

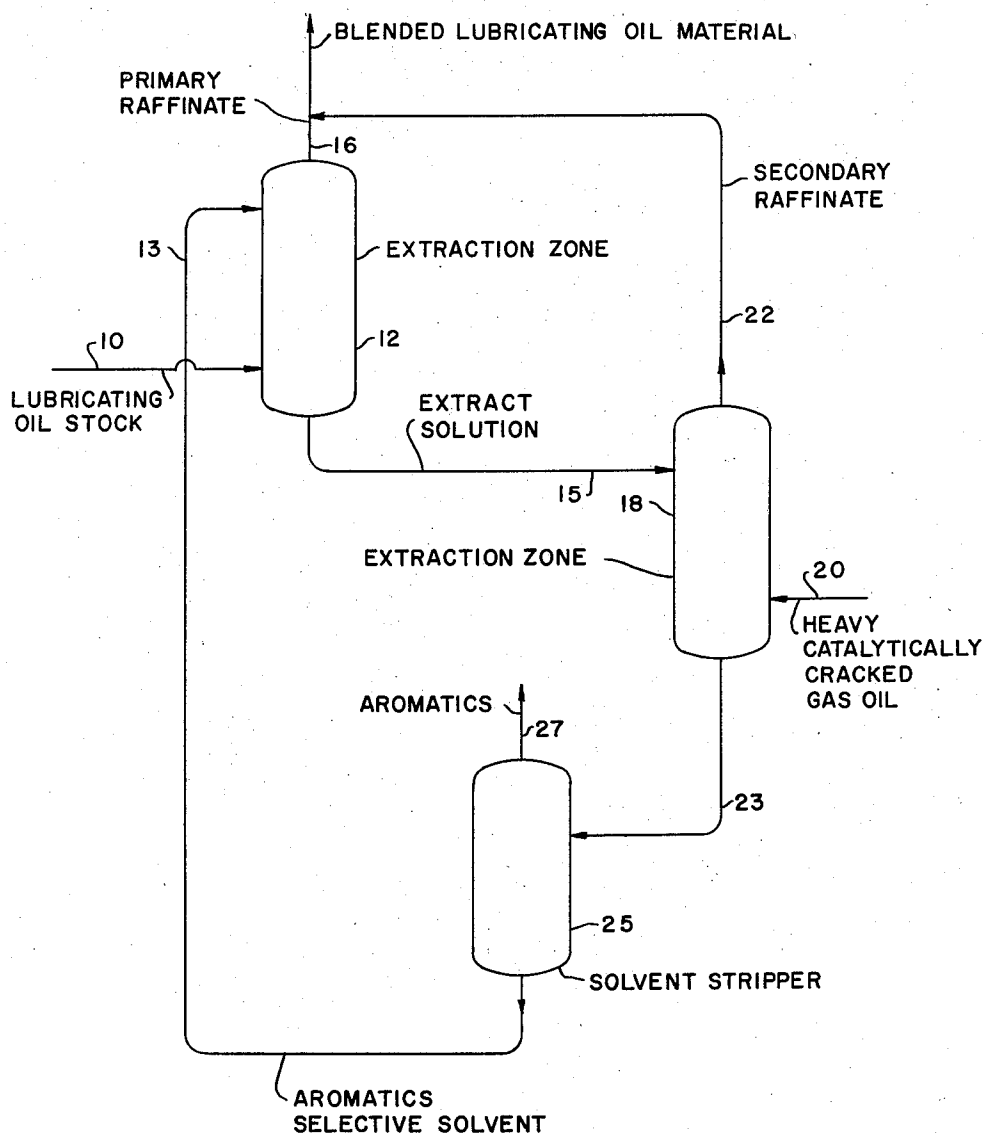
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E. L. CLARIDGE ET AL

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LUBRICATING OIL REFINING PROCESS

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INVENTORS:

ELMOND L. CLARIDGE

JOHN M. WALLIN

BY: *J. Reid Anderson*

THEIR ATTORNEY

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LUBRICATING OIL REFINING PROCESS

Elmond L. Claridge, Houston, Tex., and John M. Wallin, Pasadena, Calif., assignors to Shell Development Company, New York, N.Y., a corporation of Delaware

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This invention relates to a process for the refining of petroleum oils. It relates more particularly to an improved process for the production of lubricating oils, of catalytic cracking feed stocks and products therefrom, and of aromatic oils.

The usual practice in the art of catalytic cracking of petroleum oils to produce motor fuels is to recover the higher boiling components from a crude oil as distillate, catalytically crack this distillate feed stock to produce lighter hydrocarbons therefrom, fractionate the total product to separate the useful fractions, and to recycle the heavier material to the catalytic cracking step to increase the yield of lighter material or to subject it to a thermal cracking. A substantial portion of this heavier fraction is highly refractory to catalytic cracking, so that its recycle is a burden on the cracking operation. On the other hand, it is generally considered to be uneconomical to separate the refractory components from the more reactive components. The use of this product as an aromatic oil has the drawback that it contains a substantial proportion of paraffinic material and heretofore it has been uneconomical to separate these components.

Other valuable products of petroleum refining are the various lubricating oil fractions. These are normally produced by separating suitable high boiling fractions as distillates from the oil, as by distillation under vacuum, to minimize thermal cracking. Mixtures of the desirable lubricating oil components are usually recovered from the distillates by an extraction process, such as by physical contacting with a suitable selective solvent for the aromatic components; solvents such as phenol, cresols, furfural, nitrobenzene, and the like are used for this purpose. However, 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. As a consequence, a compromise is usually required. Maximum recovery of the desirable lubricating oil components as raffinate oil requires separation therewith of a portion of undesirable components, which are of a more or less aromatic character and of lower viscosity index. This, of course, lowers the viscosity index of the raffinate oil. On the other hand, in order to produce a raffinate having a high viscosity index, a more complete rejection of the aromatic hydrocarbons must be made and this results also in a rejection (extraction) of a substantial proportion of components which would otherwise be desirable raffinate components.

It is, therefore, a principal object of the present invention to provide an improved process for the refining of petroleum oils. A more specific object is to provide an improved process for the catalytic cracking of petroleum oils and for the solvent extraction of lubricating oil petroleum stocks. These objects will be better understood and others will be apparent from the detailed description of the invention, taken in conjunction with the drawing which is a schematic sketch of a system suitable for the production of a lubricating oil material in accordance with the process of the invention.

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It has now been found that catalytically cracked heavy gas oil is advantageously and economically separable into paraffinic and aromatic fractions, by extraction with a selective solvent extract phase from a solvent extraction of a lubricating oil stock containing paraffinic, naphthenic and aromatic components, with the recovery in a raffinate phase from this extraction of a mixture of paraffinic components derived from both the lubricating oil stock and the catalytically cracked gas oil and recovery in an extract of aromatic components also derived from both sources. The major proportion of the heavy gas oil components will, in general, have boiling points of at least about 500° F., and preferably at least about 550° F., with the 50% boiling point ranging from about 550° F. to about 800° F., while the end boiling point may be as high as 1000° to 1100° F.

In accordance with one aspect of the invention, the resulting raffinate is separated, as by distillation, into higher and lower molecular weight fractions and the higher molecular weight fraction is combined with the raffinate from the extraction of the lubricating oil stock. The lower molecular weight components, although of lower viscosity, exhibit excellent oxidation-stability properties and excellent additive response, so that their incorporation in the total lubricating oil raffinate gives an oil of improved stability characteristics. In another aspect of the invention, the recovered aromatics mixture is fractionally distilled to produce a lower boiling fraction, comprising aromatics from the catalytically cracked gas oil, and a higher boiling fraction comprising aromatics from the lubricating oil fraction and the higher boiling fraction is combined with the residual material from the catalytic cracking feed preparation to produce a suitable residual fuel oil.

Another aspect of the invention is based upon the fact that the catalytically cracked oil contains only a relatively small proportion of monocyclic aromatic hydrocarbons, which are desirable components in substantial proportion in motor lubricating oil, thus giving by ordinary solvent extraction a raffinate oil which is deficient in certain desired properties. On the other hand, in order to produce from a virgin lubricating oil stock an oil having suitable viscosity characteristics, it is usually necessary to effect the separation, as by solvent extraction, between paraffinic and aromatic components in such a manner as to remove desirable saturate components as well as desirable aromatic components in the extract phase.

Now, because of the low monocyclic aromatics content of the catalytic oil and the relatively high concentration of them in the extract phase from the extraction of the virgin stock, extraction of the catalytic oil with said extract phase results in the transfer of an effective amount of the monocyclic aromatics to the raffinate phase in this second extraction. These monocyclic aromatics are desirable in the raffinate whether it is to be utilized as a motor lubricant or as a catalytic cracking feed stock. As lubricant components, they impart cleanliness characteristics to the oil, reducing ring-sticking and carbon deposition. As catalytic cracking feed, they give rise to aliphatic and aromatic gasoline components.

The single drawing provides a flow diagram of the process of the invention when utilized to produce a lubricating oil material of improved properties. There a stream of a virgin lubricating oil stock is admitted through a line 10 to the bottom of an extraction zone 12. The lubricating oil stock passes in countercurrent flow to a solvent selective for aromatic hydrocarbons which is admitted to the other end of the zone via a line 13. An extract solution containing nearly all of the polycyclic aromatics and resins and a large portion of the monocyclic aromatics is removed from the bottom of the zone in a conduit 15. A primary raffinate enriched in paraffinic hydrocarbon leaves

the extraction zone 12 through a line 16. The extract solution is passed to a second extraction zone 18 wherein it is employed as the extractive solvent for the treatment of a heavy catalytically cracked gas oil admitted to the bottom of that zone via a line 20. A second raffinate enriched in paraffinic hydrocarbons and containing a large portion of the monocyclic aromatic hydrocarbons present in this second extraction system leaves from the top of the zone 18 via a line 22. The aromatic enriched extract phase is removed from the bottom of the zone in a conduit 23 and is introduced to a central portion of a solvent stripper 25. In the latter vessel the aromatics are removed overhead, leaving through a line 27. Stripped solvent returns to the first extraction zone through the aforementioned line 13. At least a portion of the second raffinate carried by line 22 is blended with the primary raffinate from the first extraction zone to obtain a blended product of greater oxidative stability and enhance monocyclic aromatic content compared to the oxidative stability and monocyclic aromatic content of the primary raffinate.

When the raffinate is to be utilized as a lubricating oil, it can be dewaxed, as desired, by the usual dewaxing methods, as by solvent dewaxing. However, as a catalytic cracking feed stock, the waxy hydrocarbons present, whether originating from the lube stock or the cat-cracked gas oil, or both, represent desirable cracking stock.

The relatively low content of monocyclic aromatic components in a heavy catalytically cracked gas oil is illustrated by the data in Table I, obtained by an examination of such an oil from a commercial refinery operation. The oil, containing a small amount of catalyst fines carried over from the catalytic cracking, generally referred to as cat-cracked slurry oil, was sampled under normal operating conditions of approximately 31,000 barrels per day feed to the catalytic cracking unit. The composite feed to the catalytic cracker had an API gravity of 28.2° at 60° F. and the following distillation characteristics: initial boiling point (I.B.P.), 385° F.; 10% over at 556° F.; 50% over at 710° F.; 90% over at 883° F. and an 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.....	33.1	white solid.
(5) Monocyclic aromatics.....	0.4	
(6) Polycyclic aromatics.....	32.2	green liquid.

- (c) 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, percent w..... 65 (25% w. on gas oil).
 (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.
 Viscosity index..... 131.
 (7) Viscosity index of 0° F. pour point oil..... 125.
 (8) Yield of deoiled wax at +25° F., and oil/solvent ratio of 1:3 (MEK, toluene, benzene commercial Dewaxing Solvent), percent w..... 21.
 (9) Melting point of wax, ° F..... 142 (mol wt. = 460 ± 46).
 (10) Penetration of wax..... 1.9 mm. (100 g., 5 sec. 25° C.).
 (11) Normal paraffins by urea extraction, percent w. of saturates..... 27.0 (10.2% w. of gas oil).
 (d) 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 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 50% aromatics. Dispersion data indicated the aromatics to be composed of about 5% monocyclics, 2% dicyclics, 70% tricyclics and 23% tetracyclics.

The heavy catalytically cracked gas oil, produced in the same unit while producing the slurry oil characterized in Table I, had an API gravity of 29.1 and initial and final boiling points of about 465° F. and 660° F., respectively. Further inspection gave the characteristics tabulated in Table II.

Table II.—Heavy catalytically cracked gas oil

- (1) Refractive index (70° C./D.) 1.5039
 (2) Molecular weight range 220–295
 (3) Molecular range, based on b. pt. C₁₄–C₃₀
 (4) Carbon group analysis, percent w.:
 Paraffinic carbon Ca. 52
 Naphthenic carbon Ca. 11
 Olefinic carbon Ca. 2
 Aromatic carbon Ca. 35
 (5) Chromatographic analysis:

	Percent w.	Mol wt.
(a) Saturates.....	58	291
(b) Monocyclic aromatics.....	9	
(c) Polycyclic aromatics.....	33	208
(d) Highly polar.....	3	

Although a small proportion of this heavy cat-cracked gas oil (HCCGO) is recycled to the cat-cracking operation because of its non-aromatic content, it is not a desirable feed to the cat-cracked unit because of the coke-forming polyaromatics and polar substances, so that most of it is usually used as feed to a thermal cracking process. It has not heretofore been found to be economically feasible on a large scale to separate the non-aromatics from the aromatics to provide a more suitable catalytic cracking feed stock from this heavy gas oil.

Analyses are given in Table III for a lubricating oil distillate and the complementary raffinate and extract obtained in a plant scale countercurrent solvent extraction with phenol as selective solvent. The distillate (ET 250 distillate) was a vacuum distillation fraction of an East Texas crude, selected to yield, upon extraction and dewaxing, a lubricating oil having a viscosity of 250 SUS at 100° F.

Table III

Composition	ET 250 Dist.	Raff.	Extract.
Paraffins, percent w.....	24	31	5
Naphthenes, percent w.: Non-condensed.....	29	36	8
Condensed.....	20	25	8
Aromatics, percent w.: Monocyclic.....	6	5	10
Polycyclic+resins.....	19	3	68
Molecular weight, average.....	400	411	380

The quantity and viscosity index of the saturates in the extracts and raffinates obtained by solvent extracting three different high viscosity index lube crudes and one medium viscosity index lube crude (mixture) are given in Table IV.

Table IV.—Solvent extraction of lube distillates

Distillate ^a	Mt. Poso- Coolinga, 60 SUS at 210° F. Bulk Dis- tillate ^c	ET 250 Dewaxed Dist. ^d	WTE 250 Dewaxed Dist. ^e	OC 250 Dewaxed Dist. ^f
Extract, percent w. ^b	60.6	42.0	19.0	17
Saturates lost to Ex- tract, percent w. ^b	10.7	7.7	1.3	1.1
V.I. of saturates in de- waxed dist.	59	99	116	106
V.I. of saturates in de- waxed raffinate	64	98	117	108
V.I. of saturates in de- waxed extract	33	88	87	31

^a ET, WTE and OC indicate, respectively, East Texas, West Texas Ellenburger and Oklahoma City crudes.

^b Basis dewaxed distillate.

^c Furfural extraction.

^d Phenol extraction.

^e Processed by Duosol extraction with propane-phenol-cresols solvent combination.

Although extract solutions from the extraction of different types of lube crude fractions are suitable in the practice of the invention, extract solutions resulting from the extraction of lube fractions to give high viscosity index (at least about 85) raffinates are particularly useful.

Extraction data are shown in Table V for extraction of a heavy cat-cracked gas oil with an HVI 250 extract solution. The extract solution was from plant extraction of an HVI (high viscosity index) 250 distillate (ET) to produce a 250 raffinate having a viscosity index of 88 (after dewaxing).

Table V.—Solvent extraction of heavy cat-cracked gas oil with lube extract solution

Run	1	2	3
Solvent ^a /oil ^b ratio	2	1	3
Raffinate, percent w. (basis HCCGO)	74.4	77.8	64.3
Sulfur, percent w.	0.61	0.76	0.53
Refractive index (70/D)	1.4743	1.4812	1.4720
Density (70/4)	0.8435	0.8490	0.8395
Extract:			
Sulfur, percent w.	1.64	1.70	1.49
Refractive index (70/D)	1.5634	1.5648	1.5600
Density (70/4)	0.8624	0.8508	0.9590
Total Recovery, percent w.	97.3	96.4	90.8

^a Plant phenol extract solution: contained 13.3% w. of extract oil of d_{40}^{20} 0.9553, 0.91% w. S.

^b HCCGO: percent w. S 1.12; n_D^{20} 1.4890; d_{40}^{20} 0.8696.

Although the extract solution used as solvent was quite waxy at 25° C., the extracts obtained at all solvent to oil ratios were quite fluid at 25° C., indicating that the waxy components had been transferred to the raffinate during extraction. The density of the extract in each case was greater than that of the extract obtained by stripping the phenol from the solvent extract solution and the density of the raffinate in each case was lower than that of the original gas oil.

In order to demonstrate the utility of the present process for the preparation of catalytic cracking feed stock, catalytic cracking comparisons were made between (1) a West Texas vacuum flashed distillate (heavy flasher tops, the major portion of the catalytic cracking feed stock from which the heavy cat-cracked gas oil was derived), (2) a heavy cat-cracked gas oil (HCCGO), (3) a 250 extract from the extraction of an ET 250 distillate and (4) raffinates from the extraction of the HCCGO with the 250 extract solution. From the correlations obtained between (a) space velocity and conversion, (b) coke make and conversion, and (c) gasoline make and conversion, significant illustrative data are available as shown in Table VI.

Table VI.—Catalytic cracking comparisons

Feed	Conver- sion at ^a Unit Space Vel.	Coke Make at 55% Con- version	Gasoline ^a Make at 55% Con- version
Heavy flasher tops	56	3.8	53
250 Extract	48	13	37
Cat-Cracked Gas Oil	39	13	38
Raffinate:			
At 60-70% yield ^b	48	5.9	53
At 74% yield	48	5.1	53

^a Conversion: percent v. = (100—percent v. of 400° F. + gas oil). Space velocity: weight of oil per hour per unit weight of catalyst.

^b Yield of raffinate based on HCCGO.

^c C₄ to 400° F. gasoline, percent v.

Thus, it is seen that at the same cracking severity, as indicated by constant space velocity under otherwise similar conditions, there was an increase in conversion of approximately 9 units over that for the unextracted gas oil. Although the conversion was essentially the same as for the extract, the coke make for the extracted gas oil was only about 50% (or less) of that for either the lube extract or the unextracted cat-cracked gas oil. Furthermore, at the same conversion of 55%, the gasoline yield was the same as for the flasher tops and about 40% greater than for either the lube extract or the cat-cracked gas oil. Gasoline yields at conversions ranging from about 33% to about 60% indicated the extracted cat-cracked gas oil to be equivalent to the heavy flasher tops, while those for both the lube extract and the unextracted cat-cracked gas oil showed them to be substantially inferior. In some cases raffinate yields of 100%, basis cat-cracked gas oil, of desirable cracking stock are obtainable.

Various lubricating oil extract solutions are suitable as extracting agent for the practice of the invention. Particularly suitable extract solutions are those obtained by extracting lubricating oil distillates to produce lubricating oil raffinates having a viscosity of at least about 200 SUS at 100° F., such as so-called 200, 250, 380 and heavy distillates. Expressed another way, the extract should comprise hydrocarbons having a molecular weight of at least about 300, preferably ranging from about 350 to about 500. However, extract solutions obtained in the production of so-called bright stock, by the solvent extraction of short residues, generally after deasphalting, where the molecular weights are of the order of 600 to 800, are suitable also.

Any of the usual and known selective solvents for the refinement of lubricating oils are suitable, such as furfural, phenol, nitrobenzene, sulfur dioxide, cresylic acids, sulfolane, and the like. The conditions of extraction are selected from those well known to the art and may be continuous or batchwise.

In order to demonstrate the utility of the process of this invention in the preparation of an improved lubricating oil, comparisons can be made between raffinates obtained from a catalytically cracked heavy gas oil by extraction with (1) phenol in a typical phenol extraction process and (2) a phenol extract solution obtained by the extraction of a 250 ET distillate. Upon dewaxing the resulting raffinates, and comparing them with respect to oxidation stability and susceptibility of the oil to additives, and also as to monocyclic aromatics content, it is found that the extraction of the cat-cracked heavy gas oil with the solvent-extract solution yields a superior raffinate product and that it has a higher content of monocyclic aromatic hydrocarbons than the other raffinate product.

We claim as our invention:

1. In a process for the production of a lubricating oil material from a heavy catalytically cracked gas oil and a virgin lubricating oil stock, the steps comprising (1) extracting the virgin lubricating oil stock with a solvent selective for aromatic hydrocarbons and separating an extract solution containing nearly all of the polycyclic aro-

atics and resins and a large portion of the monocyclic aromatics and a primary raffinate enriched in paraffinic hydrocarbons, (2) extracting the cracked gas oil with said extract solution and separating a second raffinate enriched in paraffinic hydrocarbons and containing a large portion of the monocyclic aromatic hydrocarbons present in this second extraction system and (3) subsequently blending at least a portion of the second raffinate with the primary raffinate to obtain a blended product of greater oxidative stability and enhanced monocyclic aromatic content compared to the oxidative stability and monocyclic aromatic content of the primary raffinate.

2. A process in accordance with claim 1, wherein the heavy catalytically cracked gas oil contains a major proportion of components having boiling points of at least about 550° F., and the extract solution is the solution resulting from the selective solvent extraction of a lubricating oil distillate fraction in which the major proportion of the components have molecular weights of at least

350 and the primary raffinate from the extraction has a viscosity index of at least about 85.

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