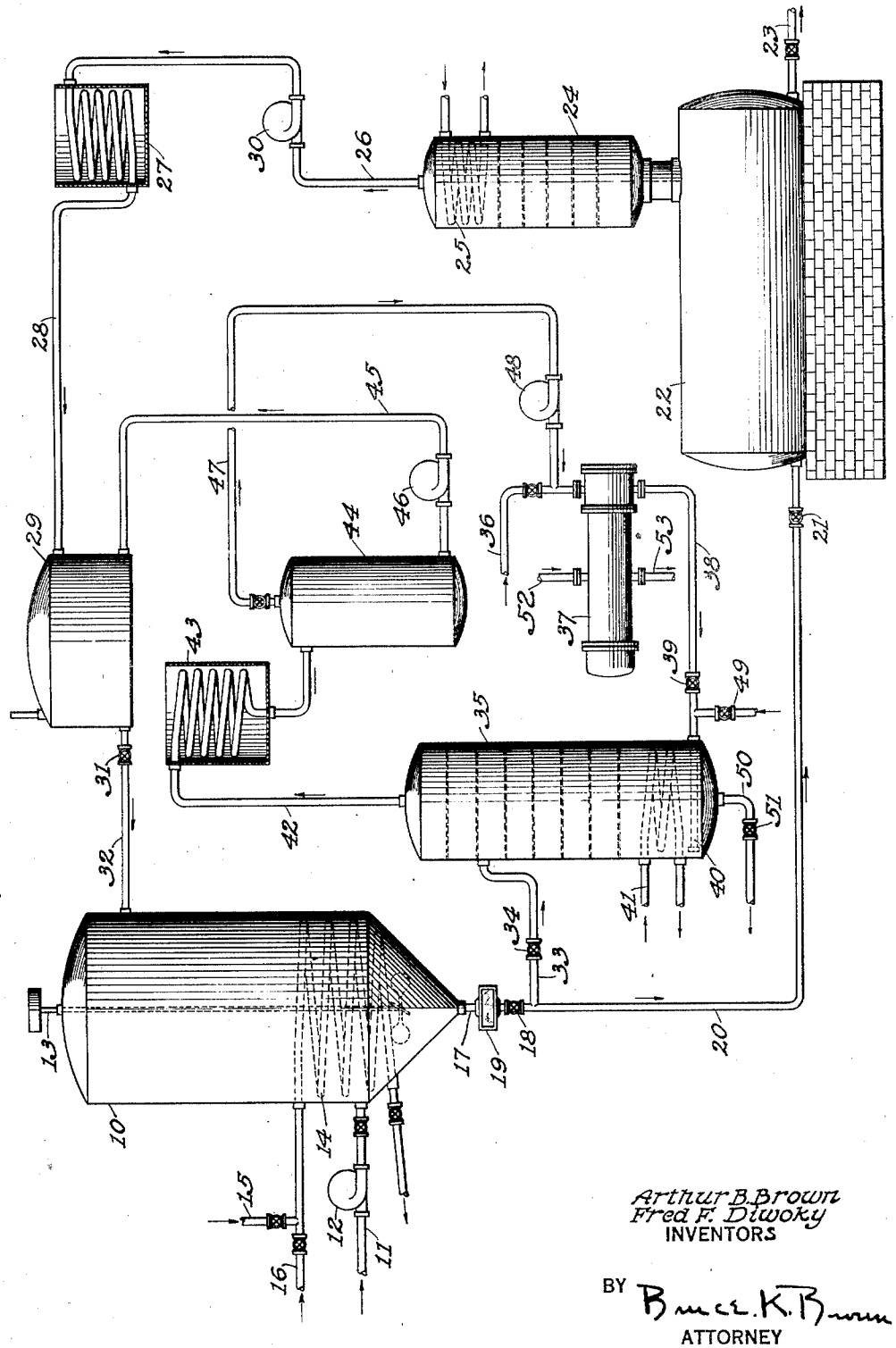
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EXTRACTION OF OILS WITH IMPROVED SOLVENTS

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EXTRACTION OF OILS WITH IMPROVED SOLVENTS

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This invention relates to the extraction of oils with improved solvents and it pertains more particularly to the extraction of lubricating oils with a mixture of solvents.

Petroleum is essentially a mixture of hydrocarbons comprising several groups or homologous series of compounds such as the paraffins, hydroaromatics, aromatics, polymethylenes, and various other series in which the hydrogen to carbon ratio is even different from that in the above classes. A large number of individual compounds of each series are present and have different boiling points, physical and chemical properties.

In the various types of crude petroleum commonly known as paraffin base, naphthenic or asphalt base, and mixed base, these various series of hydrocarbons are present in different proportions. For example, in the paraffin base oils such as those from the Appalachian field there is a relatively high proportion of paraffinic hydrocarbons having a chain structure and a high hydrogen to carbon ratio, whereas in the California and Gulf Coastal oils there is a high proportion of hydrocarbons with ring structures and low hydrogen to carbon ratio. The mixed base oils such as those from Oklahoma and the Mid-Continent area are in general intermediate between these two extreme types.

In the normal refining of crude petroleum, the fractions of varying distillation ranges which are successively obtained by distillation of the oils partake of the general character of the crude; for example, lubricating oils derived from Appalachian crudes will show paraffinic characteristics, whereas the lubricating oils derived from coastal crude show naphthenic characteristics. The distillates from the mixed base crudes, such as those from the Mid-Continent area, will show characteristics common to both the paraffinic and naphthenic oils. The crude from Winkler County, Texas, is intermediate coastal and Oklahoma crudes in its characteristics. An important property of paraffinic lubricating oils is their low viscosity-temperature coefficient or rate of change of viscosity with temperature. This property makes them particularly suitable for certain lubrication problems where high temperatures are encountered.

At low temperatures also, these oils retain their fluidity better, an important consideration in cold weather operation of automobiles, for example. For this reason it is very desirable to separate from the mixed base oils the undesirable naphthenic constituents. Various methods have been proposed for doing this and some have been used with partial success. Thus, the oil may be subjected to vigorous treatment with fuming sulfuric acid, followed by neutralization and removal of harmful sulfuric acid derivatives.

The object of our invention is to provide an improved method for extracting the naphthenic constituents from mixed base lubricating oils so that the resulting oils will have improved viscosity characteristics and will contain a high proportion of paraffinic compounds.

A further object is to provide a process for treating mixed base petroleum oils without the expense of acid treatment and without the loss of valuable petroleum constituents which accompanies the use of acid treating.

A particular object of our invention is to provide a solvent which has a very high degree of selectivity for the naphthenic constituents of mixed base lubricating oil distillates.

A further particular object of our invention is to provide mixtures of organic solvents which have greater selectivity for treating mixed base lubricating oil than the individual solvents of the mixture.

The expression "viscosity index", as used herein, refers specifically to the index defined by Dean and Davis in Chemical and Metallurgical Engineering, volume 36, 1929, page 618. The viscosity index of a lubricating oil is an indication of its composition or type, i. e., whether it is a paraffin base or naphthene base oil. Paraffin base oils are arbitrarily assigned a viscosity index of 100, naphthene base oils are assigned a viscosity index of 0, and mixed base oils lie between these extremes. By the present invention we have made it possible to obtain from mixed base lubricating oils a maximum yield of paraffin type oils (with a high viscosity index) without the nuisance or cost of acid treating and without appreciable destruction of the naphthenic constituents of the oil. Our process comprises extracting the oil with a solvent or a mixture of solvents wherein the components are chosen from two classes of compounds, one of these classes we call primary solvents and the other we call secondary solvents or promoters. The primary solvents comprise a group of aromatic, heterocyclic and aliphatic compounds, and the secondary solvents comprise the low boiling aromatic and the aliphatic ethers such as phenyl methyl ether, ethyl ether, isopropyl ether and mixed ethers. A more detailed description of the primary and secondary solvents suitable for our invention will be set forth hereinafter.

The term naphthenic hydrocarbons is employed in this application and in the claims in a generic sense to include the hydrocarbons that have a low viscosity index, a tendency to form sludge and a tendency to decrease the paraffinic characteristics of the oil. Examples of these naphthenic hydrocarbons are classified as aromatic, aromatic-like, olefinic and polymethylene hydrocarbons.

In Figure 1 of the accompanying drawing which forms a part of this specification, we have diagrammatically shown an apparatus suitable for carrying out our invention. The particular apparatus described forms no part of our invention and it should be understood that other types of extraction apparatus and processes may be used for applying our special solvent mixtures.

Our invention is applicable to the treatment of any oil but particularly a mineral oil such as asphaltic and mixed base oils and in a preferred method of extracting such oils we will describe the treatment of a heavy mixed base lubricating oil distillate having a gravity of 21.6 A. P. I., a viscosity of 114 seconds Saybolt at 210° F. and a Dean and Davis viscosity index of 56.5. Generally, our process of mixed solvent extraction gives excellent results with mixed base mineral oil distillates or mixed-base residues which have viscosities within the range of 200 to 3500 seconds Saybolt at 100° F., although it should be understood that the process is applicable to any lubricating oil of lower or higher viscosities. In the preferred example we will disclose the use of the batch method wherein one volume of oil is extracted with three volumes of the mixed solvent, said mixed solvent comprising 70% of di(2 chlorethyl) ether and 30% of isopropyl ether. It should be understood that we may use a continuous process of extraction wherein the oil is contacted with the solvent countercurrently. Also the oil may be given several successive extractions with the same or different solvents.

The mixed base mineral oil distillate is introduced into the extractor **10** by means of the conduit **11** and pump **12**. Any type of agitating means such as the stirrer **13**, may be used for contacting the oil with the mixed solvents. A closed coil **14** is provided on the inside of the agitator whereby the contents of the extractor may be heated with steam from valved pipe **15** or cooled with water or brine from valved pipe **16**. The base of the extractor is preferably conical and it terminates in a discharge pipe **17** which is provided with a valve **18** and glass window **19** so that the liquid flowing from the extractor may be seen.

After the step of extraction, which will be later described, the mixed solvents and naphthenic extract are withdrawn through pipe **20** and valve **21** to still **22** where the solvent is distilled from the extract. The extract is discharged from the still through pipe **23**. The solvents pass up through the tower **24**, around the reflux coils **25**, through the pipe **26**, condenser **27**, and pipe **28** to the storage tank **29**. The pump **30** is placed in the line between the tower **24** and the condenser **27** so that the distillation of the solvents from the extract can be performed at subatmospheric pressure, if desired. The solvent in storage tank **29** is introduced into the extractor by means of the valve **31** and pipe **32**.

The oil remaining in the extractor comprises the improved oil or the fraction high in paraffins, this fraction usually being referred to as the "raffinate." The oil is withdrawn through pipe **33** and valve **34** and introduced into the stripping tower **35** where the small amount of solvent dissolved in it is removed by a stripping gas such as carbon dioxide, nitrogen or the like. Steam may also be used in most cases if provision is made for drying the recovered solvent where it is being reused. If an inert gas, such as nitrogen, is to be used for the stripping, it is introduced into the stripper by means of pipe **36**, heater **37**, conduit **38**, valve **39** and perforated pipe **40**. The oil within the stripper may also be heated by the steam coil **41**. The inert stripping gas and solvents pass through pipe **42**, condenser **43**, and separator **44**. The recovered solvents are pumped from the separator to the storage tank **29** through the pipe **45** and pump **46**. The inert gas is withdrawn through pipe **47**, pump **48**, and recycled through the heater **37** and striper **35**. If desired, the stripping fluid may be introduced through the line **49**, thereby avoiding the initial step of heating. The paraffinic oil freed from the small portion of solvent is withdrawn through pipe **50** and valve **51**. The heating medium for the heater **37** is introduced and withdrawn through the lines **52** and **53** respectively.

In performing a batch extraction, we introduce the oil and mixed solvent into the extractor **10**. Steam may then be introduced into coils **14** to raise the temperature of the oil and solvent high enough to obtain substantially complete miscibility, but it should be understood that different temperatures will be required with different oils and solvents. Generally, the miscibility temperature falls within the range of 50 to 200° F. During this step the oil and solvent may be thoroughly mixed by the agitator **13**, in fact, if the agitation and mixing is sufficiently thorough the temperature need not be raised to effect complete miscibility. It is important, however, to obtain thorough contact of oil and solvent.

After the oil has been thoroughly mixed, it is cooled to a temperature at which the solvent and extract separate from the paraffinic oils or raffinate. The separation is generally made at least 40° F. below the temperature at which complete or substantially complete miscibility was obtained. The temperature at which this separation is effected is referred to throughout this application as the "extraction temperature." Cooling may be effected by passing cold water or cold brine through coils **14**, the agitation being preferably continued during the cooling step. In this particular example, the oil and solvents were cooled to about 10° F. and allowed to separate. The separation may require from one-half hour to five hours. We prefer to use the lowest temperature at which a good separation of the paraffinic and naphthenic fractions can be obtained. This extraction temperature is usually within the range of 0 to 95° F. Also, cooling may be effected by adding propane or other low boiling hydrocarbons to the oil and then flash the same.

If the lubricating oil were not dewaxed before being extracted, the upper layer, or raffinate, may solidify or partly solidify on cooling. The lower layer containing the naphthenic type oil and solvent remains substantially wax-free and fluid. Usually both the oil and solvent will be in a fluid state and valve **18** is closed when the raffinate appears in the sight glass **19**, then valve **21** is closed and valves **18** and **34** are opened to pass the paraffinic oil into the stripper column **35**, as hereinabove described. We may extract the oil a second time or as many times as desired to effect the degree of refining required.

In the above described process of operation,

we have used one volume of oil and three volumes of solvent, said solvent comprising 70% of di (2 chlorethyl) ether and 30% of isopropyl ether, but the ratio of the volume of solvent to the volume of oil may be varied from one-half to nine volumes of solvent for each volume of oil. Also, the solvent may comprise different proportions of primary and secondary solvents, generally from 50 to 95% of the primary solvent for each 50 to 5% of secondary solvent. When the volume of solvent is one or less to each volume of oil, we prefer to give the oil several extractions in order to produce an oil of the desired viscosity index.

The following table illustrates the results obtained from the mixed solvent extraction of the Mid-Continent lubricating distillate having a viscosity of 114 seconds Saybolt at 210° F., viscosity index of 56.5 and A. P. I. gravity of 21.6. In the above process and in the following table the results are based upon the use of one volume of oil to three volumes of solvent.

Table I

Example	Solvent		Raffinate	
	Primary solvent di (2 chlorethyl) ether	Secondary solvent isopropyl ether	Viscosity index	Extraction temperature
	Percent	*Percent*		°F.
1	100	0	85.4	10
2	90	10	86.5	10
3	80	20	89	10
4	70	30	89.5	10

By comparing the properties of the oil prepared in the above example with the properties of the oil before extraction, it will be seen that we can take a mixed base Mid-Continent lubricating oil distillate of 56.5 viscosity index and obtain an oil having a viscosity index from 86.5 to 89.5. By comparing Example 1 with Examples 2, 3 and 4, it will be seen that the viscosity index of the oil prepared by the mixed solvents is higher than the viscosity index of the oil prepared by the single solvent, or primary solvent.

Instead of using one extraction or several successive extractions with the same solvent, as set forth above, the oils may be treated with one mixed solvent and then treated with a different mixed solvent. Also, the oil may be treated with a suitable single solvent and then this treatment may be followed with a mixed solvent extraction. It is apparent that many modifications of the hereinabove described process of extraction may be used. Also, in some cases, the extraction temperature may be as low as −40° F.

Also, when sulfuric acid is used to treat oils, the acid sludge or semi-solid material obtained thereby is a waste product. It is very difficult to burn, and the acidic nature of the material makes it very difficult to handle. The acid fumes produced during the process of acid treatment of lubricating oils makes this process a hazardous, disagreeable and highly objectionable operation. The process of solvent extraction is not accompanied by objectionable fumes and can be very easily performed. Also the extract has not been changed chemically and it may be used as charging stock in the process of cracking for manufacturing gasoline. Also, this extract is very valuable in its original state as a fuel and as a source of naphthenic compounds.

It will be apparent from the above table and the table given below, that the selectivity of our mixture of primary and secondary solvents for the separation of mineral oils into a more paraffinic and a less paraffinic fraction is superior to that of the primary solvent per se.

The following table sets forth the results obtained with a halogenated ether such as di(2 chlorethyl) ether is used in combination with other organic compounds as the primary solvent, and a low molecular weight ether such as isopropyl ether is used as the secondary solvent. The oil treated in this example is a mixed base Mid-Continent lubricating distillate having a viscosity of 114 seconds Saybolt at 210° F., viscosity index of 56.5 and a gravity of 21.6 A. P. I. In the following table three volumes of solvent were used for each volume of oil.

Table II

Example	Solvent		Raffinate	
	Primary solvent: di(2 chlorethyl) ether 85%, cresylic acid 15%	Secondary solvent isopropyl ether	Viscosity index	Extraction temperature
	Percent	*Percent*		°F.
1	100	0	86.8	40
2	85	15	92.7	40
3	70	30	92.1	40
4	100	0	83.5	10
5	80	20	84.8	10
6	70	30	88.6	10

Table III

Example	Solvent		Raffinate	
	Primary solvent: dichlorethyl ether 85%, nitrobenzene 15%	Secondary solvent isopropyl-ether	Viscosity index	Extraction temperature
	Percent	*Percent*		°F.
1	100	0	85.5	10
2	80	20	87.5	10

From the above tables II and III it is apparent that the combination of mixed solvents is very effective for separating mixed base mineral oils into paraffinic and naphthenic fractions of hydrocarbon oils. By comparing the results obtained in Example 1 of Tables I, II and III with the results set forth in the other examples of Tables I, II and III, it is apparent that the selectivity of the combined primary and secondary solvents is much greater than the selectivity of the primary solvents per se.

We have used the term secondary solvent to cover the aliphatic and aromatic ethers and derivatives thereof and the term primary solvent has been used to cover the other compounds which cooperate with the secondary solvents to give our improved results. By using this combination of solvents the resulting mixture possesses greater selectivity for the undesirable naphthenic, naphthenic-like, olefinic and aromatic hydrocarbons present in the mixed base oil than for the paraffinic constituents of the mixed base oil.

Examples of the primary solvents which we employ are in general considerably higher boiling and higher in molecular weight than the secondary solvents and include the nitrogen substituted aromatic compounds such as nitrobenzene, aniline, ortho meta and para nitrotoluene,

ortho-nitro anisole, nitro xylene, xylidines, alpha and beta naphthols, such as 1-3-2-dimethyl amino benzene and 1-4-2-dimethyl amino benzene, nitro naphthalenes, ortho meta and para chloranilines, ortho meta and para chloro nitrobenzene; halogen substituted aryl compounds such as chloro benzene, ortho meta and para-dichlorobenzene, ortho chlorodiphenyl, benzyl-chloride, ortho meta and para chlortoluenes, ortho meta and para chlorophenols, ortho meta and para cresols, cresylic acid and alpha chloro naphthalene; other benzene compounds such as toluene, anisole and the like; halogenated ethers such as methyl 2-chlorethyl ether, methyl 2-3-dichloropropyl ether, methyl 2-chlorisopropyl ether, 2-chloroethyl ethyl ether, di(2-chlorethyl) ether, 1-2 dichlorethyl ethyl ether, 1-2-3-trichloroethyl ethyl ether, 2-bromethyl ethyl ether, 2-chlorethyl propyl ether, ethyl 2-3-dichloro propyl ether, chlorobutyl ethyl ether, ethyl chlorisopropyl ether, 2-chlorethyl chloropropyl ether. 2-3 dichloropropyl propyl ether, di(2-chloropropyl) ether, di(3-chloropropyl) ether, di(2-chlorisopropyl) ether, and di(2-bromethyl) ether; heterocyclic ring compounds such as dioxane, piperidine, furfural, alpha-furylacetone, thiophene, 2-3-dimethyl thiophene, 2-4-dimethyl thiophene, pyrrole, methyl pyrroles, 2-alkyl quinolines, quinoline, 2-methyl quinoline, alpha-picoline, aldehydes such as paraldehyde, parapropyl aldehyde, 2-chloropropionic aldehyde, chlor-acetaldehyde, benzaldehyde, para-anisaldehyde, halogenated aliphatic hydrocarbons and halogenated aliphatic compounds such as ethylene dichloride, 1-2 dichloropropane, 1-3 dichloropropane, 1-2-dibromopropane, tetra methylene chloride, isopropyl chloride and butyl chloride. The above primary solvents are of relatively low molecular weights and most of them boil at temperatures under 260° C. Also mixture of the above compounds may be used as the primary solvent or as the sole solvent for extracting the oil, for example, nitro benzene and aniline, nitrobenzene and cresylic acid, nitrobenzene and di(2 chlorethyl) ether, nitrobenzene and phenol, nitrobenzene and furfural, di(2 chlorethyl) ether and phenols, di(2 chlorethyl) ether and aniline, di(2 chlorethyl) ether and any of the above halogenated ethers, and other mixtures of the above primary solvents.

Examples of the secondary solvents which may be mixed in any proportion desired, but generally are the ethers, such as methyl ether, methyl ethyl ether, methyl propyl ether, methyl isopropyl ether, methyl butyl ether, methyl secondary butyl ether, methyl isobutyl ether, methyl tertiary butyl ether, ethyl ether, methyl phenyl ether, ethyl propyl ether, ethyl isopropyl ether, ethyl phenyl ether, propyl ether, propyl isopropyl ether, isopropyl ether, ethyl butyl ether, dioxane, diphenyl ether and mixtures of the above ethers. The ethers suitable for this invention have the general formula $R—O—R_1$ wherein R and R_1 represent alkyl or phenyl radicals or derivatives thereof. The ethers used as secondary solvents are normally liquid.

The above primary and secondary solvents may be mixed in any proportion desired, but generally the mixed solvents should comprise from 50 to 95% of the primary solvent. In the majority of cases the best results are obtained when 3 to 4 volumes of solvent are used to extract 1 volume of oil and said solvent comprising about 70% of primary solvent and 30% of the secondary solvent. Also one or more primary and/or secondary solvents may be used in the admixture of solvents. The solvents used for treating the oil should be substantially free from water and the commercial grade of these solvents has proven to be very satisfactory. If the primary and secondary solvents are not reactive with water, a small amount of water will not produce undesirable or injurious results.

The process of extracting the mixed base lubricating oils with a mixture of the above primary and secondary solvents is substantially the same as set forth hereinabove with di(2 chlorethyl) ether as the primary solvent and isopropyl ether as the secondary solvent or promoter. In case the admixture of primary and secondary solvents has a high boiling point or in case the solvents have a tendency to decompose when heated to relatively high temperatures, the step of removing the solvents from the extract in still 22 should be performed at subatmospheric pressures. This step of distilling at reduced pressures may be accomplished by the use of a suitable vacuum pump.

Instead of using the extraction process as the sole means for treating the oil, it may be used to supplement a preliminary acid treat, although it is preferable to follow the extraction process with a light acid treatment in order to improve the color and sludge stability of the lubricating oil, if desired. Usually it is desirable to finish the oil either by percolation or contacting with fuller's earth at somewhat elevated temperatures. If the oil was initially dewaxed, it will usually be in a marketable condition after the step of solvent extraction, however in some cases it is desirable to clay treat the oils.

While we have described a preferred embodiment of our invention, it should be understood that it is not limited to the specific details hereinabove set forth except as defined by the following claims. Also it is apparent that many modifications and alterations of the process can be accomplished by those skilled in this art without departing from the spirit of our invention.

We claim:

1. The process of removing naphthenic hydrocarbons from mixed base mineral lubricating oils, which comprises extracting the oil with a solvent comprising an aliphatic ether and a chlorinated aliphatic ether.

2. The process of treating oils containing sludge-forming constituents, which comprises extracting the oil with a solvent comprising an aliphatic ether containing not more than eight carbon atoms and a chlorinated aliphatic ether containing not more than eight carbon atoms.

3. The process of removing naphthenic hydrocarbons from mixed base mineral lubricating oils, which comprises extracting the oil with a solvent comprising a low boiling aliphatic ether and a dichlorinated aliphatic ether.

4. In the art of refining oils the process which comprises adding an admixture of isopropyl ether and di(2-chlorethyl) ether to a viscous mineral oil containing paraffinic and naphthenic hydrocarbons, heating the mixture to such a temperature as to effect solution, cooling the solution to form a two-layer system, and separating the upper layer from the lower layer.

5. In a process for producing lubricating oil having a high viscosity index from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the oil with a mixture of solvents comprising a halogenated aliphatic ether containing not more than

eight carbon atoms and an ether having the following general formula: R—O—R_1 wherein R and R_1 represent alkyl or phenyl groups.

6. In a process for producing lubricating oil having a high viscosity index from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixture of solvents comprising a chlorinated aliphatic ether containing not more than eight carbon atoms and an ether of the following general formula: R—O—R_1 wherein R and R_1 represent alkyl or phenyl groups.

7. In a process for producing lubricating oil having a high viscosity index from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains an aliphatic ether containing not more than eight carbon atoms and a beta-chlorinated aliphatic ether containing not more than eight carbon atoms, to form two liquid layers, separating said layers and removing the solvents therefrom.

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CERTIFICATE OF CORRECTION.

Patent No. 2,138,832. December 6, 1938.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 52, strike out the words "mixed in any proportion desired, but generally" and insert instead used in combination with the primary solvents; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 10th day of January, A. D. 1939.

(Seal)

Henry Van Arsdale
Acting Commissioner of Patents.