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PREPARATION OF OILS OF HIGH SOLVENT CHARACTER

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The present invention is concerned with a process for preparing petroleum lubricating oils of increased aromaticity from naphthenic distillates.

For certain uses such as in agricultural spray oils, or in the manufacture of lubricating greases or of metal working oils, in the plasticizing of rubber and similar materials, etc., it is desirable to employ base oils that have good solvent characteristics. Generally such oils have a high density, a high refractive index, a high percentage of aromatic hydrocarbons, negligible acidity, and a pale colour. While certain crude oils such as Lagunillas will supply distillates, which by means of slight treatment with sulfuric acid or by light solvent treats, as for example with phenol or sulfur dioxide, can supply the solvent characteristics required for the uses mentioned above, there is need for a process that will provide oils of the desired properties from distillates that are relatively low in aromatic hydrocarbon content.

In accordance with the present invention, a petroleum fraction of the desired viscosity is obtained by conventional distillation processes, as for example by atmospheric distillation or vacuum distillation from a selected crude oil or from a selected distillate of wider distillation range, and a portion of this fraction is subjected to solvent extraction to obtain a solvent extract of selected aromaticity. This solvent extract is then blended with an unextracted portion of the same distillate in proportions ranging from 20 to 80 weight precent of extract and from 80 to 20% of distillate. The mixture is then subjected to a hydrofining operation to obtain the desired lubricating oil fraction having the required solvent properties.

The petroleum lubricating oil stocks that are to be treated by he process of the present invention are distillates having boiling ranges within the limits of about 500° to 900° F. and viscosities within the range of about 75 to 100 SUS at 100° F. The lubricating oil base stocks are preferably derived from naphthenic crude oils and preferably have aromatic hydrocarbon contents no higher than about 40 weight percent in C_A. Particularly suitable crudes are Webster and Tia Juana crudes. The lubricating oils which may be treated according to this invention include transformer oils, spindle oils, machine oils, base stocks for grease manufacture, cutting oils, and the like. The boiling point ranges used herein are meant to embrace the temperature at which 5 volume percent of the distillate is first distilled off and the final boiling point of the distillate.

The solvent extraction processes employed in the present invention may comprise any of the conventional methods such as furfural extraction, aniline extraction, sulfur dioxide extraction (Edeleanu process), and phenol extraction. Phenol extraction is preferred. All of these extraction processes are well-known in the art. An important aspect of the invention is that the solvent extract must not be too aromatic and preferably the mixture to be hydrofined (viz. solvent extract and distillate) should contain not more than 40% in C_A weight percent of aromatics. The aromaticity is determined by Brandes infra-red method (Brennstoff Chemie, 1956, vol. 37, page 263) and is expressed as the percentage of aromatic carbon. This is represented by the symbol C_A. The solvent extraction is carried out so as to provide a raffinate having viscosity-gravity constants within the range of 0.815 to 0.830 and preferably within the range of 0.820 to 0.825.

The hydrofining operation conducted in accordance with the present invention may be conducted under the broad and preferred conditions set forth in Table I.

TABLE I

	Broad Range	Narrow Range	Preferred Range
Temperature, ° F	400-700	400-600	520-555
Feed Rate (v./hr./v.)	0.3-5.0	0.5-3.5	0.5-2.0
Pressure (bars)	10-100	20-80	40-70
Hydrogen Treat, vol. (NTP) H_2/vol. oil	50-1000	100-500	150-300

The hydrofining catalysts that can be used in the hydrofining step include the conventional catalysts such as the oxides and/or sulfides of metals such as vanadium, chromium, manganese, iron, cobalt, nickel, molybdenum, tungsten, tin, and the like. Specific examples of such catalysts are cobalt molybdate, molybdenum oxide, nickel-tungsten sulfide, cobalt sulfide, tungsten sulfide, molybdenum sulfide, nickel sulfide, tin sulfide, nickel-cobalt molybdenum, iron-cobalt-molybdenum and the like. Preferably the catalysts are carried out on a support or suitable carrier such as alumina, magnesia, silica, zirconia, spinel, and the like. A particularly preferred support is alumina, and a particularly preferred catalyst is cobalt molybdate supported on alumina. The cobalt molybdate catalyst will comprise from 2 to 6 weight percent of cobalt oxide and from 6 to 15 weight percent of molybdenum oxide. While the catalyst may be employed in the form of a fluidized bed or slurry in the oil being treated, it is preferably employed as a fixed bed catalyst. Periodic regeneration of the catalyst bed to remove carbonaceous deposits is done by passing an oxygen-containing gas such as air, or one in which the oxygen content may be lower or higher than in air, through the catalyst bed. Regeneration is normally conducted at a temperature in the range of about 750° to 1000° F.

In the hydrofining operation the mixture of distillate and extract is contacted with a fixed bed of catalyst in a reaction vessel by continuous downward flow through the vessel. The oil feed to the vessel may be preheated by means of a furnace or other means such as heat exchangers to a temperature between about 400° and 700° F. The hydrogen may or may not be preheated. The hydrogen-containing gas may be pure hydrogen or may comprise a mixture of hydrogen and gaseous material such as light hydrocarbons. After the hydrofining step has been carried out, the treated mixture of distillate and extract is passed through a steam stripping column to remove residual hydrogen sulfide. The hydrofined product may then be subjected to conventional treatment such as redistillation under reduced pressure, contacting with alkaline metal or alkaline as metal hydroxides or oxides such as sodium hydroxide, potassium hydroxides, calcium oxide, lime or the like.

This invention is illustrated by the following example:

Example

A light lubricating oil distillate obtained from a Tia Juana crude was extracted with phenol to obtain a raffinate having a viscosity-gravity constant of 0.822.

Mixtures of the light distillate and the extract in various proportions were subjected to hydrofining treatment at about 550° F. (280° C.) using as the catalyst cobalt molybdate on alumina, the catalyst containing 3.5 weight

percent cobalt oxide and 12.5% molybdenum oxide. The feed rate was at 1 volume of oil per volume of catalyst per hour and hydrogen was supplied at the rate of 300 volumes (at NTP) per volume of oil. The characteristics of the oils obtained in comparison with those of the original distillate and the original extract are shown in Table II.

TABLE II.—TREATMENT OF LIGHT DISTILLATE FROM TIA JUANA CRUDE

Characteristics	Light Distillate	Solvent Extract	Product Obtained by Hydrofining					
			Light Distillate	Distillate and Extract Mixture				Solvent Extract
				80% Dist. 20% Extr.	60% Dist. 40% Extr.	50% Dist. 50% Extr.	40% Dist. 60% Extr.	
Acid Number	1.78	4.2	Trace	0.03	0.03	0.05		Trace
Specific Gravity (15° C.)	0.908	0.977	0.894	0.905	0.930	0.929	0.939	0.959
Centistokes Viscosity at—								
37.8° C. (100° F.)	21.49	38.40	17.67	19	20.5	23.3	19.3	27.85
50° C. (122° F.)	13.38		11.3	11.5	12.5	13.9	11.75	16
98.8° C. (210° F.)			3.31	3.21	3.4	4.4		3.80
Aniline Point, ° C	70.8	28.4	74.4	66	55.8	56.2	51.2	34
Pour Point, ° C	−42	−27	−36	−36	−39	−45	−42	
Refractive Index (20° C.)			1.497	1.507	1.520	1.520		
Aromatics, wt. percent	18.7	38.6	18	25	31.8	30.8	35	45–50
Naphthenes, wt. percent	36.1	51.4	33					
Paraffins, wt. percent	45.2	10.0	49					
Sulfur, wt. percent	1.5	3.35	0.53	1.05	1.68	1.73		2.01
Colour Hold Test: Tag-Robinson Colour—								
Initial					9¼	11½	14½	4½
After 16 hrs. (100° C.)					9¼	10	11½	2½

The Colour Hold Test was made by comparing the Tag-Robinson colour (Tag Manual for Inspection of Petroleum, page 57; colour of lubricating oils, Test No. 3) both before and after heat treatment for 16 hours at 212° F. (100° C.) in the open air. The sample was placed in a bottle 13 cm. high and 3.7 cm. in diameter to an oil level of 8.5 cm.

The product obtained by hydrofining a mixture of 40% extract and 60% distillate was quite similar to a spindle oil obtained from Lagunillas crude. The latter spindle oil had a specific gravity of 0.925, a viscosity of 21.2 centistokes at 100° F. and 12 centistokes at 122° F., an aniline point of 60° C., a pour point of −12° C., and a refractive index of 1.514 at 20° C. It contained 26% of aromatic hydrocarbon and 2% of sulfur. In the Colour Hold Test the spindle oil had a Tag-Robinson colour originally of 14 and a colour of 11½ after 16 hours at 100° C.

What is claimed is:

1. A process for preparing a lubricating oil fraction of increased armoatic hydrocarbon content which comprises:

(a) extracting a petroleum distillate having an aromatic hydrocarbon content of up to 40% in C_A weight percent and a viscosity at 100° F. within the range of 75 to 100 SUS with a selective solvent to obtain a raffinate having a viscosity-bravity constant within the range of 0.815 to 0.830, and a solvent extract;

(b) blending said extract with an unextracted portion of said distillate in proportions containing from 20 to 80 weight percent of extract and 80 to 20 weight percent of distillate;

(c) hydrofining the said mixture at a temperature in the range of 400° to 700° F. and 10 to 100 atmospheres pressure at a feed rate in the range of from 0.3 to 5 volumes of oil per volume of catalyst per hour using from 50 to 1000 volumes of hydrogen (at NTP) per volume of oil.

2. Process as defined by claim **1** wherein said viscosity-gravity constant is within the range of 0.820 to 0.825.

3. Process as defined by claim **1** wherein said mixture comprises from 35 to 50 weight percent of extract and from 65 to 50 weight percent of distillate.

4. Process as defined by claim **1** wherein said distillate is a spindle oil.

5. Process as defined by claim **1** wherein said hydrofining step is conducted in the presence of a catalyst comprising cobalt molybdate on alumina.

6. Improved lubricating oil fraction prepared by the process of claim **1**.

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