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SEPARATION OF SOLVENT FROM RAFFINATE PHASE IN
THE SOLVENT REFINING OF LUBRICATING OIL
STOCKS WITH N-METHYL-2-PYRROLIDONE
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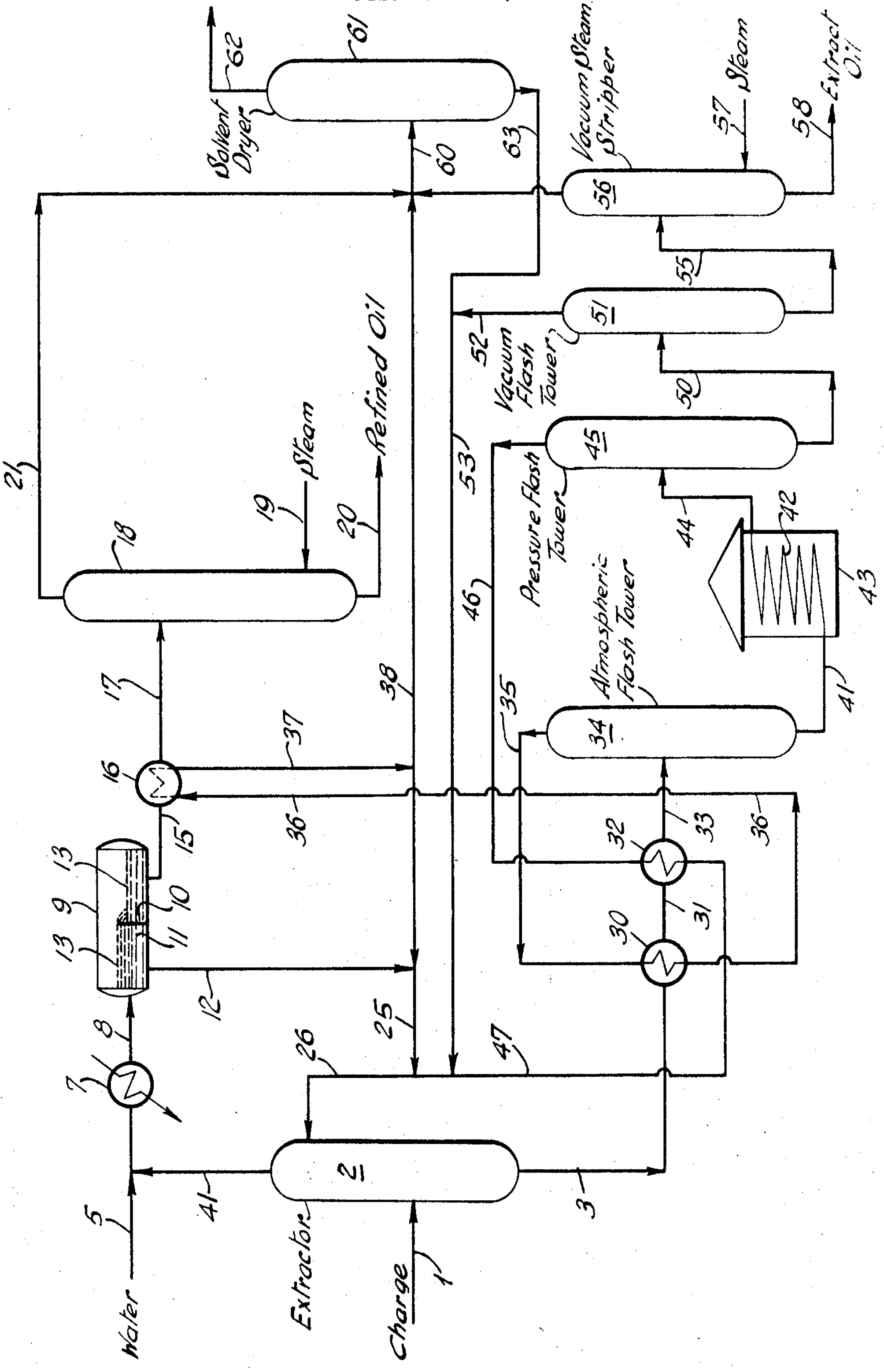

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SEPARATION OF SOLVENT FROM RAFFINATE PHASE IN THE SOLVENT REFINING OF LUBRICATING OIL STOCKS WITH N-METHYL-2-PYRROLIDONE

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U.S. Cl. 208—326 **9 Claims**

ABSTRACT OF THE DISCLOSURE

In the solvent refining of a lubricating oil charge stock for the removal of constituents having a low viscosity index and poor stability, said lubricating oil charge stock is contacted with a solvent comprising N-methyl-2-pyrrolidone effecting separation of a raffinate-mix comprising a major portion of oil with a minor portion of said solvent dissolved therein and an extract-mix comprising a major portion of said solvent with said constituents having a low viscosity index and poor stability dissolved therein. Solvent is separated from raffinate-mix by adding water in an amount of at least 2.0 weight percent of the N-methyl-2-pyrrolidone dissolved therein effecting separation of an oil phase and a wet solvent phase comprising at least 2.0 weight percent water. Refined oil is separated by distilling remaining solvent therefrom. Wet solvent is recycled with solvent of lower water content to comprise at least a part of the solvent charged in contact with said lubricating oil charge stock.

BACKGROUND OF THE INVENTION

Field of the invention

In the manufacture of lubricating oils from crude petroleum, one or more fractions containing the lubricating oil constituents are separated by distillation, usually by vacuum distillation. The raw lubricating oil fractions contain unstable naturally occurring materials which tend to form deposits or become corrosive in operating equipment as a result of heating or oxidation or both. Additionally, in the case of paraffinic oils, it is often desirable to increase the viscosity index by removing the more aromatic lower viscosity index constituents from the oil. To accomplish this it is necessary to remove or destroy a significant amount of material present in the raw stock, typically ranging from 10 to 60 percent depending on the qualities desired in the product oil. The most common way to do this is by extraction with a solvent having selectivity for the more unstable molecules which are predominantly aromatic and non-hydrocarbon materials. Prior to the advent of solvent extraction, severe treatment with concentrated sulfuric acid was commonly used to destroy these undesirable materials.

In the treatment of oils to remove unstable, corrosive, and low viscosity index constituents of oil, a substantial amount of material is removed from the charge stock, that is, an amount in excess of about 10 volume percent. This is distinctly different from decolorizing treatment in lubricating oil manufacture where only trace amounts of coloring material are removed, typically less than 1.0 percent. Here, handling losses are usually greater than the amount of material removed. Common methods used for color improvement are, for example, clay treating, mild acid treating and hy-finishing (mild hydrogenation). Such color improvement steps are often used after solvent refining. A raw stock that is only treated for color improvement is usually unsatisfactory as regards thermal and oxidating stability or viscosity index.

This invention is directed to the solvent refining of lubricating oil charge stocks with N-methyl-2-pyrrolidone hereinafter referred to as NMP. In the solvent refining process, the lubricating oil charge stock is contacted with a solvent stream comprising NMP and not more than about 1.0 weight percent water forming a raffinate-mix comprising a major portion of oil with a minor portion of NMP dissolved therein. An extract-mix is also separated comprising a major portion of solvent with the extract constituents dissolved therein. This invention relates to an improved method of separating the NMP dissolved in the raffinate-mix.

Description of the prior art

Heretofore, NMP has been known as a solvent for the separation of olefins, diolefins, and aromatic hydrocarbons. The usual method of separation of solvent from the resulting extract and raffinate-mix has been by simple distillation. Disadvantages of simple distillation are that the entire raffinate-mix must be subjected to distillation thereby subjecting the refined oil to an additional distillation step and requiring relatively large distillation facilities.

SUMMARY OF THE INVENTION

It has now been found that a major portion of the solvent may be separated from the raffinate-mix by the addition of a small amount of water thereby reducing the solubility of the NMP in the oil and separating a wet solvent phase. The remaining NMP dissolved in the raffinate-mix is readily separated by a stripping distillation for example by steam stripping or vacuum steam stripping. The wet NMP phase separated from the raffinate-mix by water dilution, although a major portion of the NMP dissolved in the raffinate-mix, is a minor portion of the total solvent employed in the extraction system. This small stream of wet solvent may be combined with other solvent streams containing less water, for example, solvent separated from the extract-mix, and the combined stream having a water content less than about 1.0 weight percent water recycled to the extraction zone.

Solvent extraction with NMP may be applied to paraffin base oils for example, oils used in the manufacture of crankcase lubricants for internal combustion engines, and naphtenic oils for example, oils used in the manufacture of turbine lubricating oils. In the case of paraffin base oils, an extraction temperature within the range of about 120 to 250° F. and preferably within the range of about 140 to 180° F. is employed and a solvent dosage within the range of about 50 to 450 percent and preferably about 100 to 340 percent is employed. The corresponding extraction temperatures and dosages when refining naphthene oils are within the range of about 50 to 200° F., preferably within the range of about 75 to 150° F. and about 50 to 300 percent, and preferably about 75 to 200 percent respectively. Significantly the dosage of solvent employed is only about half that employed with furfural, a widely used selective solvent. Typically the viscosity index of paraffin base lubricating oil charge stocks is within the range of about 40 to 105 and the viscosity index of the refined lubricating oil stock is at least ten units higher.

In accordance with this invention water in an amount within the range of about 2 to 20 weight percent and preferably about 5.0 weight percent of the NMP in the raffinate-mix is added thereto to effect separation of a wet solvent phase. The effect of water addition to a raffinate-mix containing 30 weight percent NMP produced in the treatment of a wax distillate at 195° F. is shown in the following Table I.

TABLE I

Water Added, Wt. % basis NMP	5.0	10.0	20.0
Oil layer:			
Yield, wt. percent	76.4	75.0	70.8
NMP, wt. percent	10.6	8.0	6.0
Water, wt. percent	0.4	2.0	2.7
Oil, wt. percent	89.0	90.0	91.3
RI at 71° C. of stripped oil	1.4564	1.4565	1.4565
Wet solvent layer:			
Yield, wt. percent	23.6	25.0	29.2
NMP, wt. percent	90.8	92.5	82.5
Water, wt. percent	5.0	5.9	12.7
Oil, wt. percent	4.2	1.6	4.8
RI at 71° C. of stripped oil	1.4638	1.4786	1.4641
Wt. percent NMP rejected from raffinate-mix	65	73	80

The amount of wet solvent layer separated may be increased by cooling the diluted raffinate-mix to a temperature below the treating temperature. The degree of separation of wet solvent from the refined oil phase is a function of the boiling range of the charge stock, the temperature of the raffinate-mix leaving the extractor, the amount of water added, and the degree of cooling. Generally, the lower the boiling range of the charge stock and the higher the raffinate-mix temperature leaving the extractor, the greater is the amount of solvent soluble in the oil phase. The greater the amount of water added and the lower the separation temperature, the greater is the volume of solvent removed in the separator. For a given charge stock, operating with the lowest possible raffinate-mix outlet temperature necessary to obtain the desired quality and the lowest practical wet solvent separation temperature minimizes the volume of solvent remaining in the oil phase and permits the separation of the desired amount of wet solvent with a minimum of water. The use of a minimum amount of dilution water permits the use of the largest volume of wet solvent from other processing steps while controlling the water content to 1.0 weight percent maximum. The volume of aromatic oil contained in the wet solvent is less than 0.3 weight percent of the recycled solvent which does not have any significant effect on the solvent power of the solvent recycled in the extraction step. The aromatic oil dissolved in the wet solvent is similar to the extract oil and does not build up in the recycle solvent since it is, in effect, displaced into the extract oil.

Dissolved water has a substantial effect upon the solvent refining characteristics of NMP. The effect is shown in a series of tests wherein a vacuum distillate from crude distillation referred to as a Wax Distillate 7 and having a refractive index at 70° of 1.4741 is solvent refined with NMP at constant conditions of solvent dosage and extract outlet temperature with varying amounts of water dissolved in the NMP solvent. Results of this series of tests are shown in Table II following:

TABLE II

Extraction conditions:					
Solvent dosage, volume percent	200	200	200	200	200
Extraction temperature, ° F	154	154	154	154	154
Solvent composition:					
NMP, weight percent	100.0	99.5	99.0	98.0	95.0
Water, weight percent	0	0.5	1.0	2.0	5.0
Yields:					
Refined oil, weight percent	76.0	78.0	78.5	84.6	89.4
Extract oil, weight percent	24.0	22.0	21.5	15.4	10.6
Product Tests:					
Refined oil RI at 71° C	1.4605	1.4605	1.4608	1.4620	1.4630
Extract oil RI at 70° C	1.5030	1.5072	1.5077	1.5194	1.5349
Solvent in raffinate-mix: Volume percent	16.8	--------	13.8	--------	10.6
Solvent in extract-mix: Volume percent	89.0	89.6	90.0	92.5	95.1

It will be noted that as water is added to the NMP solvent, the amount of oil extracted decreases. The effect of this reduced extraction of undesired constituents however, does not affect the refined oil quality until the amount of water in the solvent exceeds about 1.0 percent. The solvent's efficiency in producing a refined oil of high quality is then significantly affected as shown by the higher refractive index of the refined oil at solvent water levels of 2.0 and above. It will also be noted that at 0.5 percent water, a higher yield of refined oil is obtained having the same quality as the product obtained with water-free solvent as indicated by the fined oil refractive index.

A series of tests is made to show the effect of water addition and cooling on the separation of solvent from the raffinate-mix. The raffinate mix is produced by refining a Vacuum Distillate 20 with NMP at a solvent dosage of 150 volume percent, an extract-mix outlet temperature of 160° F. and a raffinate-mix outlet temperature of 190° F. The resulting raffinate-mix comprises 19.3 weight percent oil which upon stripping produces a stripped oil having a refractive index at 70° C. of 1.4605. Other portions of said raffinate-mix are treated by water addition, water addition with cooling, or by cooling alone to effect separation of two phases, an upper oil layer containing dissolved solvent and water and a bottom solvent layer containing dissolved oil and water. The yields and compositions of the resulting layers are shown in Table III following:

TABLE III

Raffinate-mix treatment:				
Water added, basis wt. percent NMP in raffinate-mix	5.0	5.0	5.0	None
Cooling from 190° F to	None	160	130	130
Separate oil phase:				
Yield, wt. percent	93.1	86.5	85.7	88.4
Oil, wt. percent	85.1	91.6	92.8	89.0
Solvent, wt. percent	14.1	8.2	6.9	11.0
Water, wt. percent	0.8	0.2	0.3	None
Stripped oil, RI at 70° C	1.4600	1.4602	1.4600	1.4605
Separated solvent phase:				
Yield, wt. percent	6.9	13.5	14.3	11.6
Oil, wt. percent	0.5	5.5	3.2	4.8
Solvent, wt. percent	87.5	88.7	91.8	95.2
Water, wt. percent	12.0	5.8	5.0	None
Stripped oil, RI at 70° C		1,4730	1,4745	1,4710

The marked effect of water upon the solvent power of NMP is shown in a series of tests made with a stock identified as Wax Distillate 40. This stock is produced by the vacuum distillation of crude oil and the stock used in this test has a refractive index at 70° C. of 1.4890. This stock is treated with NMP containing varying amounts of water from 0 to 5.0 percent at the conditions with the results shown in Table IV following:

TABLE IV

Solvent composition, volume percent:				
NMP	100.0	98.0	100.0	95.0
Water	0	2.0	0	5.0
Solvent refining condition:				
Solvent dosage, volume percent charge	200	414	107	411
Extraction temperature, ° F	200	200	200	200
Refined oil yield, volume percent	45.2	50.5	60.0	66.2
Refined oil quality: RI at 70° C	1,4622	1,4620	1,4665	1,4667

Reference to Table IV shows that the solvent efficiency of NMP is significantly reduced by the presence of water levels of 2.0 and 5.0 volume percent. This is clearly shown by the substantial increase in solvent dosage which is necessary to maintain the same refined oil refractive index which is a criterion of the quality of the refined oil. It will be noted that when 2.0 volume percent water is present, about twice as much solvent must be used to maintain the same refractive index, and when 5.0 volume percent water is present, about 4 times the amount of solvent is necessary to maintain the same refined oil refractive index.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying figure is a flow diagram of a solvent refining system employing the process of this invention. Although the figure illustrates particular arrangements of apparatus in which the invention may be practiced, it is not intended to limit the invention to the particular apparatus, materials, or conditions described.

A lubricating oil charge stock is passed through line **1** into the lower section of extractor **2**. The charge stock may be any petroleum fraction boiling above about 600° F. Extractor **2** may be any liquid-liquid contacting apparatus, suitably a tower having 4 to 10 theoretical stages such as packed, spray or sieve tray towers, or rotating disc contactor, and it may include mechanical means to improve contacting such as sonic generators or pulsing means. Solvent is introduced in the top of extractor **2** through line **26**. The charge oil constituents soluble in the solvent leave the extractor as extract-mix through line **3** at a temperature of about 185° F. with the bulk of the solvent. The charge stock constituents insoluble in the solvent leave the extractor through line **4** at a temperature of about 190° F. as raffinate-mix containing some dissolved solvent. Water in an amount of about 5 weight percent of the dissolved solvent in line **5** in injected into the raffinate-mix and the mixture passed to cooler **7**. Cooled, diluted raffinate-mix at about 130° F. is passed through line **8** to separator **9**. Separator **9** is divided into two compartments by wier **10**. Wet solvent phase having an upper level **11** is separated in the compartment behind wier **10** and is withdrawn through line **12**, and recycled with dry solvent through lines **25** and **26** to extractor **2**. Separated oil phase, having an upper level **13**, rises above interface **11**, overflows wier **10** and collects in the outlet compartment of separator **9**. Separated oil phase is withdrawn through line **15**, heated in exchanger **16** to about 350° F. and passed through line **17** to vacuum steam stripper **18**. Steam is introduced through line **17** to vacuum steam stripper **18**. Steam is introduced through line **19** into the lower portion of vacuum steam stripper **18** operated at a top tower pressure of about 11 pounds per square inch absolute stripping the remaining NMP from the oil. Distillate comprising NMP and steam is discharged through line **21**. Refined oil product is withdrawn from stripper **18** through line **20**.

Extract-mix at a temperature of about 185° F. leaving extractor **2** through line **3** is passed through exchanger **30**, line **31**, exchanger **32** and line **33** to atmospheric flash tower **34** operated at a top tower pressure of about 20 pounds per square inch absolute. Heat supplied by exchangers **30** and **32** raises the extract-mix temperature to about 418° F. and effects vaporization of about 40 percent of the solvent present in the extract-mix which is removed together with dissolved water as distillate through line **35**. This distillate stream is used to supply heat to exchanger **30**, is passed through line **36** to supply heat to exchanger **16**, and is then passed through **37**. The distillate in line **37** comprising solvent and dissolved water is then split between the solvent recycled to extractor **2** in line **25** and fed to the solvent drying tower in line **38** in a ratio controlled to maintain the maximum water desired in the recycled solvent. As the water content and volume of the stream in line **12** is increased, less of the atmospheric flash tower distillate in line **37** is included in the recycled solvent passed through line **25**. Recovery is optimized by injecting a volume of water into the raffinate-mix and controlling the temperature to which this phase is cooled in balance with the amount of atmospheric flash tower overhead split to the recycle stream.

Atmospheric flash tower bottoms of reduced solvent content is withdrawn through line **41**, through heating coil **42** in furnace **43** where it is heated to about 538° F. and discharged through line **44** to pressure flash tower **45** at a top tower pressure of about 55 pounds per square inch absolute. About 90 percent of the solvent remaining in the extract-mix is removed as dry distillate through line **46**. This stream is passed through heat exchanger **32** and line **47** to comprise the dry solvent combined with the wet solvent in line **25**. Extract oil with a small amount of remaining solvent is withdrawn through line **50** and passed at about 523° F. to vacuum flash tower **51** which is operated at a top tower pressure of about 2 pounds per square inch absolute so that about 95 percent of the remaining solvent is flashed overhead through line **52**. Since this solvent is also dry, it is passed through line **53** and combined with the dry solvent in line **47**. The extract oil containing the remaining solvent is withdrawn from the bottom of vacuum flash tower **51** through line **55** and passed at about 460° F. to vacuum steam stripper **56** operated at a top tower pressure of about 11 pounds per square inch absolute wherein it is contacted with steam introduced through line **57** to remove the remaining traces of solvent. Extract oil free of solvent is withdrawn through line **58** and discharged to storage. Distillate from vacuum steam stripper **56** comprising steam and solvent is combined with the wet streams in lines **38** and **21** and passed through line **60** to solvent dryer **61**. Solvent dryer **61** is a fractional distillation tower which is operated at a top tower pressure of about 18 pounds per square inch absolute to remove water as distillate which is discharged through line **62**. Dry solvent is withdrawn from the bottom of solvent dryer **61** through line **63** and is recycled to extractor **2** through lines **53** and **26** with the dry solvent from lines **52** and **47**.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In an embodiment of this invention, a vacuum distillate from crude distillation is refined with NMP in the apparatus and at the conditions described in connection with FIGURE 1, NMP solvent containing 1.0 weight percent water is employed at a solvent dosage of 151 volume percent. A yield of refined oil of 68.9 weight percent is obtained which refined oil has a gravity °API of 31.1, and a viscosity index before dewaxing of 105.0. A material balance showing the distribution of NMP, water, and oil fractions in the refining of 10,000 barrels per day of the Wax Distillate 20 charge stock is shown in Table V, following.

TABLE V.—MATERIAL BALANCE

[Thousands of pounds per day]

	Charge oil	NMP	Water	Refined oil	Extract oil
Oil charge	3,164		0.633		
Raffinate-mix		539	5.767	2,180	
Water injected into raffinate-mix			26.959		
Extract-mix		3,753	38.225		998
NMP charge		4,293	43.359		14
Separator solvent phase		416	22.674		14
Separator oil phase		123	10.052	2,165	
Refined oil stripper overhead		123	132.923		
Refined oil product				2,165	
Steam to refined oil stripper			122.871		
Extract atmospheric flash tower overhead		1,501	38.225		
id. Split to treating tower		813	20.685		
id. Split to solvent dryer		688	17.540		
Extract atmospheric flash tower bottoms		2,252			998
Extract pressure flash tower overhead		2,027			
Extract pressure flash tower bottoms		225			998
Extract vacuum flash tower overhead		214			
Extract vacuum flash tower bottoms		11			998
Extract vacuum steam stripper overhead		11	11.260		
Extract vacuum steam stripper bottoms					998
Steam to extractvacuum steam stripper			11.260		
Wet solvent charge to solvent dryer		822	161.723		
Solvent dryer overhead			161.723		
Solvent dryer bottoms		822			

We claim:

1. In the solvent refining of a lubricating oil charge stock produced by vacuum distillation of the crude oil for the removal of constituents having a low viscosity index and poor stability wherein said lubricating oil charge stock is contacted with a solvent stream comprising N-methyl-2-pyrrolidone and not more than about 1.0 weight percent water affecting separation of a raffinate-mix comprising a major portion of oil with a minor portion of said solvent dissolved therein and an extract-mix comprising a major portion of said solvent with said constituents having a low viscosity index and poor stability dissolved therein, the improvement which comprises:

adding water to said raffinate-mix in an amount of at least about 2.0 weight percent of the N-methyl-2-pyrrolidone dissolved therein effecting separation of an oil phase and a wet solvent phase comprising at least 2.0 weight percent water,

distilling said oil phase effecting separation of remaining solvent as distillate from bottoms comprising refined oil,

recycling at least a portion of said wet solvent in admixture with solvent of lower water content to comprise at least a part of said solvent stream comprising N - methyl - 2 - pyrrolidone and not more than about 1.0 weight percent water,

and distilling said extract mix to effect separation of a distillate comprising solvent containing less than 1.0 weight percent water and recycling said distillate as at least a part of said solvent of lower water content.

2. The method of claim 1 wherein said lubricating oil charge stock is contacted with said solvent stream at a solvent dosage within the range of about 50 to 450 percent of said lubricating oil stock.

3. The method of claim 1 wherein said lubricating oil charge stock is contacted with said solvent at a temperature within the range of about 50 to 250° F.

4. The method of claim 1 wherein said lubricating oil charge stock is a paraffinic base oil having a viscosity index within the range of about 40 to 105 and the viscosity index of said refined oil is at least 10 units higher than said lubricating oil charge stock.

5. The method of claim 1 wherein said lubricating oil charge stock is paraffin based, the solvent dosage is within the range of about 100 to 340 volume percent and the contacting temperature is within the range of about 140 to 180° F.

6. The method of claim 1 wherein said lubricating oil charge stock is naphthene based, the solvent dosage is within the range of about 75 to 200 volume percent and the contacting temperature is within the range of about 75 to 150° F.

7. The method of claim 1 wherein said raffinate-mix is separated at a first temperature within the range of 50 to 250° F. and said oil phase is separated from said wet solvent at a second temperature below said first temperature.

8. The method of claim 1 wherein the amount of water added to said raffinate-mix is within the range of about 2 to 20 weight percent of the N-methyl-2-pyrrolidone dissolved therein.

9. The method of claim 1 wherein the amount of water added to said raffinate-mix is about 5 weight percent of the N-methyl-2-pyrrolidone dissolved therein.

References Cited

UNITED STATES PATENTS

2,923,680	2/1960	Bushnell	208—321
2,963,427	12/1960	Nevitt	208—326

FOREIGN PATENTS

610,414	12/1960	Canada.

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,470,089 **Dated** September 30, 1969

Inventor(s) Herbert C. Morris and John I. Nixon

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 7, "71°C." should read --70°C.--; column 3, line 11, "71°C." should read --70°C.--; column 3, line 45, "The" should read --This--; column 3, line 63, "71°C." should read --70°C.--; column 4, line 13, after "cent" insert --solvent, and 80.7 weight percent--.

SIGNED AND
SEALED
JAN 27 1970

(SEAL)
Attest:

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Attesting Officer

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Commissioner of Patents