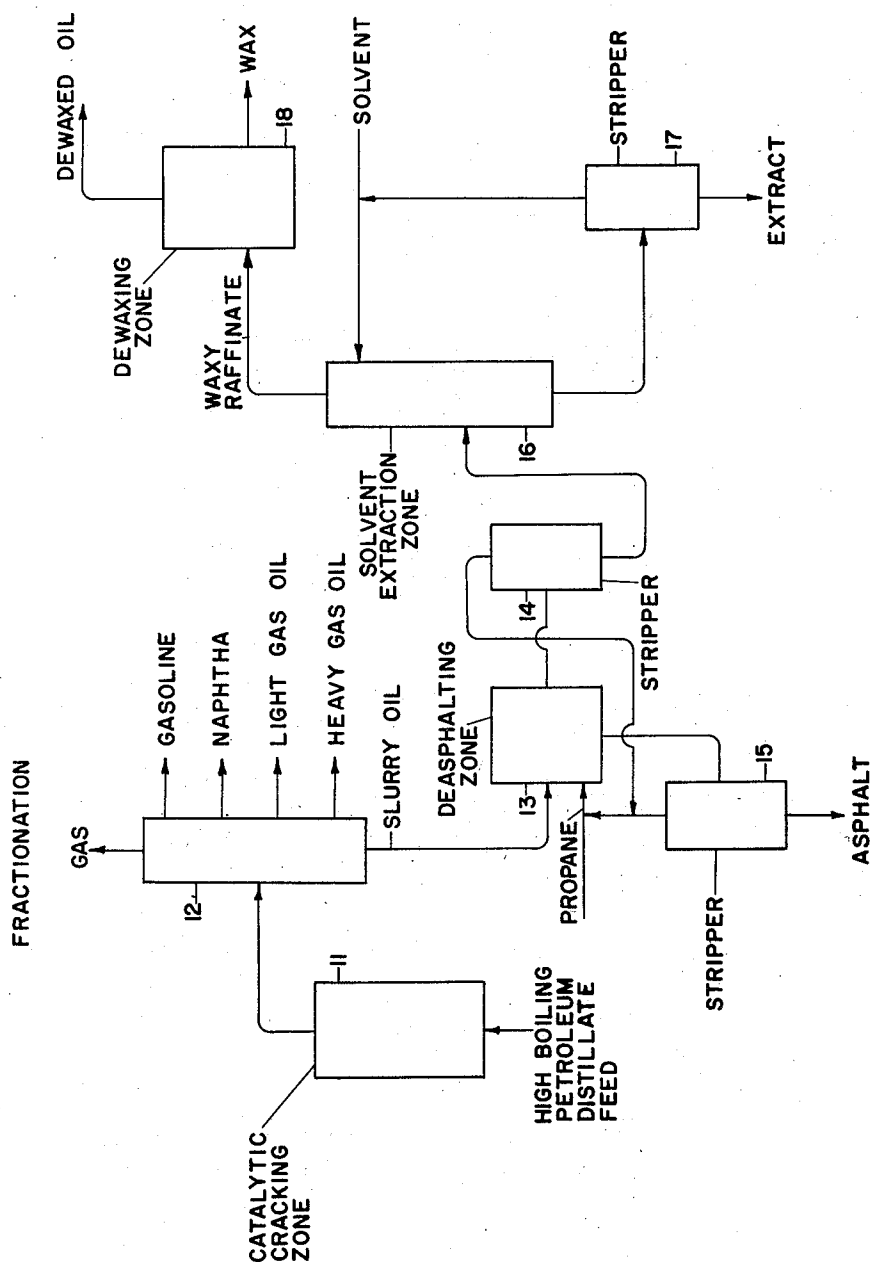


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PRODUCTION OF LUBRICATING OIL

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1

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PRODUCTION OF LUBRICATING OIL

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This invention relates to a process for producing lubricating oils, and particularly the production of mineral lubricating oils of high quality, including high viscosity index.

Heretofore, it has been the general practice to recover quality lubricating oil components from those crude oils and distillate fractions thereof in which they occur in economically recoverable proportions. It is generally recognized that considerable selection is required in order to secure proper crude stocks in adequate supply for the ever increasing demands for high quality lubricating oils. As the proportion of paraffinic crude oil available for processing decreases and the proportion of naphthenic, and particularly of mixed naphthenic and asphaltic base crudes increases, the demands on processing techniques increase in order to recover the smaller proportion of components of lubricating characteristics.

It is now common practice to recover the desirable lubricating components from various straight-run distillate oil fractions by the use of selective solvents to extract out and thereby remove the low quality components such as sulfur compounds, oxygenated compounds and aromatics, from the higher quality paraffinic hydrocarbons. However, such an attempt to separate all of the desirable components from the undesirable ones is not practical by solvent extraction because of the wide variety of types of compounds present. Furthermore, the relative solubilities of the various types present do not bear any exact correspondence to the qualities which are desired in them as lubricants.

As a consequence, oils which contain a marginal proportion of desired components of different types and which contain undesirable components of an intermediate solubility characteristic, cannot be processed economically to obtain a satisfactory yield of an oil of suitable quality. This is particularly true of certain oils of a more naphthenic and aromatic character.

It is, therefore, a principal object of the present invention to provide an improved process for the production of mineral lubricating oils. A more specific object is to provide a process whereby oils and oil fractions, which contain a relatively minor proportion of components of desirable lubricating oil characteristics admixed with other components of undesirable characteristics for a lubricating oil, of which a substantial proportion has solubility characteristics in selective solvents closely similar to those of the desirable components, are effectively processed by a combination of operations to recover the desirable components as a high quality lubricating oil composition. Still another object is to provide a process in which the difficultly separable undesirable components are modified so that an improved selective solvent separation can be effected. The foregoing objects will be better understood and others will be apparent from the detailed description of the invention, which will be made with reference to the accompanying drawing in which the sole

2

figure is a diagrammatic process flow sheet for the practice of the invention.

It has now been found that lubricating oils of high quality can be obtained from what are normally considered to be non-lube stocks of high molecular weight petroleum fractions by a process comprising: (1) a chemical conversion at an elevated temperature; (2) a deasphalting as by the use of an anti-solvent therefor, such as a light hydrocarbon, e. g. propane, and (3) a selective physical extraction of the non-lube from the lube components as by means of a selective solvent or adsorbent. The deasphaltized oil is suitably and preferably dewaxed to reduce the pour point of the oil, either before or after the dearomatization step.

Described in somewhat greater detail, lubricating oils of high quality can be obtained from higher boiling petroleum fractions which contain paraffinic, naphthenic, and both simple and condensed ring aromatic components by a combination process wherein the oil is first modified by a treating process, which effects chemical changes including one or more of dehydrogenation, cracking, isomerization and condensation with a splitting of aliphatic radicals from aromatic radicals and a condensation of aromatic radicals to form condensed aromatics and asphaltenes, as by catalytic or thermal cracking, or both, then treated with a deasphalting agent, such as a light hydrocarbon, to separate the original and the resulting asphaltic material as by precipitation therefrom, and subsequently recovering the desirable components from the deasphalted oil by extraction of the undesirable components in a selective solvent, such as phenol, furfural, nitrobenzene, sulfur dioxide, and the like. The thus deasphalted and extracted oil is then preferably dewaxed, preferably by a solvent dewaxing process, in order to recover the waxes and to lower the pour point of the oil. The dewaxed oil can be suitably clay treated, or otherwise treated chemically, as desired.

The invention is particularly applicable to the production of lubricating oils from the higher-boiling petroleum distillate fractions which are utilized as feed stock to catalytic cracking operations for the production of motor fuels, such as gasoline. By means of the catalytic conversion conditions to which the oil is subjected, there is recoverable, as by distillation from the mixture of cracked products, a higher-boiling oil fraction, representing only a small proportion of the usual cracking feed stock, which not only is deleterious in recycle cracking because of its inordinate propensity to produce coke on the catalyst, but it is suitable for the recovery of the lube oil components therefrom by deasphalting and selective extraction of the aromatic components.

The foregoing will be made clear by an examination of significant data obtained in connection with a catalytically cracked slurry oil from a commercial refinery operation, as set forth in Table I. The slurry oil was sampled under normal operating conditions of approximately 31,000 barrels per day feed to the catalytic cracking unit, and with a production of about 700 barrels per day of the slurry oil. The feed charge was a mixture of various distillate fractions and products produced in other operations of the refinery, some fractions of course being too low boiling to contain any components within the lubricating oil range. The composite feed had an API gravity of 28.2 at 60° F. and the following distillation characteristics: initial boiling point (IBP), 385° F.; 10% over at 556° F.; 50% over at 710° F.; 90% over at 883° F. and end boiling point of 1000° F.; the pour point was 80° F.

Table I.—Catalytically cracked slurry oil

(a) General properties:		
(1) API gravity.....	7.2	
(2) Pour point, ° F.....	+90	
(b) Hydrocarbon type analysis (by isopentane deasphalting and alumina and silica gel Chromatography):		
	Percent w.	Appearance
(1) Isopentane asphalt.....	20.9	black solid.
(2) Catalyst fines.....	0.64	
(3) Resins.....	7.8	red solid.
(4) Saturates.....	38.1	white solid.
(5) Monocyclic aromatics.....	0.4	
(6) Polycyclic aromatics.....	32.2	green liquid.
(c) Properties of asphalt of b(1):		
(1) Softening point, ° F.....	121.8	
(2) Penetration value.....	34.0	
(d) Properties of saturates of b(4):		
(1) n_D^{20}	1.4301.	
(2) d_4^{20}	0.797 (API 43.4 at 60° F.).	
(3) Specific dispersion at 90° F.....	100.	
(4) Pour point, ° F.....	120.	
(5) Yield of 0° F. pour point oil, % w. basis.....	65 (25% w. on slurry oil basis).	
(6) Viscosity data on 12° F. pour point oil:		
Visc. at 100° F., cs.....	22.66 (109 Saybolt).	
Visc. at 210° F., cs.....	4.54 (41.1 Saybolt).	
Viscosity index.....	131.	
(7) Viscosity index of 0° F. 125. pour point oil.		
(8) Yield of Deoiled Wax at 21. +25° F., and oil/solvent ratio of 1:3 (MEK, toluene, benzene commercial dewaxing solvent), percent w.		
(9) Melting point of wax, ° F.....	142 (mol. wt. = 460 ± 46).	
(10) Penetration of wax.....	1.9 mm. (100 g., 5 sec. at 25° C.).	
(11) Normal paraffins by urea extraction, percent w. of saturates.	27.0 (10.2% w. of slurry oil).	
(e) Properties of Polycyclics from b(6):		
(1) Pour point, ° F.....	30	
(2) Density (90/4).....	1.028	
(3) Viscosity:		
At 210° F., cs.....	6.85	
At 240° F., cs.....	4.09	

Analysis of another catalytically cracked slurry oil, obtained from a different operating refinery catalytic cracking unit, by conventional silica gel adsorption techniques with 5% benzene in petroleum ether and acetone as eluting agent for the adsorbed hydrocarbons, gave, on a deasphalted and deresined basis, 41% paraffins and naphthenes (saturates) and 59% aromatics. Dispersion data indicated the aromatics to be composed of about 5% monocyclics, 2% dicyclics, 70% tricyclics and 23% tetracyclics. Solvent extraction and distillation fractionations indicated C₂₁ to C₂₈ normal paraffins to be present as major components of the 41% saturates portion of this slurry oil.

Based upon the foregoing results, another portion of slurry oil, taken from the same catalytic cracking unit for which the data are given in Table I was processed by subjecting it to the combination of a propane deasphalting, phenol extraction, solvent dewaxing, and clay contacting. Based on the slurry oil charge, yields in the different steps were approximately as follows: asphalt 36 percent w., extract 32 percent w., slack wax 20 percent w. and finished lubricating oil 12 percent w. The finished oil had a gravity of 31.9° API, viscosity index of 107, Saybolt Universal viscosity of 132.4 seconds at 100° F., and a pour point of +25° F. Pertinent data, including processing conditions and properties of the various products, are given in Tables II–V.

Table II.—Properties of slurry oil

Gravity, API at 60° F.....	8.2
Viscosity, SU at 170° F., sec.....	72.7
210° F.....	48.5
Pour point, ° F.....	95
Average molecular weight.....	288±9

Hempel vac. distillation:

	Percent w. Overhead, Cumulative	Temp., ° F.*
5 IBP.....		465
18.5.....		650
47.0.....		780
56.5.....		805
76.3.....		850
94.9.....		989

* Converted to 760 mm. Hg pressure by U. O. P. Method E-76.

Table III.—Deasphalting slurry oil (tower process)

Propane-to-oil ratio.....	6.4
Temperature gradient, ° F.....	122–137
Recovery, slurry oil basis, percent w.:	
Deasphalted oil.....	61.2
Asphalt.....	35.1
Unaccounted for.....	3.7
Properties:	
Deasphalted oil	
Gravity, API at 60° F.....	19.4
Viscosity, SU at	
170° F., sec.....	48.9
210° F.....	40.9
Refractive index (n_D^{20}).....	1.5233
Hempel vac. distillation:	

	Percent w. Overhead, Cumulative	Temp., ° F.*
25 IBP.....		454
50.1.....		745
99.3 (EP).....		885

* Converted to 760 mm. Hg pressure by U. O. P. Method E-76.

30 Asphalt	
Gravity, Specific d_{40}^{20}	1.1696
Viscosity, SU at	
170° F., sec.....	3564
210° F., sec.....	418.2
Flash point, FMCC, ° F.....	230
Softening point, ° F.....	96
Penetration, mm./10 g.....	103
35 Penetration index.....	-3

Table IV.—Phenol extraction of deasphalted slurry oil

Run conditions (countercurrent tower extraction):	
Phenol-to-oil ratio.....	2.98.
Temperature gradient.....	160–180 (linear gradient).
Water addition:	
With phenol, percent w.....	0.647.
At bottom, percent w.....	10.7.
Recovery—	
Raffinate.....	49.5.
Extract.....	50.5.
Properties—	
Raffinate:	
Gravity, API at 60° F.....	35.3.
Viscosity, SU at	
170° F., sec.....	49.4.
210° F.....	41.9.
Flash point, COC, ° F.....	410.
Refractive index (n_D^{20}).....	1.4505.
Extract—	
Gravity, API at 60° F.....	6.0.
Viscosity, SU at	
170° F., sec.....	79.5.
210° F.....	49.2.
Flash point, COC, ° F.....	400.

Table V.—Dewaxing raffinate

Solvent.....	100% methyl ethyl ketone.
Solvent-to-oil ratio.....	3.0.
60 Filtration temperature, ° F.....	+5.
Wash solvent oil ratio.....	1½.
Wash solvent temperature, ° F.....	+5.
Recovery:	
Dewaxed oil, percent w.....	37.
Slack wax (71% soft wax, 29% deoiled wax).....	62.

For color improvement, the dewaxed oil was treated with about 30 pounds per barrel of Filtril clay at 425° F. for 15 minutes in a clay contacting unit. Properties of the finished oil are shown in the first column of Table VI. A further portion of the phenol raffinate was treated with a 15 lb./bbl. dosage of 98% sulfuric acid, followed by a 20 lb./bbl. clay treat at 300° F. The properties of the thus acid and clay treated oil are given in the second column of Table VI.

Table VI.—Properties of finished oil

	Clay Treated Oil	Acid and Clay Treated Oil
Gravity, API at 60° F.....	31.9	31.9
Viscosity, SU at 100° F., sec.....	132.4	136.1
Viscosity Index.....	107.3	111
Pour Point, ° F.....	+25	+40
Flash Point, PMCC, ° F.....	290	—
Color, NPA.....	5+	5+
Refractive Index (n_D^{20}).....	1.4604	—
Specific Dispersion.....	—	110.5

The properties of the deoiled wax of Table V are given in Table VII, including its fractionation by filtration in solvent at progressively lower temperatures. Thus it has a melting point of about 140° F., an index of refraction at 90° F. of about 1.427, and is a mixture of waxes having melting points ranging from about 117° F. to about 147° F. and most of which throughout the melting point range, by their refractive indices, are normal paraffinic hydrocarbons, with a small proportion of isoparaffinic waxes throughout the melting point range and essentially free from naphthenic and aromatic hydrocarbons.

Table VII.—Slurry oil deoiled wax

Melting point, ASTM, ° F.....	140.1
Refractive index (n_D^{90}).....	1.4272
Melting point distribution:	

Filtration Temp., ° F.	Yield, Percent w. Cumulative	M. P., ° F.	Δn_D^{90} (Fraction—n-Paraffin of same M. P.)
108.....	8.9	147	0.0025
105.....	16.6	144	0.0032
98.....	25.5	140	0.0040
91.....	40.8	140	0.0036
85.....	56.6	134	0.0059
80.....	63.0	132	0.0039
71.....	76.6	132	0.0036
60.....	87.0	127	0.0043
36.....	95.1	126	0.0043
15.....	97.9	122	0.0048
-35.....	99.2	117	0.0072
Filtrate.....	100.0	—	—

The acid and clay finished oil, for which specifications are given in Table VI, was evaluated to determine its suitability for various uses. The London Heat Test and the Continental Oxidation Test indicate good color and oxidation stability for the oil. The susceptibility of the oil for additives is shown by the Dornite Oxidation Test. The response to octyl formol, the calcium salt of the octylphenol-formaldehyde condensation product containing an average of about 4–5 octylphenol units per molecule, was excellent, particularly for iron catalyst. The finished oil was tested in a hot wire quench test to determine its utility as a metal quenching oil. Performance here was essentially the same as that of a good commercial quench oil. Since the slurry oil has already exhibited high resistance to cracking in the catalytic cracking, it was expected that it would exhibit good thermal stability. A study of its thermal stability under quenching and Martempering conditions demonstrated that it was outstanding in its resistance to cracking. Oxidation stability of the oil at a high temperature (400° F.), to determine its stability under Martempering conditions, was determined to be good. The results of the foregoing evaluations are tabulated in Table VIII.

Table VIII.—Evaluation of finished slurry oil

	Orig.	3 hr.	18 hr.	30 hr.	48 hr.
5 London Heat Test (Color)-----	D5+	D5+	D5+	D5+	6+
[Continental Oxidation Time]					
10	10 mg. time		100 mg. time		
Oxygen uptake-----	22 hr.		72 hr.		
15	24 hr.		48 hr.	72 hr.	
Viscosity Increase-----			1.5	1.9	
Sludge-----	12.1		41.7	87.5	
20	[Dornite oxidation test at 313° F., time in minutes]				
	Cu Catalyst		Fe Catalyst		
25 Finished Slurry Oil-----	40		160		
Finished Slurry Oil +0.25% w-2, 6-ditertiarybutyl-4-methylphenol-----	220		150		
Finished Slurry Oil +0.5% w-2, 6-ditertiarybutyl-4-methylphenol-----	390		240		
Finished Slurry Oil +0.02% (sulfate ash) of Octyl Formol-----	830		1,670		
30					
Hot wire quench test: Max. amp. ²					
	Finished slurry oil----- 500				
35	Refined HVI lube oil of 100 SUS visc. at 100° F----- 470				
	Refined HVI lube oil of 100 SUS visc. at 100° F.+sodium sulfonates----- 530				
40	[Thermal Stability (Temperature: Boiling Point; 80 minutes).				
	Percent Drop in SUS Visc. at 100° F.	Drop in B. P., °F.	Gas Collected, cc.		
45					
Refined Slurry Oil-----	7.6	40	400		
Refined HVI lube oil of 100 SUS visc. at 100° F-----	17.4	27	550		
Tellus 72-----	31.8	120	1,000		
50	[Oxidation test (400° F., 72 hr. 1 cm. ² iron wire/cc. oil—5 liter air/hr.).				
	Orig. Visc. SUS at 210° F.	Visc. After Oxid. SUS at 210° F.	Percent Increase		
55					
Finished Slurry Oil-----	42.7	74.95	76		
Refined Bright Stock Lube Oil (WTE)-----	88.3	154.8	75		
Refined Bright Stock Lube Oil (East Texas)-----	83.4	181.8	* 118		
60					

* 76 hour test.

It is to be seen from the foregoing that the present invention provides an effective method for the production of suitable lubricating oils of high quality, from what is normally considered to be a non-lube stock. This is accomplished by subjecting the heavy oil components within the lubricating oil boiling range, either alone or admixed with lighter oils, to cracking conditions of an elevated temperature, which may of course be done in the presence of a cracking catalyst, such as a siliceous material, including acidified clays, certain natural clays of an acidic nature, and synthetic siliceous catalyst, such as the commercial alumina/silica cracking catalysts. The

cracked products are then fractionated by distillation to separate a higher boiling fraction with a boiling range corresponding to that of at least a substantial portion of hydrocarbons of lubricating viscosity. It may of course contain some of the even lower boiling components, but it is preferred to eliminate by the distillation the larger proportion of such hydrocarbons which are outside (below) the boiling range of lubricating oil components. Thus, only a minor proportion of the material should boil below about 650° F. and it is preferable that the major portion boil above about 745° F. at 760 mm. Hg. The heavier oil fraction is then treated to effect a rejection of the asphaltic materials, as by dilution of the oil with an asphalt anti-solvent. For this purpose, the C₂-C₆ hydrocarbons are particularly suitable, such as propane, butane, isopentane, hexane and mixtures thereof. This prior deasphalting is advantageous in that it minimizes difficulties, such as associated with phase separations, in the subsequent extraction operations and at the same time makes it possible to obtain an effective separation between the lubricating components and the aromatics. The deasphalted oil is separated by selective extraction into a saturate fraction comprising the desirable non-aromatic hydrocarbons, and an aromatic fraction, predominantly polynuclear in character. This selective extraction, as already shown, can be carried out readily now by selective solvent extraction, as by use of any of the well-known selective solvents, such as phenol, furfural, nitrobenzene and liquid sulfur dioxide. On the other hand, a selective adsorbent extraction can be utilized, as already shown, using any of the well-known selective solid adsorbent agents, such as silica gel, alumina, and the like.

The non-aromatic fraction obtained by the selective extraction, called the raffinate, is suitably dewaxed, preferably by dissolving the raffinate in any of the well-known dewaxing solvents, such as methyl ethyl ketone, methyl isobutyl carbinol, acetone, and the like, and mixtures thereof with aromatic hydrocarbons, such as benzene and toluene. A suitable common commercial dewaxing solvent mixture is composed of methyl ethyl ketone (MEK), toluene and benzene. These solvents can be used together with a light hydrocarbon, such as propane, a portion of which can be evaporated from the resulting mixture to effect the required refrigeration.

In some cases, because of economies in equipment and utility requirements, as well as ease of operation, it is desirable to carry out the dewaxing operation ahead of the selective extraction. This, of course, increases the refrigeration requirements, but it reduces the amount of material to be handled in the extraction process, and particularly the higher melting materials, the waxes.

The foregoing description of the invention may be more readily understood by a description of the practice thereof made with reference to the accompanying drawing. A high boiling petroleum distillate feed, such as a vacuum flashed distillate as is conventionally used as a catalytically cracking feed stock, is conventionally cracked in the catalytic cracking zone 11. The cracked products are then fractionated by a conventional method such as by fractional distillation in a fractionation zone 12 with the separation of gas, gasoline, naphtha, light gas oil and heavy gas oil distillate fractions and a residual slurry oil comprising essentially a heavy gas oil fraction containing catalyst fines suspended therein. The slurry oil is then suitably deasphalted in a deasphalting zone 13 by the use of a suitable deasphalting agent, such as propane. The separated asphalt phase is transferred to stripper 15 wherein the propane is stripped from the asphalt as by a pressure reduction, steam stripping or the like, and the propane removed overhead is transferred to the deasphalting zone. The deasphalted oil is processed in stripper 14 to remove the propane, which is recycled to the deasphalting zone and the stripped deasphalted oil is transferred to solvent extraction zone 16 wherein it is suitably solvent extracted with a conven-

tional selective solvent, such as phenol, furfural and the like. The solvent selectively extracts aromatic components from the oil to produce an extract phase and a waxy raffinate phase. The extract phase is transferred to a stripper, or solvent recovery zone, 17 wherein the solvent is separated from the extracted aromatic components and the solvent is recycled to the solvent extraction zone. The waxy raffinate from the solvent extraction zone is dewaxed in dewaxing zone 18 by suitable conventional dewaxing process such as a solvent dewaxing process utilizing a dewaxing mixture of methyl ethyl ketone, toluene and benzene. The dewaxed oil and the wax are thereby separated and are recovered as separate products for utility as desired.

We claim as our invention:

1. The process of producing a lubricating oil comprising the steps of: cracking a substantially non-lube oil, gas oil feed stock, boiling in the boiling range of hydrocarbon lubricating oil components, at an elevated hydrocarbon-cracking temperature; fractionating a high boiling oil fraction from the cracked products boiling in the range of the boiling range of hydrocarbon lubricating oil components; deasphalting the separated fraction by mixing it with an asphalt anti-solvent to insolubilize the asphalt in the oil; selectively extracting aromatic components from non-aromatic components of the deasphalted oil; and including the step of dewaxing the high boiling oil fraction subsequent to the deasphalting step, whereby a high viscosity index lubricating oil is obtained.

2. The process of producing a lubricating oil comprising the steps of: cracking a high boiling petroleum oil stock, containing components having boiling points in the boiling range of hydrocarbon lubricating oil components, at an elevated hydrocarbon-cracking temperature; fractionating a high boiling oil fraction from the cracked products and containing components boiling in the boiling range of hydrocarbon lubricating oil components; deasphalting said oil fraction with a light C₂-₆-hydrocarbon; selectively extracting aromatic components from non-aromatics of the resulting deasphalted oil with a selective solvent therefor; and dewaxing the non-aromatics fraction resulting from the solvent extraction, whereby a high viscosity index lubricating oil is obtained.

3. The process of producing a lubricating oil and a distillate hydrocarbon wax comprising the steps of: catalytically cracking a high boiling, substantially non-lube oil, gas oil feed stock; fractionating a high boiling oil fraction including lubricating oil hydrocarbons from the cracked products; deasphalting the lubricating oil-containing fraction with a light C₂-₆-hydrocarbon; solvent extracting the deasphalted oil with a selective solvent to produce a substantially non-aromatic waxy raffinate; dewaxing the raffinate, whereby a high viscosity index lubricating oil is obtained; and deoiling the oily-wax produced in the dewaxing step, whereby a distillate wax consisting predominantly of n-paraffinic hydrocarbons and a minor amount of isoparaffinic hydrocarbons throughout its melting point range is obtained.

4. The process of producing a lubricating oil comprising the steps of: catalytically cracking a high boiling, substantially non-lube oil, petroleum oil feed stock; fractionating a high boiling oil fraction containing lubricating oil hydrocarbons from the cracked components; deasphalting the oil fraction with a C₂-₆-hydrocarbon; selectively extracting aromatic components from non-aromatic components of the deasphalted oil; and solvent dewaxing the non-aromatic raffinate separated in the preceding selective extraction step, whereby a high viscosity index lubricating oil is obtained.

5. The process in accordance with claim 4, wherein the C₂-₆-hydrocarbon is propane and the selective ex-

traction is carried out with a phenol-water selective solvent.

6. The process in accordance with claim 4, wherein the C₂-6-hydrocarbon is isopentane and the selective extraction step is carried out with a selective solid adsorbent. 5

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