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HIGH VISCOSITY INDEX LUBRICATING OIL

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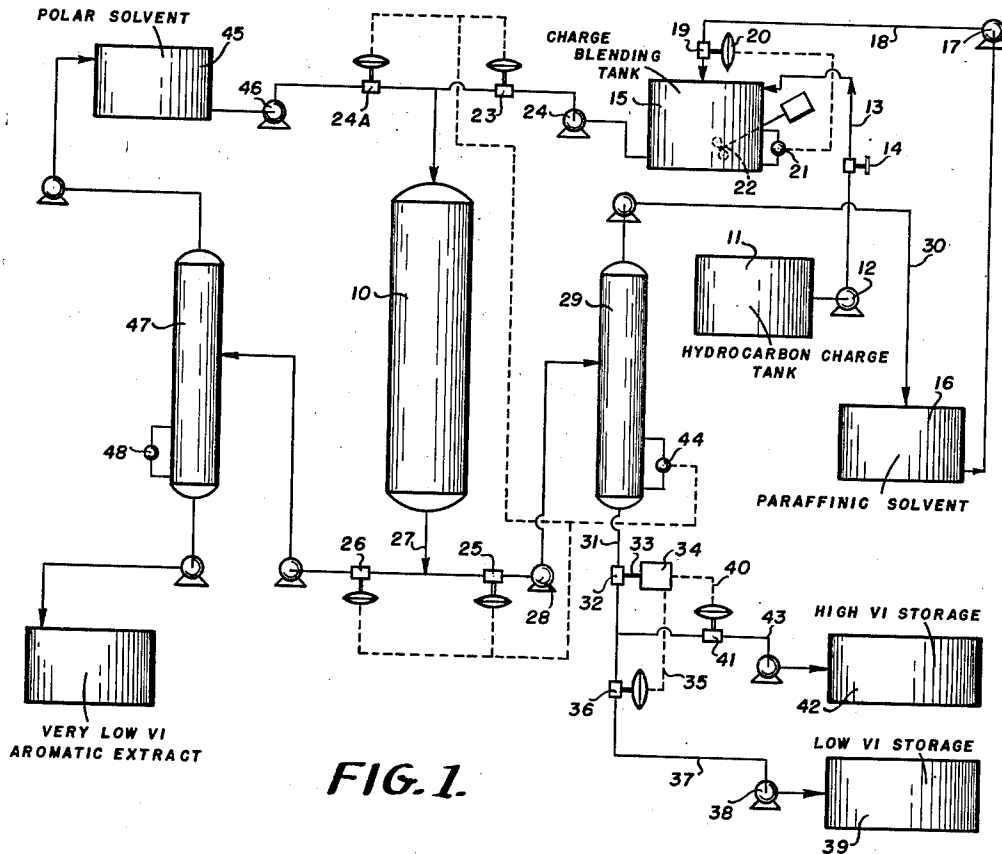


FIG. 1.

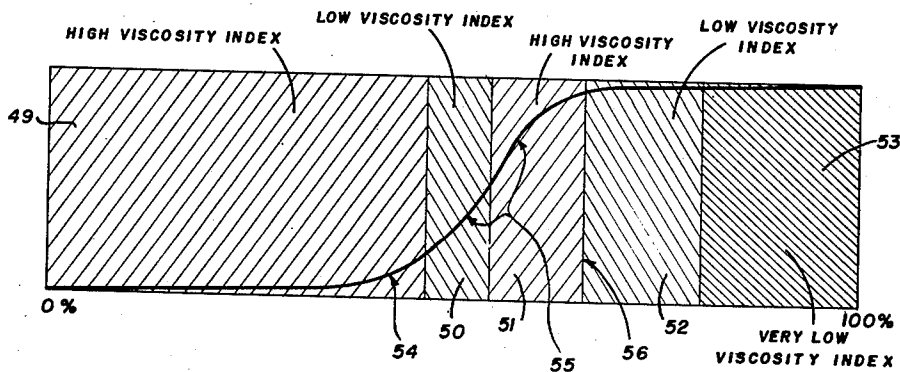


FIG. 2.

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HIGH VISCOSITY INDEX LUBRICATING OIL

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1 Claim. (Cl. 196—151)

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The present invention may be described briefly as a high viscosity index lubricating oil composition containing only components which will allow the composition to have a high viscosity index. The composition of the present invention consists of a mixture of paraffinic naphthenes and aromatic naphthenes boiling in the lubricating oil boiling range. The ratio of paraffinic naphthenes to aromatic naphthenes may be approximately 7:1.

Paraffinic and aromatic naphthenes employed in the lubricating oil of the present invention may be characterized by the following formula:

$$M(n_p^{20} - 1.4750) < 8^*$$

in which M is the average molecular weight and n_p^{20} is the index of refraction at 20° F. of said naphthenes using the sodium D line. The numeral 1.4750 is obtained by plotting the reciprocal of the molecular weight of a large number of hydrocarbons of different types against the refractive index of these hydrocarbons to obtain a series of straight lines. Each type of hydrocarbon will follow along a separate straight line but all hydrocarbons of the same type will follow in the same line. These lines are not parallel to one another and may be extended to a point corresponding to infinite molecular weight at which they converge. The point of convergence for infinite molecular weight occurs at a refractive index of 1.4750 when using the D line of sodium at a temperature of hydrocarbons of 20° C.

It has been observed that the various hydrocarbons in lubricating oil fractions have factors, as determined from the foregoing equation, which vary widely. Generally, it has been found that paraffins have values (F) or factors determined from the foregoing equation substantially less than 8 and similar values have been found for the naphthenes. On the other hand, the aromatics have values or F factors as a general rule above 8 while the aromatic naphthenes in the lubricating oil boiling range have F factors below 8. It has also been observed that the fractions having F factors or a value below 8 have high viscosity indexes while those fractions having F factors or a value above 8 have low viscosity indexes.

It has been found that lubricating oil may be separated by silica gel percolation into about 5 fractions having widely different viscosity index.

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characteristics. These various fractions each consist of a large number of compounds of a certain type. Silica gel percolation separates as a first fraction of lubricating oil a paraffinic-naphthene fraction containing from 1 to 3 naphthene rings, aromatic-naphthenes containing on the average 1 aromatic and 1 naphthenic ring, and condensed naphthenes containing 2 or more naphthene rings, naphthalenes containing 2 or more aromatic rings of which only 2 are condensed and higher condensed aromatics containing 3 or more aromatic rings of which at least 3 are condensed.

The paraffinic naphthenes may be considered as paraffinic and naphthenic fractions, whereas the aromatic naphthenes may be considered as single ring aromatic fractions which has a naphthenic ring attached thereto, as described by Watson et al. in Patent 2,643,217, issued June 23, 1953, where identical compounds are described. Terminology of a similar nature is described by Rossini in Refiner and Natural Gasoline Manufacturer, vol. 17, No. 11, November, 1938.

When F factors or values for these various compound types are obtained from lubricating oil, for example, by silica gel percolation thereof, the compounds are separated largely as shown in the following table:

Table I

Compound Type	F
Paraffinic Naphthenes.....	-4 to +6.
Condensed Naphthenes.....	8 to 10.
Aromatic Naphthenes.....	2 to 6.
Naphthalenes.....	10 to 20.
Higher Condensed Aromatics.....	Greater than 40.

In employing the F value to characterize the various components in a lubricating oil fraction for a particular stock it may be determined by assuming a constant molecular weight for the lubricating oil fraction for which the value is to be obtained. Since the molecular weights of the narrow fractions secured by silica gel percolation of the lubricating oil fraction have a maximum variation of about 10%, the F factor may have a maximum variation of about 10% due to the molecular weight change.

The paraffinic-naphthenes and aromatic-naphthenes forming the composition of the present invention may be blended together in any ratio to give the desired viscosity index. However, since both the paraffinic-naphthenes and the aromatic-naphthenes have high vis-

* "Ring Analysis of Hydrocarbon Mixtures," Report PRL-4-48, Issued by the Petroleum Refining Laboratory, The Pennsylvania State College, State College, Pa. June 7, 1948.

cosity indexes as compared to the low viscosity indexes of the other components of the lubricating oil, it will be desirable to utilize all of the aromatic-naphthenes with the paraffinic-naphthenes obtainable from a given lubricating oil fraction. It has been determined that the paraffinic-naphthenes and aromatic-naphthenes are present in lubricating oil fractions from the Panhandle field in Texas and from the Texas Coastal crudes in the approximate ratio of 7 parts by volume of paraffinic-naphthene to about 1 part by volume of aromatic-naphthene. While this is the preferred ratio, it will be understood that greater amounts of the paraffinic naphthenes may be used depending on the viscosity index of the particular aromatic-naphthene secured from a particular lubricating oil.

In order to illustrate the invention further, lubricating oil fractions obtained from Panhandle crude from the Panhandle field in Texas and from Texas Coastal crudes were subjected to contact with a column of silica gel. The lubricating oil fractions from the Panhandle crude were a dewaxed medium motor oil distillate and a finished Bright Stock. The dewaxed motor oil distillate on percolation through the column of silica gel gave the following results:

Table II

Crude Source Sample Compound Class	Panhandle Dewaxed Medium Motor Oil Distillate	
	Vol. Per-cent	VI
Paraffinic-Naphthenes.....	60	124
Condensed Naphthenes.....	10	47
Aromatic-Naphthenes.....	8	97
Naphthalenes.....	12	38
Higher Condensed Aromatics.....	10	-81

The data in the foregoing table show the percentage and the viscosity index of the various fractions. It will be noted that the paraffinic-naphthenes have a viscosity index of 124 whereas the condensed naphthenes have a viscosity index of only 47. On the other hand, the aromatic-naphthenes have a viscosity index of 97. Both of these fractions, therefore, are suitable for blending together to form the composition of the present invention. It will be noted that the ratio of paraffinic naphthenes to aromatic naphthenes is 7½:1; consequently it is desirable to blend the paraffinic naphthenes with the aromatic naphthenes in this ratio to obtain maximum yields.

The paraffinic-naphthenes in Table II contain 1 to 3 naphthene rings. The condensed naphthenes contain 3 or more rings, at least 2 of which are condensed, while the aromatic naphthenes contain on the average 1 naphthene ring and 1 aromatic ring.

A finished Bright Stock from Panhandle crude was also percolated through a silica gel column and was found to contain 60% by volume of paraffinic-naphthene having a viscosity index of 109. The Bright Stock also contained 8% by volume of naphthenes having a viscosity index of 97. These fractions may also be blended to obtain a composition in accordance with the present invention.

A medium motor oil distillate from a Texas Coastal crude was also percolated through a silica gel column and was found to contain 57% by volume of paraffinic naphthenes and 7% by volume of aromatic naphthenes, the paraffinic-

naphthenes had a viscosity index of 102 while that of the aromatic naphthenes was somewhat lower. In this particular instance, it will be noted that the ratio of paraffinic naphthenes to aromatic naphthenes is not quite 7½:1. It will be desirable, therefore, to blend the paraffinic-naphthenes and the aromatic-naphthenes in this particular ratio.

It has been mentioned that the composition of the present invention may be obtained by percolating a lubricating oil fraction through silica gel and blending the segregated fractions. The segregation of a lubricating oil fraction into components of varying viscosity index characteristics by means of silica gel may be carried out on a batch or continuous basis. The optimum ratio of hydrocarbon oil to silica gel for a batch operation is well known, a value of 1:10 by volume being typical. The silica gel is charged into a column whose ratio of diameter to length is governed by the degree of separation desired. For the type of separation described in this memorandum, a ratio of diameter to length of 1:300 is preferred.

The temperature at which the percolation is conducted may be a temperature in the range of about 60 to about 150° F. A temperature of 80° F. will give quite satisfactory results, if the viscosity of the oil is reduced by dilution with a light paraffinic solvent, such as normal heptane.

The invention will be further illustrated by reference to Fig. 1 in which a mode is described allowing the segregation of the high viscosity index fractions necessary to provide the composition of the present invention, and

Fig. 2 wherein the composition of a given lubricating oil is shown graphically with reference to the composition of the present invention.

The segregation of a lubricating oil fraction into fractions of varying viscosity index characteristics and recombination of certain fractions to obtain an oil of improved viscosity index is illustrated in Figure 1. Column 10 is filled with silica gel. The quantity of oil, which is optimum for the amount of silica gel placed in column 10, is withdrawn from hydrocarbon charge tank 11 by means of pump 12 through line 13 and valve 14 and discharged into charge blending tank 15. After valve 14 is closed, paraffinic solvent is withdrawn from tank 16 by pump 17 through line 18 and valve 19 until the desired ratio of paraffin solvent to oil for control of the viscosity of the mixture is obtained. Valve 19 is then closed and connected to controller 20 which keeps it in a closed position until activated by liquid level control 21. It is not necessary that the oil and paraffinic solvent be mixed in a tank before charging them to the silica gel column; if it is more convenient, the two may be continuously pumped in the proper ratio into a line containing an incorporator and go directly from the incorporator into the silica gel column. After the hydrocarbon and paraffin solvent have been thoroughly mixed by mixer 22, valve 23 is opened and the charge passes from the charge blending tank through pump 24 into the silica gel column. Before valve 23 is opened, valves 24A and 26 are closed and outlet valve 25 is opened. As the mixture of hydrocarbon and paraffin solvent passes through the silica gel, it is separated into various fractions, depending upon the affinity of the silica gel for the various compound types. The order of increasing affinity of silica gel for the various compound types is: paraffinic-naphthenes,

condensed naphthenes, aromatic-naphthenes, naphthalenes, and higher condensed aromatics. If both the condensed aromatic compound types are contained in the charge, both are held strongly by the silica gel in the presence of paraffinic solvent under the condition being described. The effluent from the silica gel column 10 passes through line 27 and valve 25 where it is pumped by pump 28 into fractionating column 29. This column causes a separation between the hydrocarbon and the paraffinic solvent admixed with it. The paraffinic solvent is taken as overhead through line 30 and pumped into the paraffinic solvent storage tank 16. The hydrocarbon is withdrawn as bottoms through line 31 and all, or a portion of it, passes through a refractive index indicating-recording device 32. The signal from the refractive index indicator is transmitted through line 33 into recorder 34 which converts it into an F value. The recorder 34 is adjusted for the molecular weight of the lubricating oil being percolated in column 10. Since the molecular weight of the particular narrow lubricating oil fraction recovered from column 10 will not vary greatly, the F value will not be effected substantially by any slight variation thereof. If the F value is 8 or greater, a signal is transmitted through line 35 to valve 36 causing it to open and through line 40 to valve 41 causing it to close; the material is discharged through line 37 and pump 38 into tank 39 which contains the lower viscosity index fractions. If the F factor is less than 8, a signal is transmitted through line 40 to open valve 41 and through line 35 to close valve 36. Thus, material for which F is less than 8 is passed into tank 42 through line 43. This tank 42 contains the higher viscosity index components of the lubricating oil fraction. When the charge contained in the charge blending tank 15 is depleted, liquid level control 21 causes valve 20 to be opened and a paraffinic solvent is pumped through the charge blending tank into the silica gel column 10. This solvent flushes remaining materials for which silica gel does not have a relatively strong affinity from column 10 into fractionator 29. When the paraffinic solvent no longer desorbs appreciable quantities of material from the silica gel in column 10, the liquid level in column 29 decreases and causes liquid level control 44 to close valve 23, open valve 24A, close valve 25, and open valve 26. When the valves are positioned in this manner, a polar solvent such as benzene or alcohol is withdrawn from tank 45 and forced into silica gel column 10 by pump 46 to cause the material remaining adsorbed on the silica gel to be desorbed and pass out of the column 10 through line 27 and valve 26 and be pumped into fractionator 47 which effects a separation between the polar solvent and the material which it has desorbed. When desorbing the silica gel in column 10 with a polar solvent, the output of the column 10 does not pass through a refractive index determining device because it has been found that all hydrocarbons that have to be desorbed from silica gel by using a polar solvent have F factors considerably greater than 10 or 15. Therefore, all of the material desorbed by the polar solvent will have undesirable lower viscosity index characteristics. When the silica gel in column 10 has been completely desorbed as indicated by liquid level indicator 48, all valves are closed and the silica gel is regenerated. This regeneration may be carried out in the silica gel column 10 by any one

of several methods such as by blowing with steam or hot air. The facilities for the regeneration operation are not shown or described since they are well known to the art. In some cases it may be preferable to discard the spent silica gel and recharge the column with fresh silica gel. As a matter of convenience, a second column may be connected in parallel with the first column so that another charge of hydrocarbon and paraffinic solvent may be passed through this second column while the first is being regenerated. Thus, it is possible to operate more than one silica gel column with the same auxiliary equipment and the necessary equipment for the segregation of the hydrocarbon into the desired viscosity index components is simplified.

The action of column 10 in combination with control of its operation by means of the characterization factor F may be readily understood by referring to Fig. 2 wherein the various shaded bands indicate different silica gel fractions from a lubricating oil. The horizontal axis of the bar represents the volume per cent distribution of the hydrocarbon fraction, with zero volume per cent being taken in the left of the figure and 100 volume per cent being taken at the right. The area 49 represents the paraffinic-naphthenes fraction, 50 represents the condensed naphthenes fraction, 51 represents the aromatic-naphthenes fraction, 52 represents the naphthalenes fraction, and the shaded area 53 represents the higher condensed aromatics fractions. The viscosity index characteristics of these various fractions is indicated within the rectangle representing each fraction. The line 54 indicates the separation usually obtained by phenol extraction, the material below the line being that extracted by the phenol. Increasing the severity of a conventional phenol treat causes the central portion 55 of the line 54 to move to the left, thus extracting more of the low viscosity index fraction 50 and also of the high viscosity index fraction 51 with the total effect being to increase the viscosity index of the material not taken up by the phenol. In the same manner decreasing the severity of the phenol treat causes the central portion 55 to move to the right which not only causes more of the high viscosity index fraction 51 to be included in the raffinate, but also includes more of the low viscosity index fractions 50 and 52, thus decreasing the total viscosity index of the material not taken up in the phenol. The present method of separation controlled by the characterization factor F does not allow these various fractions to be smeared into one another, and, thus, at all times allows a sharp separation of the high and low viscosity index components. The line 56 separating fractions 51 and 52 is the "natural cut point" for compounds adsorbed on silica gel between the desorbing powers of paraffinic and polar solvents, with the material to the left of this line being removed from silica gel by paraffinic solvents, and the material to the right of the line requiring polar solvents for elutriation.

From the foregoing description taken with the two figures, it will be seen that two components of the lubricating oil of the present invention may suitably be obtained by silica gel extraction. The lubricating oil may be separated into paraffinic-naphthenes and into aromatic-naphthenes by extraction with solvents but this may be a tedious, time-consuming operation.

In obtaining the paraffinic-naphthenes and aromatic-naphthenes for the lubricating composition of the present invention, it is desirable to

extract untreated lubricating oil fractions. Otherwise, if a lubricating oil is subjected to a treatment with sulfuric acid such, for example, as practiced in the petroleum refinery, or to contact with clay, such as Super Filtrol or other types well known in the refining industry, there is danger that the aromatic-naphthenes may be lost either by chemical action or by physical adsorption. While it is desirable to work with the total or untreated lubricating oil fraction, it is within the purview and scope of my invention to work with solvent extracts or raffinates which contain paraffinic-naphthenes and aromatic-naphthenes for segregation thereof for use in the composition of my invention.

The nature and objects of the present invention having been fully described and illustrated, what I desire to claim as new and useful and to secure by Letters Patent is:

A lubricating oil composition consisting of a mixture of approximately 7 parts of a paraffinic and naphthenic fraction having from 1 to 3 naphthene rings and approximately 1 part of a single ring aromatic fraction having an average of one naphthene ring and one aromatic ring

boiling in the lubricating oil boiling range, said fractions being characterized by the formula $M(n_D^{20}-1.4750)<8$ where M is the average molecular weight and n_D^{20} is the index of refraction at 20° F. for the sodium D line of said naphthenes, said fractions having viscosity indexes of 102 to 124 and 97, respectively.

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