

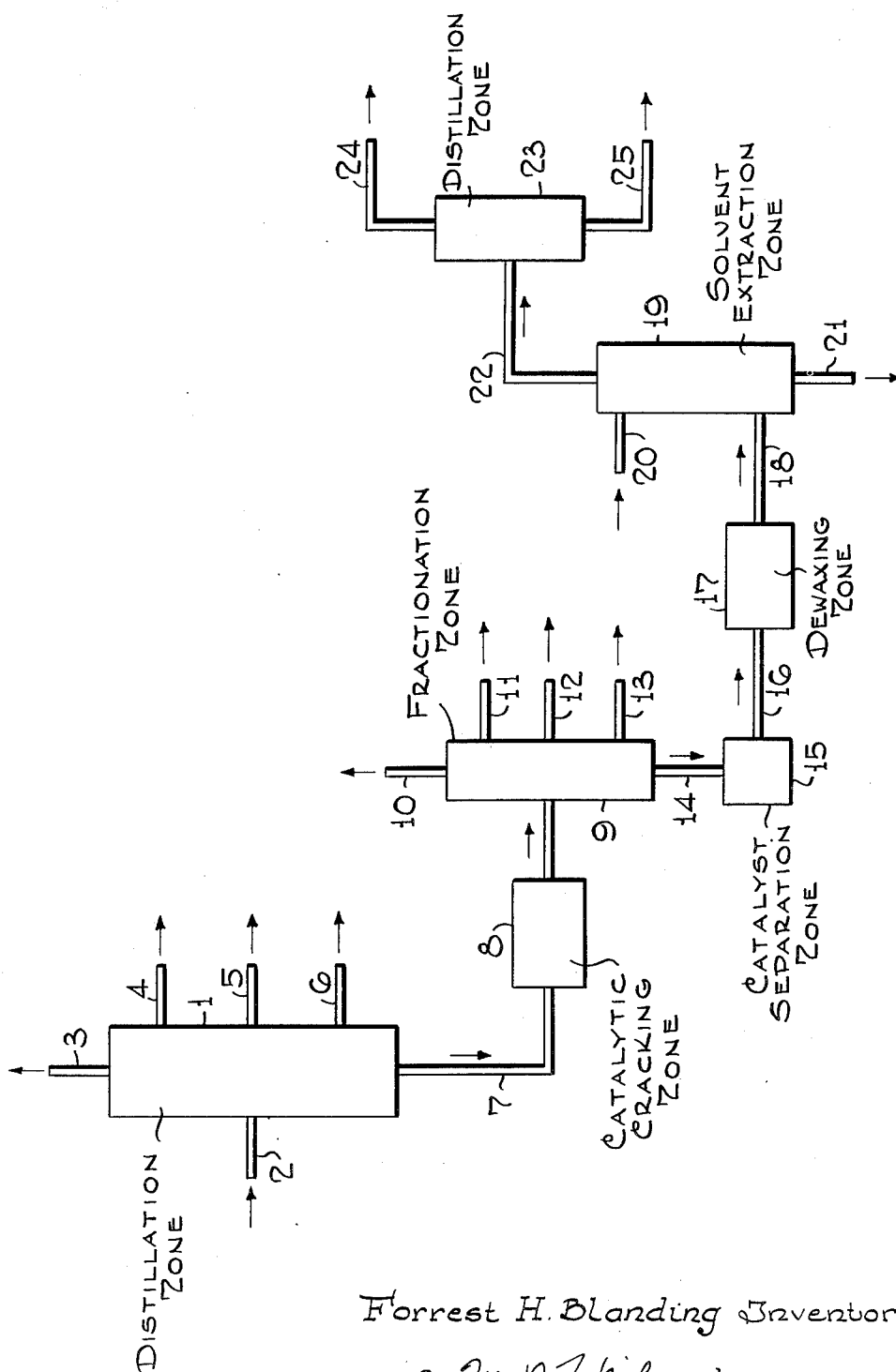
Nov. 24, 1953

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2,660,552

COMBINATION PROCESS FOR PRODUCING LUBRICATING OILS

Filed Sept. 30, 1950



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UNITED STATES PATENT OFFICE

2,660,552

COMBINATION PROCESS FOR PRODUCING LUBRICATING OILS

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Application September 30, 1950, Serial No. 187,709

4 Claims. (Cl. 196—14.42)

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This invention concerns a novel process for producing lubricating oils of particularly high quality. In accordance with this invention, a suitable petroleum feed stock is subjected to a catalytic cracking operation and thereafter a distillate boiling in the lubricating oil boiling range is separated from the cracked product. This distillate is then dewaxed and subjected to a solvent extraction operation to provide a paraffinic lubricating oil of remarkably high viscosity index.

As is generally known, an important criterion of a lubricating oil relates to the viscosity characteristics of the oil. For many applications, temperatures at which a lubricant must be employed are several hundred degrees Fahrenheit above temperatures existent prior to use of the particular mechanism. Consequently, it becomes a real problem to provide lubricating oils having the proper viscosity over the entire operating temperature range due to the decrease in viscosity of a lubricating oil as the oil becomes heated. This characteristic of a lubricating oil is generally identified as the "viscosity index" of the oil and essentially provides information as to the change in viscosity of the oil over the temperature range of 100 to 210° F. It is apparent that for many applications it is desirable to employ lubricating oils having the highest possible viscosity index.

In general, three types of chemical compounds are to be found in the lubricating oil fraction of a crude petroleum. These types of chemical compounds are paraffinic, aromatic, and naphthenic hydrocarbons. It is now known that the paraffinic hydrocarbons have by far the highest viscosity indices. Thus, paraffinic hydrocarbons have viscosity indices of about 125 to 180. Naphthenic and aromatic hydrocarbons have materially lower viscosity indices and materials rich in ring structures have viscosity indices far below 0. Because of this, paraffinic type crude oils have long been considered to be the best source of lubricating oil. However, truly paraffinic crude oils are unusual, and more often, crude oils are of the mixed base type, containing a combination of paraffinic, naphthenic and aromatic hydrocarbons, all of which are present in substantial proportions. Examples of such crude oils are Panhandle, Louisiana, Mississippi and East Texas crude oils.

Many efforts have been made to provide suitable processing methods for producing high quality, high viscosity index lubricating oils from such mixed base crude oils. In particular, it has

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been found that by employing solvent extraction processes, lubricating oils may be made more paraffinic by the selective removal of aromatic compounds. However, the solvents which may be employed for this general process, while being highly selective for the removal of condensed ring aromatic constituents, are less selective for removing naphthenic constituents and one or two ring aromatic constituents. As a result, lubricating oils obtained by solvent extraction processing are characterized by containing large proportions of naphthenic compounds and one or two ring aromatic compounds having long side chains, thus lowering the potential viscosity index of the oil.

In accordance with this invention, means have now been found for increasing the viscosity index of lubricating oils by not only selectively removing aromatic hydrocarbons, but also by selectively removing naphthenic hydrocarbons. The end result is a paraffinic lubricating oil containing only minor proportions of naphthenic and aromatic hydrocarbons and having viscosity indices approaching those of paraffinic hydrocarbons or approaching the value of 125 or higher.

The process by which this may be accomplished depends upon a combination of treating steps. In a first step of the operation, a suitable feed stock is subjected to a catalytic cracking operation. The catalytic cracking operation is effective to substantially eliminate naphthenic hydrocarbons present in the raw feed stock. Thereafter, the products of the catalytic cracking step may be subjected to solvent extraction operations so as to selectively remove the aromatic constituents.

The general nature of this process may be well understood by reference to the accompanying drawing referred to in the following description of one example by which the requisite processing may be conducted.

Referring now to the drawing illustrating the entire integral process to be employed, numeral 1 designates a crude petroleum distillation zone. A crude petroleum oil such as a mixed base crude oil is introduced to distillation zone 1 through line 2. The distillation operation is conducted to permit removal of volatile fractions overhead through line 3 and of heavier boiling products such as gasoline, kerosene and heating oils through side stream withdrawals 4, 5, 6 and so on. The heavier boiling fractions having initial boiling ranges of from 800 to 1100° F. and higher are withdrawn as a bottoms product through line 7. It is particularly contemplated that in

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the practice of this invention, distillation zone 1 be of such a nature as to provide a higher boiling fraction boiling in the range of about 700 to 1100° F., preferably as obtained by vacuum distillation operations. This fraction is then conducted to a catalytic cracking zone identified by the rectangle 8. The cracking operation to be conducted in zone 8 is of any desired type employing a catalyst such as modified natural or synthetic clay or gel type catalysts. Examples of these are montmorillonite clays, silica-alumina, silica-magnesia composites and other conventional cracking catalysts. The operation may be of a continuous or batch nature employing fixed beds, moving beds, fluidized, or suspensoid systems. The heat required for cracking may be supplied as preheat of processed materials and/or as the sensible heat of exothermically regenerated catalyst or in any other conventional manner. The cracking is carried out at temperatures of about 800 to 1000° F. and pressures of about atmospheric to 25 p. s. i. g. or higher in a manner well known. The total cracked products are removed from cracking zone 8 and are conducted to a product fractionator 9. Fractionator 9 is operated to remove lighter fractions of the cracked products through overhead 10, side streams 11, 12 and so on. A bottoms product is obtained from fractionator 9 which may be removed through line 14. In the event the cracking operation conducted in zone 8 was of a fluidized nature, the material withdrawn through line 14 will contain a small percentage of catalyst particles carried over from zone 8. In this case, it is necessary to pass the product stream of line 14 to a settler 15 or otherwise to permit separation of the liquid hydrocarbon product from the catalyst. Thus, a clarified hydrocarbon stream is removed from zone 15 through line 16. This stream is conventionally designated as "clarified cycle oil." For the purposes of this invention, the bottoms product of fractionator 9 corresponding to the stream of lines 14 or 16 boils in the range of about 700 to 1100°.

As the conduct of the process as described heretofore is generally well known to the art, no further description of this phase of the process is considered necessary. The stream of line 16 derived, as indicated, is then conducted to suitable dewaxing facilities identified by rectangle 17 in the drawing. The operation conducted in zone 17 may be chosen from any of the conventional dewaxing processes of a nature to reduce the wax content of the hydrocarbon fraction treated to any desired extent. In general, it is preferred that a solvent dewaxing operation be employed. For example, the hydrocarbon oil of line 16 may be diluted with about 2 to 4 parts per volume with a solvent such as propane or methyl ethyl ketone. The mixture of hydrocarbon oil and solvent is then heated sufficiently to secure the solution of all wax present. Thereafter, the mixture of oil and solvent is cooled to a temperature of about 25° F. to -10° F. so as to secure the crystallization of the wax present. The chilled mixture of oil, solvent and wax is then filtered to eliminate this wax, permitting removal from zone 17 through line 18 of a dewaxed hydrocarbon oil.

The dewaxed oil is then passed to a solvent extraction zone 19 wherein the oil is subjected to contact with a solvent exerting a selective solvent action towards aromatic constituents. It should be noted that, as described, the oil is dewaxed prior to solvent extraction. However, if desired, the dewaxing operation may follow the

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solvent extraction operation so that, as will be seen, the raffinate of the solvent extraction operation may be subjected to dewaxing.

As is well known, a variety of solvents may be employed to secure the desired selective removal of aromatic constituents. Thus, for example, sulfur dioxide, phenol, furfural, nitrobenzene and other solvents may be employed. While the contacting of the solvent and oil may be conducted in any desired contacting equipment of a batch or continuous nature, countercurrent treating technique is preferably employed. In such a system, the oil feed of line 18 is introduced to a countercurrent contacting tower 19 at a point near the bottom thereof. Tower 19 is provided with packing, perforated plates or equivalents to secure effective liquid-liquid contacting. A solvent such as phenol is introduced at an upper portion of the tower as through line 20. The oil passes upwardly through the tower while the solvent passes downwardly through the tower, permitting removal from the bottom of the tower of what is known as an extract phase through line 21. The extract phase will consist principally of the solvent such as phenol together with the constituents selectively extracted from the oil consisting principally of aromatic hydrocarbons. The material withdrawn from the top of tower 19 through line 22 is known as the raffinate phase and consists principally of the initial oil feed minus the aromatic constituents originally present in the feed, admixed with small proportions of the solvent employed during the contacting. The raffinate is preferably passed to a final distillation zone 23 wherein residual solvent is driven overhead through line 24 while the final lubricating oil product is removed as a bottoms product through line 25.

As described, the process of this invention, preferably necessitates the segregation of a crude petroleum oil into a heavy boiling fraction boiling in the range of about 700-1100° F. This fraction is then subjected to a catalytic cracking operation operative to substantially eliminate naphthenic hydrocarbons from the fraction. The cracked products are then fractionated to provide a clear oil boiling in the range of about 700-1100° F. This oil is then subjected to processing effective to selectively remove the aromatic constituents present in the oil. As indicated, this processing preferably entails contacting of the oil with a solvent selective for aromatic hydrocarbons. However, it is within the scope of this invention to employ equivalent operations such as contact with an adsorbent such as silica gel which is also suitable for selectively removing aromatic hydrocarbons. Either before or after the selective removal of the aromatic hydrocarbons, the oil is to be subjected to a dewaxing operation so as to eliminate a material quantity of the wax present in the oil.

As a specific example of the operation and utility of this invention, a gas oil was subjected to a fluidized catalytic cracking operation. The gas oil boiled in the range of about 650-1100° F. and was derived from a mixture of West Texas and similar types of crude oil. The products of the catalytic cracking operation were fractionated and treated to provide a clarified oil boiling in the range of 700-1100° F. This clarified oil was then subjected to contact with a selective solvent consisting of phenol containing 7% of water as a solvent modifier. Contact was carried out in a contacting tower providing 7 extraction stages while injecting 2.8% of water

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at the bottom of the tower. A 160% treat of solvent, based on feed, was employed. Data as to this operation is provided in Table I below:

*Phenol extraction of catalytic cycle stock*¹

[160% treat, 140 to 125° F., 7% H₂O in phenol, 2.8% H₂O injection, 7 extraction stages, 1 H₂O injection stage]

	Feed	Raffinate	
		Waxy topped to 700°	Dewaxed topped
Yield on feed, vol. percent.....	100	31.0	22
Inspections:			
Gravity, ° API.....	9.7	34.7	32.1
Vis. at 100° F., SSU.....	2 208	2 117	162
Vis. at 210° F., SSU.....	43.6	42.2	44.4
Vis. index.....	24	137	106
Flash.....	340	415	430
Pour.....	+95	+110	+15

¹ Clarified oil from a catalytic cracking operation.

² By extrapolation from viscosity at 210° F. and 150° F.

Referring to Table I, it will be noted that inspections of the feed and the raffinate obtained from the phenol extraction are given. In addition, data is presented as to the nature of the raffinate after having been dewaxed in a ketone dewaxing operation reducing the raffinate to a pour point of about 0°. It is to be understood that as indicated in the table, the raffinate was fractionated so as to secure the fraction boiling in the lubricating oil boiling range of about 700 to 1100° F.

It will be observed that the final dewaxed raffinate product consisted of a lubricating oil having a viscosity index of 106, indicating that the process as conducted was operative to provide a high viscosity index lubricating oil.

In this example, the initial gas oil, subjected to cracking, had a content of about 26% aromatics, 25% naphthenes, and 49% paraffinic compounds. After cracking, the clarified oil was found to contain 67% aromatic compounds and 33% non-aromatic compounds, more than 85% of the non-aromatic compounds being paraffinic in nature. This shows the substantial elimination of naphthenic compounds achieved by the catalytic cracking. Finally, after the solvent contacting, the raffinate was again analyzed and it was found that the aromatic content had been reduced to about 12%, while the non-aromatic content was 88%. Two points of particular note are to be made from this data. First, the phenol extraction operation provided a yield of final lubricating oil of about 67% based on the non-aromatic content of the oil subjected to phenol extraction. Secondly, the phenol extraction conducted was not carried out to the extent of complete aromatic removal so that by a somewhat more severe extraction operation, greater aromatic removal could have been achieved providing a higher viscosity index product. This was demonstrated by segregating the non-aromatic portion of the raffinate by silica gel treatment, after which it was determined that this portion had a viscosity index of 119.

As a further example to bring out the advantages of the process of this invention, the following considerations are presented.

An ordinary high boiling gas oil, boiling in the range of about 700 to 1100° F., may contain about 23% aromatic hydrocarbons, and 20% naphthenic hydrocarbons. Such an oil has a viscosity index of only about 65 and would not be considered a good feed material to be subjected to processing for the production of high viscosity

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lubricating oils. To demonstrate this, on phenol treating a gas oil of this type at 150° F., employing phenol containing 3% of water, injecting 3% of water into the final stage, and conducting the contacting in a tower containing four theoretical contacting stages, the following results may be secured:

	Feed			
Percent treat.....		100	200	300
Yield, vol. percent.....	100	76	67	61
V. I. (undewaxed).....	65	95	105	110

Referring to this table, it should be noted that the viscosity indexes given are for the undewaxed phenol treated raffinate. Depending upon the wax content of the treated raffinate, dewaxing would lower the reported viscosity indexes by 10 to 30 units. It is apparent from this data that phenol treating of such a gas oil would not be attractive for the production of high quality lubricating oil. This is particularly true since a phenol treat of about 200% is the maximum percent treat employed in practical commercial operations.

By contrast, however, if the gas oil referred to is subjected to the process of this invention, necessitating the catalytic cracking of this oil and the fractionation of the portion boiling in the range of 700 to 1100° F., the following phenol treating results may be obtained, employing the conditions of the preceding example:

Percent treat.....	50	100	200	300
Yield.....	67	51	47	41
V. I. (undewaxed).....	108	129	140	149

It will be noted from this table that in phenol treating the catalytically cracked gas oil a much higher viscosity index product may be achieved. In this case only a 50 or 60% phenol treat is required to produce a lubricating oil having a viscosity index of 110 contrasted to the 300% treat required in processing the virgin gas oil. In addition to this a somewhat better yield is obtained. In view of the fact that much of the cost of a commercial plant depends upon the extent treat applied, large savings in phenol treatment to achieve a given quality lubricating oil is thus possible.

What is claimed is:

1. The process of producing a lubricating oil comprising the steps of: catalytically cracking a gas oil feed stock boiling in the range of about 650° to 1100° F., fractionating an oil fraction from the cracked products boiling in the range of about 700° to 1100° F., and thereafter contacting said fraction with a selective solvent for aromatic compounds to remove aromatic compounds from the said fraction, said process including the step of dewaxing the said fraction after the catalytic cracking step, whereby a high viscosity index lubricating oil is obtained.

2. The process defined by claim 1 in which the said fraction after treatment with the said selective solvent for aromatic compounds is treated with silica gel.

3. The process defined by claim 1 in which the said gas oil contains substantial portions of aromatic, naphthenic, and paraffinic hydrocarbons.

4. The process for producing a high viscosity index lubricating oil from a gas oil feed stock containing substantial portions of aromatic, naphthenic and paraffinic hydrocarbons and boiling in the range of about 650 to 1100° F., com-

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prising the steps of catalytically cracking the said gas oil, segregating a clarified oil from the said cracking operation having a boiling range of about 700 to 1100° F., and thereafter contacting said clarified oil with about 50 to 400 volume percent of phenol, said process including the step of dewaxing the clarified oil, whereby aromatic hydrocarbons are selectively removed and a high viscosity index lubricating oil is obtained.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,025,965	Whitely -----	Dec. 31, 1935
2,070,383	Tuttle -----	Feb. 9, 1937
2,379,966	Johnson -----	July 10, 1945
2,429,875	Good et al. -----	Oct. 28, 1947
2,448,489	Hirschler -----	Aug. 31, 1948