomplished at a temperature of about 0° F. The high VI oil recovered in zone 104 is removed therefrom by conduit 106 with the remaining wax being recovered at 108.

Having thus presented a general description of the improved method and sequence of process steps of this invention and set forth specific examples relating thereto, it is to be understood that minor modifications may be made thereto without departing from the scope thereof and no undue restrictions are to be imposed by reasons of the specific examples presented.

We claim:

1. A method for producing lubricating oils which comprises recovering a resin extract having a viscosity at 210° F. of between about 700 SSU and about 4100 SSU of a substantially asphalt-free residual crude oil, catalytically hydrocracking the resin extract under conditions to produce naphtha boiling range material, fuel oil and a high boiling lubricating oil fraction, separating by fractionation and dewaxing the high boiling lubricating oil fraction into a plurality of oil fractions of different boiling range and thereafter combining portions of the lubricating oils of different boiling range to produce a desired lubricating oil.

2. A method for producing lubricating oil which comprises recovering a resin extract having a viscosity at 210° F. of between about 700 SSU and about 4100 SSU of a substantially asphalt-free residual crude oil comprising aromatics and resins, hydrocracking the extract phase under relatively severe hydrocracking conditions in the presence of a hydrocracking catalyst, recovering a lube oil product having an initial boiling point above about 600° F. from the hydrocracking step, separating the high boiling lube oil product under conditions to obtain a plurality of separate lube oil fractions of different boiling range and thereafter separately dewaxing the plurality of lube oil fractions to obtain a plurality of 0 to 20° F. pour point lube oils.

3. The method of claim 2 wherein the resin containing extract phase is obtained from an asphalt containing residual oil fraction by contacting the residual oil with a solvent in a plurality of steps.

4. The method of claim 1 wherein the dewaxing is carried out at a temperature selected from within the range of from about 0° F. to about minus 80° F.

5. The method of claim 1 wherein the resin extract contains waxy materials.

6. The method of claim 1 wherein the resin extract is dewaxed prior to being subjected to catalytic hydrocracking.

7. The method of claim 1 wherein the residual oil comprises a paraffinic non-asphalt residual oil.

8. The method of claim 1 wherein dewaxing of the separated lube oil fractions of different boiling range is effected at a temperature less than minus 65° F. and the waxy constituents obtained therefrom is deoiled at a temperature of about 0° F.

9. The method of claim 2 wherein a dewaxed resin extract is the feed to the hydrocracking steps and 0° F. pour point lube oils are prepared therefrom by effecting dewaxing of the hydrocracked product lube oil fractions at a temperature of about 0° F.

References Cited

UNITED STATES PATENTS

2,960,458	11/1960	Beuther et al.	208—19
2,967,146	1/1961	Manley	208—87
3,046,218	7/1962	Henke et al.	208—19
3,142,634	7/1964	Ireland et al.	208—95

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,328,287 June 27, 1967

Michael T. Smilski et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, lines 61 and 62, for "hydrocrack" read -- hydrocracking --; column 3, line 71, for "Pt=Al" read -- Pt-Al --; column 4, line 58, for "SCG/B" read -- SCF/B --; columns 5 and 6, in Table IV, ninth column, line 7 thereof, for "11" read -- 115 --; column 5, line 18, for "ot" read -- to --.

Signed and sealed this 18th day of June 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents