June 4, 1963

A. W. FRANCIS

SOLVENT REFINING LUBRICATING OILS WITH A DUAL SOLVENT SYSTEM

3,092,571

Filed Sept. 2, 1960

3 Sheets-Sheet 1

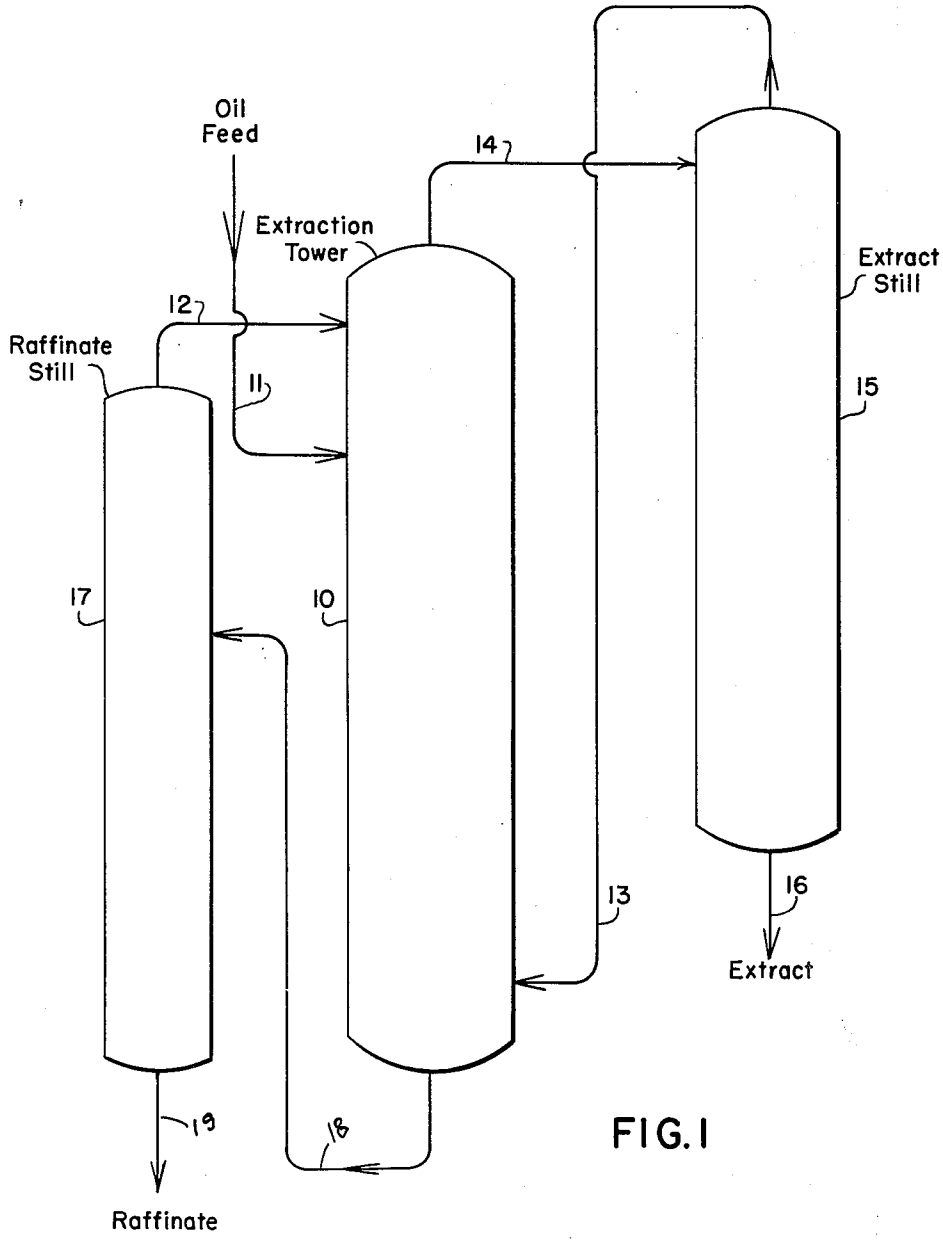


FIG. 1

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Filed Sept. 2, 1960 3 Sheets-Sheet 2

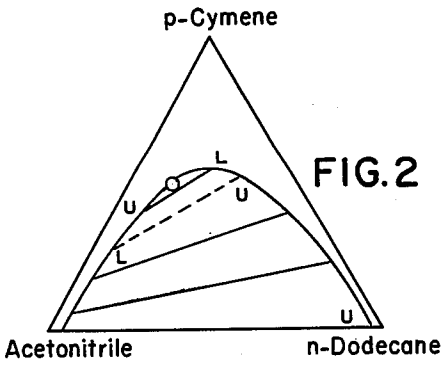


FIG. 2

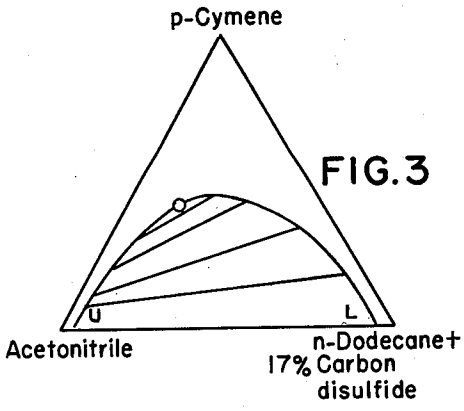


FIG. 3

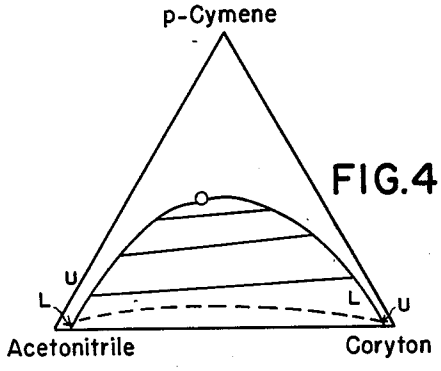


FIG. 4

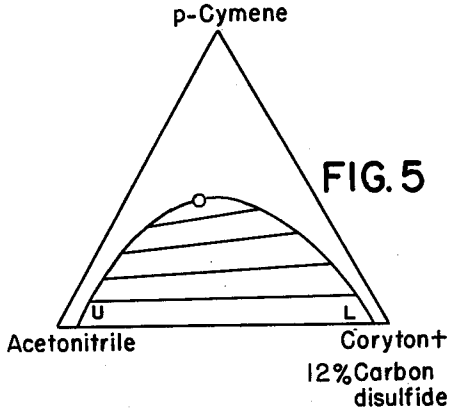


FIG. 5

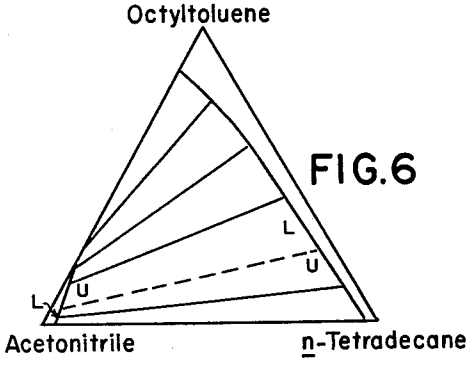


FIG. 6

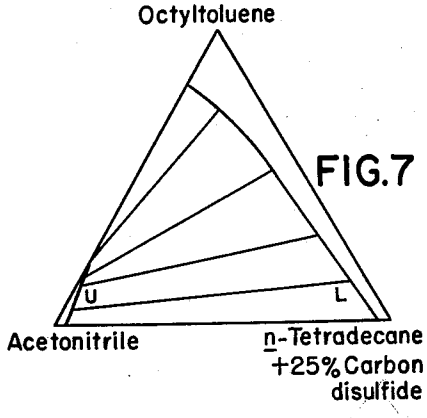


FIG. 7

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June 4, 1963 A. W. FRANCIS 3,092,571

SOLVENT REFINING LUBRICATING OILS WITH A DUAL SOLVENT SYSTEM

Filed Sept. 2, 1960 3 Sheets-Sheet 3

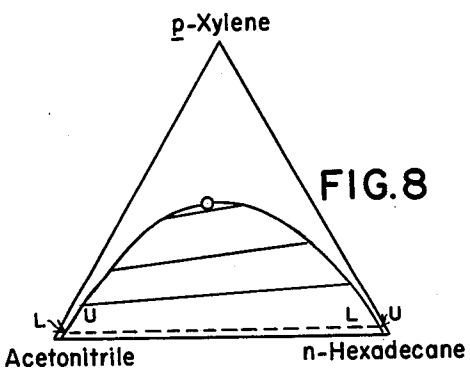


FIG.8

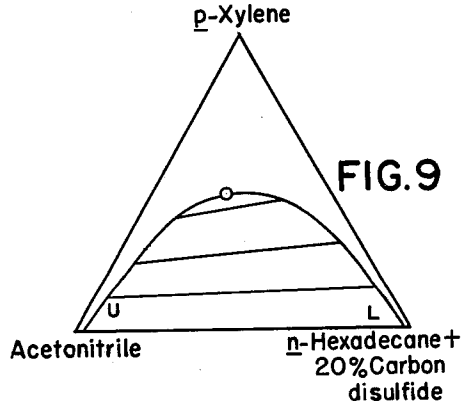


FIG.9

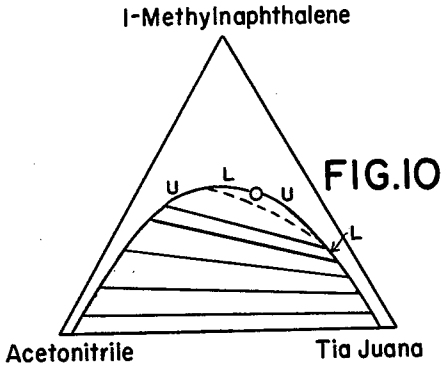


FIG.10

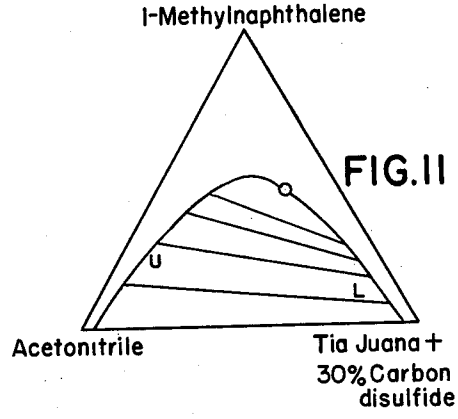


FIG.11

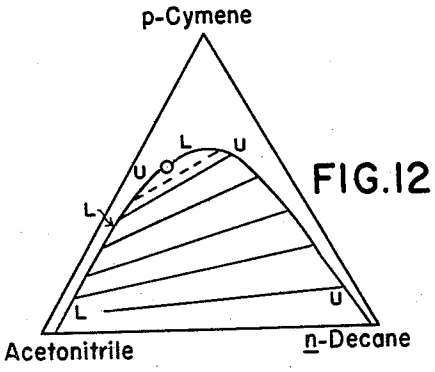


FIG.12

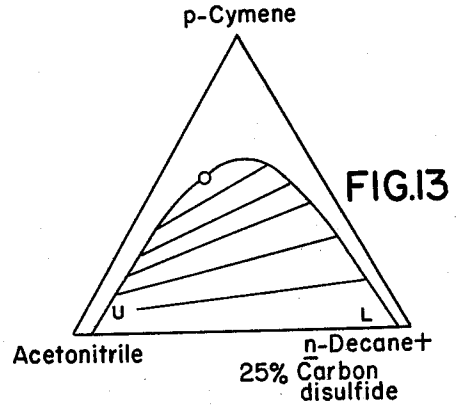


FIG.13

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United States Patent Office 3,092,571 Patented June 4, 1963

3,092,571

SOLVENT REFINING LUBRICATING OILS WITH A DUAL SOLVENT SYSTEM

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Filed Sept. 2, 1960, Ser. No. 53,737
2 Claims. (Cl. 208—324)

This invention relates to solvent refining of petroleum lubricating oils. The invention relates more particularly to the use of selective solvents found to produce highly desirable refined lubricating oils which exhibit high viscosity index, high stability toward oxidation and sunlight and high removal of wax or asphalt.

Many solvents have been proposed in the prior art for removing from lubricating oil stocks undesirable components, such as aromatics, olefins, asphaltenes, waxes and other unstable components. By such processes, stocks satisfactory for use as high quality lubricants can be upgraded to premium quality motor oils. The most common commercially adopted solvents for this purpose are furfural and a combination of propane and cresylic acid.

Acetonitrile has been proposed in the prior art as a suitable solvent for treating lubricating stocks, both with and without other cooperating solvents. The acetonitrile has been found to be highly selective and stable to heat, light and oxidation. The acetonitrile is also convenient as a selective solvent since it has a low boiling point of about 81.7° C. This low boiling point compares very favorably with the high boiling points of the alternate solvents suggested in the prior art, since a high boiling point makes quantitative recovery of the solvent difficult and requires long continued heating of the oil at high temperature with possible deterioration in oil quantity. While sulfur dioxide has a low boiling point and is known to have some solvent power, it is undesirable for use in treating lubricating stocks because it is poor in selectivity and low in solvent power.

Unfortunately acetonitrile has such a low solvent power for most oil stocks that excessive volumes of solvent are required to provide satisfactory treatment of the oil. Furthermore, the density of acetonitrile is so near to that of the oil being treated that separation or settling of the layers is slow. For example, the density of acetonitrile at 20° C. is 0.7828 which is slightly less than those of the oils being treated. As the aromatics dissolve in the acetonitrile the density of the solvent is increased to a level even closer to that of the oils being treated. These defects are serious and are sufficient to form a basis for rejecting acetonitrile as a selective solvent.

Efforts have been made to overcome the defects of acetonitrile. For example, U.S. Patents No. 2,023,375 and 2,091,078 employ in addition to acetonitrile a suitably selected diluent such as benzol, another aromatic hydrocarbon or an ether. These patents teach the combination of acetonitrile with a solubility enhancing agent. As a practical matter, however, enhancement of a solvent with low solvent power is not very effective generally except with a high concentration of enhancing agent. For example, a mixture of 42% of ethyl ether and 58% acetonitrile dissolves only 3.2% of a typical lubricating oil stock at room temperature and yet ethyl ether is a recommended enhancing agent. Other agents, such as benzene, are even less effective. Unfortunately, higher concentrations of enhancing agent decrease the selectivity considerably. The prior art does not teach the correction of the density problem of acetonitrile for use as a selective solvent in treating lubricating stocks.

I have discovered that when carbon disulfide is used with acetonitrile both prior objections of this solvent are corrected. The correct amount of carbon disulfide will provide adequate enhancement of the solvent power of acetonitrile and also provide a satisfactory solution of the density problem providing a wide enough density differential to make separation sufficiently rapid for practical purposes. Furthermore, I have found that the use of carbon disulfide and acetonitrile decreases the viscosity of the oil greatly so that separation of the layers by settling is very rapid. Besides providing these unusual results, carbon disulfide has the additional advantage of a low boiling point, 46° C., sufficiently below that of acetonitrile (81.7° C.) so that the two solvents are removed by distillation together readily and completely from both raffinate and extract, and recycled to the appropriate points in the process.

It is an object of this invention to provide an improved process for treating lubricating stocks to provide improved lubricating base oils.

It is a further object of this invention to provide an improved process for removing aromatics, olefins, asphaltenes and waxes from lubricating stocks to provide more stable and satisfactory lubricating base oils.

It is a further object of this invention to provide an improved process for treating lubricating oil stocks with acetonitrile to provide high viscosity index, stable base oils.

These and other objects of the invention will be clarified in the following detailed discussion of the invention, which is to be read in conjunction with the attached figures.

FIGURE 1 discloses a diagrammatic arrangement of apparatus for carrying out the invention.

FIGURE 2 shows a ternary diagram for p-cymene and n-dodecane with acetonitrile as a solvent medium.

FIGURE 3 shows a ternary diagram for p-cymene and n-dodecane plus 17% carbon disulfide with acetonitrile as a primary solvent medium.

FIGURE 4 shows a ternary diagram for p-cymene and Coryton gas oil with acetonitrile as a solvent medium.

FIGURE 5 shows a ternary diagram for p-cymene and Coryton gas oil plus 12% carbon disulfide with acetonitrile as a primary solvent medium.

FIGURE 6 shows a ternary diagram for octyltoluene and n-tetradecane with acetonitrile as a solvent medium.

FIGURE 7 shows a ternary diagram for octyltoluene and n-tetradecane plus 25% carbon disulfide with acetonitrile as the primary solvent.

FIGURE 8 shows a ternary diagram for p-xylene and n-hexadecane with acetonitrile as a solvent medium.

FIGURE 9 shows a ternary diagram for p-xylene and n-hexadecane plus 20% carbon disulfide with acetonitrile as the primary solvent medium.

FIGURE 10 shows a ternary diagram for 1-methylnaphthalene and Tia Juana gas oil with acetonitrile as a solvent.

FIGURE 11 shows a ternary diagram for 1-methylnaphthalene and Tia Juana gas oil plus 30% carbon disulfide with acetonitrile as the primary solvent medium.

FIGURE 12 shows a ternary diagram for p-cymene and n-decane with acetonitrile as a solvent medium.

FIGURE 13 shows a ternary diagram for p-cymene and n-decane plus 25% carbon disulfide with acetonitrile as the primary solvent.

Referring now to FIGURE 1, the lubricating oil feed is introduced into the extraction tower through the con-

duit **11** at an intermediate level. Carbon disulfide is introduced into the tower **10** through the conduit **12** at a level near the top of the tower. Acetonitrile is introduced into the tower **10** through the conduit **13** at a level near the bottom of the tower.

The extract layer is taken overhead through the conduit **14** to an extract still **15**. This extract layer is predominantly acetonitrile with small amounts of carbon disulfide, aromatics, olefins and asphaltenes. The extract is withdrawn from the bottom of the still through the conduit **16** free of solvent. The solvent, being primarily acetonitrile with a small amount of carbon disulfide is taken overhead from the still **15** through the conduit **13**. Condensing apparatus of a conventional type may be used in the conduit **13** to condense the solvent vapors.

The paraffin or stable hydrocarbons are removed from the bottom of the tower with the carbon disulfide and a small portion of acetonitrile to the raffinate still **17** through the conduit **18**. The solvent mixture of carbon disulfide and a minor portion of acetonitrile is taken overhead from the raffinate still and returned to the top portion of the extraction tower through the conduit **12**. Suitable condensing apparatus of a conventional kind may be located in the conduit **12**. The stable oil raffinate is removed from the bottom of the raffinate still **17** through the conduit **19**. This oil may be used directly as lubricating oil or may be given further treatment, such as filtration and may be improved by the addition of detergent and other additives before being marketed as highly stable, high viscosity index motor oil.

The FIGURES 2 to 13 show 12 ternary diagrams of acetonitrile, a pure aromatic hydrocarbon and a pure paraffin hydrocarbon or a commercial oil. These figures are arranged in pairs. The even numbered graphs 2, 4, 6, 8, 10, 12 have no carbon disulfide, and each contains a dashed line indicating compositions which separate into phases of equal density. Such systems do not settle, even on centrifuging, but remain as emulsions. In ternary systems the dashed lines are straight and are tie lines called "isopycnics." When a commercial oil is a component, the dashed lines are curved and are called "twin density lines," since the equal densities are not uniform. The letters U and L indicate respectively the upper and lower layers. These relations are explained in the paper, Ind. Eng. Chem., 45, 2789 (1953).

The odd numbered graphs 3, 5, 7, 9, 11 and 13 are the same systems respectively, to which a small amount of carbon disulfide has been added. The latter is distributed mostly to the hydrocarbon-rich phase, making it heavier and eliminating the isopycnic or twin density line. Two-phase compositions in these systems all settle readily.

In extractions with acetonitrile, even in combinations which do not show an isopycnic, the densities of the layers may be so close as to cause slow settling. The addition of at least a little carbon disulfide greatly accelerates the settling, illustrating the synergistic action of the solvent combination.

The amount of carbon disulfide required will vary from 1 to 50% by volume of the oil being treated, but will usually be between about 1 and 20% by volume.

Another result obtained by combining carbon disulfide with acetonitrile is an improvement in the solvent power of the acetonitrile. This is generally an improvement when treating heavy oils. The effect on selectivity is, however, generally slight.

The carbon disulfide does not act as a diluent for the acetonitrile there being a synergistic cooperative action of the commingled solvents. The two reagents are not completely miscible. The carbon disulfide first dilutes the oil and the two reagents are recycled to the extraction by different routes.

Several examples of extraction with a commercial oil

A which illustrate the effectiveness of the invention are presented in Table I herein below:

Table I

Run No.	1	2	3	4
Oil A, g.	53.14	42.65	42.65	44.75
CS_2, g.	25.2	12.6	12.6	25.2
Acetonitrile, g.	31	31	47	39
Extract:				
g.	14.67	5.95	8.83	8.53
percent	27.6	13.95	20.7	19
N_D^{20}	1.5659	1.5988	1.5886	1.5838
Raffinate:				
g.	38.40	36.7	33.82	35.88
percent	72.4	86.0	79.3	80.7
N_D^{20}	1.4838	1.4886	1.4848	1.4870
D_4^{20}			0.8782	0.8774

In the examples illustrated by FIGURES 2–13, and in Table I above, three gas oils are referred to as constituents. The properties of two of these gas oils are enumerated in Table II hereinbelow:

Table II

Gas Oil	A	Tia Juana
Specific Gravity	0.9055	0.9123
N_D^{20}	1.5057	1.5060
Molecular Weight	369	
Pour Point, ° F.	+25	−45
Color, Lovibond	1.20	8
Kinematic Viscosity:		
100° F.	51.65	
210° F.	6.23	
Saybolt Universal Viscosity:		
at 100° F.		122
at 210° F.		39.4
Viscosity Index	65	19
Viscosity Gravity Coefficient		0.873
Atomic Ratio, H/C	1.74	
Flash, ° F.		373

The properties of the third gas oil, Coryton oil, is enumerated in Table III hereinbelow:

Table III

[Gravity 46.2 A.P.I. or 0.795 density]

ASTM:		
I.B.P.	° F.	335
5%	° F.	358
10%	° F.	365
50%	° F.	404
90%	° F.	466
E.P.	° F.	500
Hydrogen, Wt.	percent	13.8
Aniline point	° F.	142.8
Diesel index		66
Aromatics	percent by volume	18
Smoke point	mm.	24.5
Luminosity No.		63
Color, Saybolt		21
Sulfur	percent	0.33
Total mercaptan Sulfur	p.p.m.	90
I.P. freeze point	° F.	−46
ASTM freeze point	° F.	−59
Wick char	mg./kg.	79
Heat of Combustion:		
B.t.u./lb.		18,625
B.t.u./gal.		123,485
N_D^{20}		1.4400

This invention has been illustrated above to provide an understanding thereof. The illustration of the invention is not intended to limit the scope of the invention. The only limitations intended are found in the attached claim.

I claim:

1. A process for removing aromatics, olefins, waxes and asphaltenes from hydrocarbon lubricating oil to provide an oil of increased stability and improved viscosity

index which comprises: introducing a lubricating oil charge stock predominantly formed of paraffin hydrocarbons and containing a minor amount of the unstable and undesired hydrocarbons into an extraction zone at an intermediate level of said zone, introducing carbon disulfide in the amount of 1–50% by volume of the oil being treated into the extraction zone near the top thereof, introducing acetonitrile into the extraction zone near the bottom thereof, taking the acetonitrile and said unstable and undesired hydrocarbons overhead from said extraction zone to an extract distillation zone, removing substantially pure acetonitrile vapor from the top of said extract distillation zone, condensing said acetonitrile vapor and introducing the liquid acetonitrile into the lower portion of said extraction zone, withdrawing the unstable hydrocarbons from the bottom of said extract distillation zone, taking the carbon disulfide and stable hydrocarbon lubricating oil from the bottom of said extraction zone to a raffinate distillation zone, removing substantially pure carbon disulfide vapor from the top of said raffinate distillation zone, condensing said carbon disulfide vapor and introducing the liquid carbon disulfide into the upper portion of said extraction zone, and withdrawing the stable hydrocarbon lubricating oil from the bottom of said raffinate distillation zone, substantially free of undesirable unstable hydrocarbons.

2. A process for removing aromatics, olefins, waxes and asphaltenes from hydrocarbon lubricating oil to provide an oil of increased stability and improved viscosity index which comprises: introducing a lubricating oil

charge stock predominantly formed of paraffin hydrocarbons and containing a minor amount of the unstable and undesired hydrocarbons into an extraction zone at an intermediate level of said zone, introducing carbon disulfide in the amount of 1–20% by volume of the oil being treated into the extraction zone near the top thereof, introducing acetonitrile into the extraction zone near the bottom thereof, taking the acetonitrile and said unstable and undesired hydrocarbons overhead from said extraction zone to an extract distillataion zone, removing substantially pure acetonitrile vapor from the top of said extract distillation zone, condensing said acetonitrile vapor and introducing the liquid acetonitrile into the lower portion of said extraction zone, withdrawing the unstable hydrocarbons from the bottom of said extract distillation zone, taking the carbon disulfide and stable hydrocarbon lubricating oil from the bottom of said extraction zone to a raffinate distillation zone, removing substantially pure carbon disulfide vapor from the top of said raffinate distillation zone, condensing said carbon disulfide vapor and introducing the liquid carbon disulfide into the upper portion of said extraction zone, and withdrawing the stable hydrocarbon lubricating oil from the bottom of said raffinate distillation zone, substanially free of undesirable unstable hydrocarbons.

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