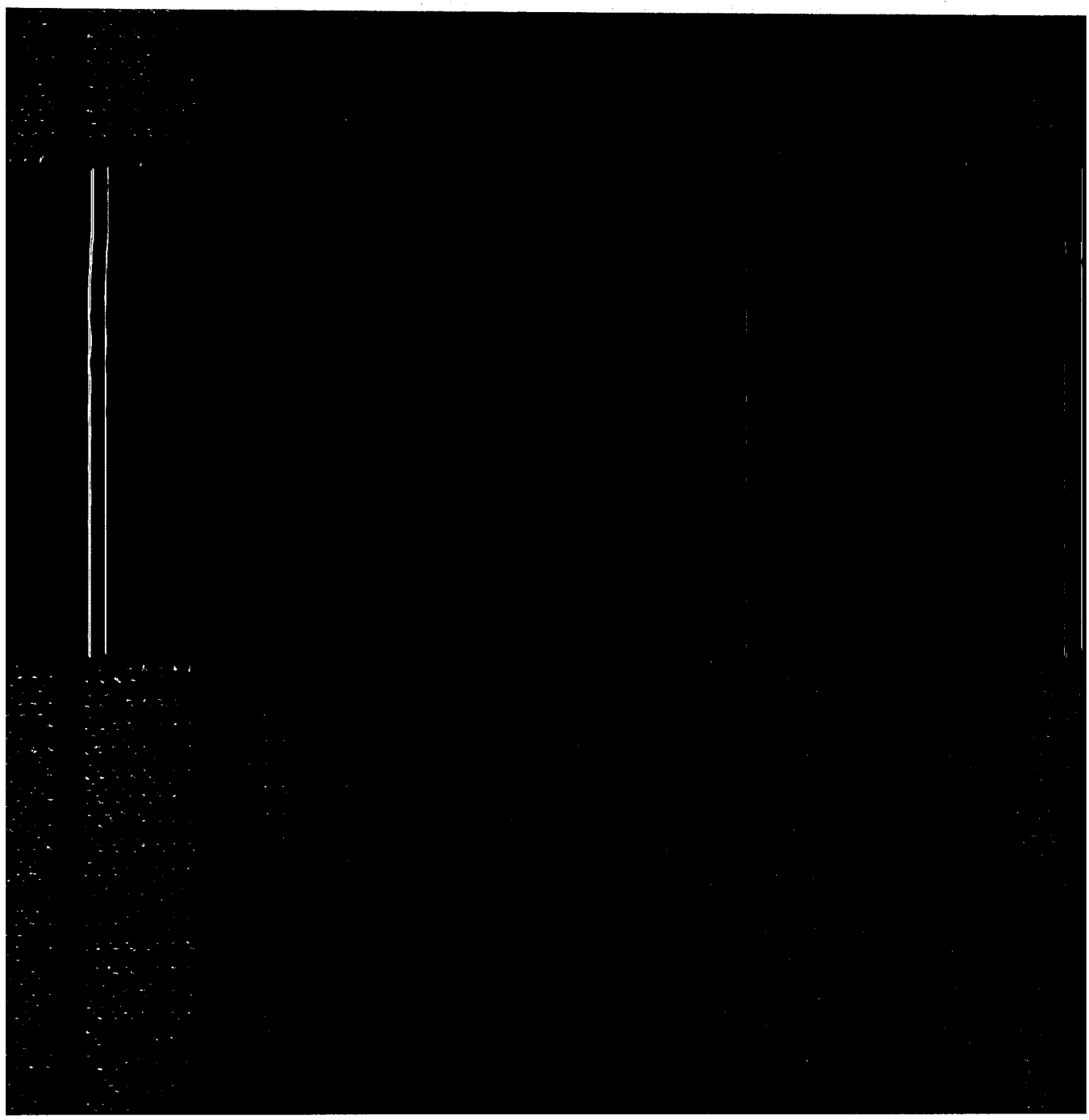
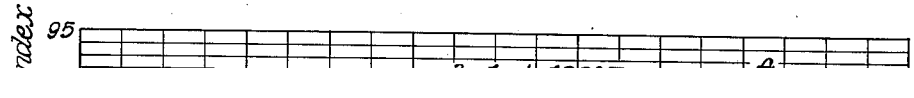


Dec. 6, 1938. A. B. BROWN ET AL 2,138,833

PROCESS FOR EXTRACTING OILS

Filed April 2, 1934 2 Sheets-Sheet 1



Dec. 6, 1938. A. B. BROWN ET AL 2,138,833

PROCESS FOR EXTRACTING OILS

Filed April 2, 1934 2 Sheets-Sheet 2

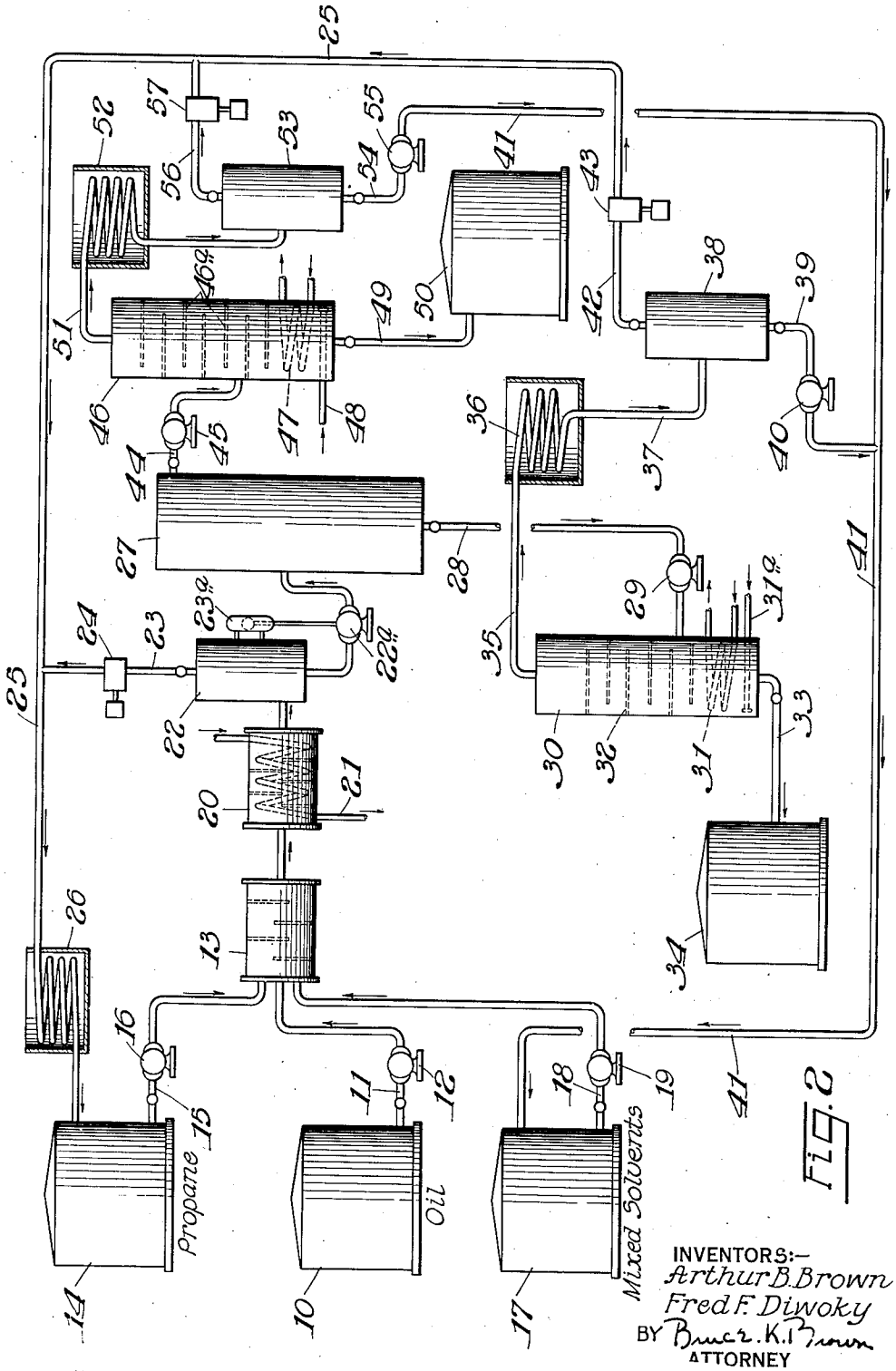


Fig. 2

INVENTORS:-
Arthur B. Brown
Fred F. Diwoky
BY Bruce K. Brown
ATTORNEY

Patented Dec. 6, 1938

2,138,833

UNITED STATES PATENT OFFICE

2,138,833

PROCESS FOR EXTRACTING OILS

Arthur B. Brown, Hammond, Ind., and Fred F. Diwoky, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application April 2, 1934, Serial No. 718,586

8 Claims. (Cl. 196—13)

This invention relates to the extraction of oils with organic solvents or mixtures of solvents.

Petroleum is essentially a mixture of hydrocarbons comprising several groups or homologous series of compounds such as paraffins, hydroaromatics, aromatics, poly-methylenes, and various other series in which the hydrogen to carbon ratio is even lower than in the above series. 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 paraffinic base, naphthenic or asphalt base and mixed base oils, 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 the Gulf Coastal oils have a high proportion of hydrocarbons with ring structures and a low hydrogen to carbon ratio, which are generally referred to as non-paraffinic or naphthenic constituents. The mixed base oils such as those from Oklahoma and the Mid-Continent areas 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 show paraffinic characteristics, whereas the lubricating oils derived from Texas crude show naphthenic characteristics. The distillates from the mixed base crudes, such as those from the Mid-Continent area, show characteristics common to both the paraffinic and naphthenic oils. Similarly, the undistilled oils or residuums have properties resembling the crude from which they are prepared. An important property of paraffinic lubricating oils is the low viscosity temperature coefficient or the rate of change of viscosity with temperature. This property makes them particularly suitable for certain lubricating problems where high temperatures are encountered. At low temperatures also, these oils retain their fluidity, an important consideration in cold weather operation of automobiles. For this reason, it is very desirable to separate from the mixed base oils and other oils containing non-paraffinic constituents the undesirable non-paraffinic and naphthenic constituents. Various methods have been proposed for doing this. For example, the oil may be subjected to vigorous treatment with fuming sulfuric acid, followed by neutralization and removal of harmful sulfuric acid derivatives.

An object of this invention is to provide an improved admixture of solvents for extracting the naphthenic or non-paraffinic constituents from mixed base mineral or lubricating oils and asphalt base oils so that the resulting oil will have improved viscosity characteristics and will contain a high proportion of paraffinic hydrocarbons. These new solvents may be used for extracting lubricating oil distillates or residual lubricating oils.

Another object of our invention is to provide an improved admixture of solvents for extracting these mineral lubricating oils in order to improve the color of the oil and at the same time remove the sludge forming or non-paraffinic constituents.

A further object is to provide a method for treating petroleum oils containing non-paraffinic constituents without the expense and nuisance of acid treatment, and without the loss of valuable petroleum constituents which accompanies the use of acid treating. A further object is to provide a lubricating oil with a minimum tendency toward sludge formation when exposed to oxidizing conditions.

A further object of our invention is to provide an admixture of solvents which may be used in combination with a non-viscous, normally gaseous liquid hydrocarbon for extracting mineral oils containing paraffinic and non-paraffinic constituents.

A particular object of our invention is to provide an admixture of solvents which can be used at ordinary temperatures to separate the oil into paraffinic and non-paraffinic constituents.

The expression "viscosity index" as used herein refers specifically to the index defined by Dean and Davis in Chemical and Metallurgical Engineering, vol. 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. An object of the present invention is to obtain from mixed base lubricating oils or oils containing some non-paraffinic constituents a maximum yield of paraffin type oils having a low true color (with a high viscosity index) without the nuisance or cost of acid

treating and without appreciable destruction of the naphthenic constituents of the oil.

In accordance with one feature of this invention, we have discovered that an admixture of two or more of the following solvents may be used for the extraction of the hereinbefore described mineral oils: nitrobenzene, aniline, pyridine, furfural, cresylic acid, phenol, chloraniline or a mixture of ortho, meta, and para chloraniline, chlorophenols such as ortho chlorophenol, chlorocresols or mixtures of chlorocresols, and beta chlorinated aliphatic ethers such as di (2-chloroethyl) ether and 2-chloroethyl-propyl ether.

Some of the preferred combinations of the above solvents are

Di (2-chlorethyl) ether and cresylic acid,
Di (2-chlorethyl) ether and nitrobenzene.
Di (2-chlorethyl) ether and phenol,
Di (2-chlorethyl) ether and aniline,
Di (2-chlorethyl) ether and ortho chlorophenol,
Di (2-chlorethyl) ether and pyridine,
Di (2-chlorethyl) ether and furfural,
Cresylic acid and nitrobenzene,
Cresylic acid and chloraniline,
Cresylic acid and aniline,
Cresylic acid and chlorophenols,
Nitrobenzene and aniline,
Nitrobenzene and phenol,
Nitrobenzene and furural, and
Nitrobenzene and pyridine.

In fact, one preferred embodiment of our invention is to use di (2-chlorethyl or cresylic acid in combination with any of the hereinbefore mentioned compounds or classes of compounds. Briefly, the invention is performed by mixing the mineral oil with two, and in some cases three, of the above solvents at a temperature where substantially complete miscibility is obtained, and then cooling the mixture until phase separation occurs. The temperature at which miscibility is obtained is termed the "miscibility temperature" and the temperature at which phase separation is effected is termed the "extraction temperature." It should be understood that the oil and admixture of solvents may be mixed and then heated to any desired temperature or miscibility temperature, or the oil and the admixture of solvents may be mixed and then permitted to separate into a raffinate and extract phase without heating to the miscibility point. In most cases, however, we prefer to mix the oil and solvents at about the temperature where phase separation can be effected. The upper layer or phase which consists mainly of the paraffinic fraction is referred to as the "raffinate" and the compounds which are dissolved in the solvent in the lower phase are called the "extract." The respective liquid phases may be separated from each other by decantation or other suitable means. The raffinate consists of hydrocarbons which exhibit a high viscosity index, excellent color and good sludge stability, and it is particularly suitable for lubricants. These lubricants may be used for any purpose. Generally it is not necessary to give the raffinate a further refining treatment in order to produce suitable lubricating oils; however, if desired, the raffinate may be given a further light refining treatment such as treating with clay, sulfuric acid or alkaline. However, our novel combination of solvents usually makes it unnecessary to further refine the oil. The solvents may be recovered from the extract by distillation and reused.

The process may also be performed by extracting the oil with one of the above admixtures of solvents in the presence of a non-viscous, normally gaseous liquid hydrocarbon such as propane, ethane, butane, isobutane, hexane or light petroleum distillate or mixtures of these. Hydrocarbon gases may be obtained by the cracking of hydrocarbon oils, rectification of natural gasoline, and the like; and propane from this source usually contains small quantities of hydrocarbons such as methane, ethane, isobutane, and butane. A purer grade of propane may also be used. These non-viscous, normally gaseous liquefied hydrocarbons are generally referred to as "diluents". One of the reasons for using a diluent is to raise the extraction temperature. This is particularly advantageous when an admixture of solvents is used to extract wax-containing oils.

This invention is applicable to the treatment of any mixed base oil or residual oil; for example, it may be used to improve the color and remove the naphthenic and other non-paraffinic constituents from oils having a viscosity within the range of 200–3500 seconds Saybolt at 100° F. The diluent may be used to reduce the viscosity and/or increase the extraction temperature of the oils falling within this range of viscosities. It should be understood that oils having viscosities above or below this range may also be extracted with our combination of solvents.

As an example of the method of carrying out one embodiment of our invention, one volume of dewaxed, Mid-Continent S. A. E. 50 distillate having a viscosity of 114 seconds Saybolt at 210° F., viscosity index of 56.5, true color 1100, and a gravity of 21.6 A. P. I. was mixed with three volumes of a solvent consisting of equal parts of di (2-chloroethyl) ether and cresylic acid. The resulting mixture was heated to the miscibility temperature or the temperature at which the oil and solvent are substantially completely miscible; generally this temperature is not above 135–150° F. In this case we used a miscibility temperature of less than 135° F. The mixture of oil and solvent was then cooled to the extraction temperature, 100° F., where phase separation occurred. One of the important features of our admixture of solvents is the high extraction temperatures which may be used. Our admixture of solvents gives excellent phase separation at extraction temperatures ranging from 50° F. to 100° F. Such extraction temperatures may be obtained without resorting to artificial cooling methods. It is obvious, however, that lower extraction temperatures can be used without departing from our invention. The admixture of solvents and dissolved non-paraffinic or naphthenic constituents separate to form the lower layer and the paraffinic oil or raffinate separates to form the upper layer. The lower layer is withdrawn or removed from the upper layer by any convenient means and the admixture of solvents removed therefrom by distillation. The distilled solvents are then condensed and reused in the extraction of mineral oils. The raffinate may contain a small quantity of dissolved or entrained solvents and they may be removed therefrom by distillation or by stripping with an inert gas or fluid such as carbon dioxide or steam. With our admixture of solvents, one extraction is usually sufficient to produce a satisfactory lubricant; however, the raffinate may be given an additional extraction treatment with the same or different admixtures of solvents or with a single solvent. The following table shows the properties of the

raffinate of the above mentioned oil after one extraction with an admixture of solvents:

Table I

Example	Solvents: Percent cresylic acid	Solvents: Percent di(2-chlorethyl) ether	Ratio of solvent to oil	Extraction temperature	Viscosity index	Percent yield of raffinate	True color
				°F.			
I	50	50	3:1	100	91	62.4	150
II	100		3:1	100	91	59.6	275
III		100	3:1	100	91	57.6	450
IV	50	50	3:1	50	88.4	73.6	235
V	100		3:1	50	89	66.8	350
VI		100	3:1	50	88	75	550

The data with respect to the true color, yield, and viscosity index for Examples I, II, and III are also shown by the curves designated as A in Figure I. It will be observed that the admixture of di(2-chlorethyl) ether and cresylic acid gives a substantial increase in the color of the raffinate over the single solvents. In view of the good color produced by this admixture of solvents, it is not necessary to use additional refining. Furthermore, it will be observed that the extract in Examples I, II, and III was obtained at an "extraction temperature" of 100° F. This feature of our invention is very important because the process may be used without using refrigeration means to effect phase separation. The curves designated as A in Figure I also show the results which can be obtained by varying the percent of di(2-chlorethyl) ether and cresylic acid used to make up the solvent.

The data set forth in Examples IV, V, and VI with respect to an admixture of equal proportions of di(2-chlorethyl) ether and cresylic acid are also shown by curves B in Figure I. This set of data was obtained at an extraction temperature of 50° F. It will be observed that the true color of the oil obtained by this extraction was somewhat inferior to the true color of the oil obtained at an extraction temperature of 100° F. The data set forth in Figure I by curves C represent the properties of the oil when the ratio of solvent to oil is 2:1 and an extraction temperature of 100° F. is used. The three sets of curves shown in Figure I also represent the true color, viscosity index, and yield of raffinate when varying proportions of di(2-chlorethyl)-ether and cresylic acid are used to extract a Mid-Continent 50 distillate having a viscosity index of 56.5 and a true color of 1100. The same magnitude of results is obtained with other admixtures of solvents as is illustrated by Figure I. It is obvious, therefore, that various proportions of the solvents may be used, but generally the ratio of the two solvents will be within the range of 25 to 75%. Also the ratio of solvent to oil may be varied, namely, we may use from 2 to 5 volumes of solvent for each volume of oil.

The following table illustrates the results obtained from the mixed solvent extraction of Mid-Continent 50 lubricating distillate having a viscosity of 114 seconds Saybolt at 210° F., viscosity index of 56.5, true color 1100, and an A. P. I. gravity of 21.6:

Table II

Example	Solvents: Percent cresylic acid	Solvents: Percent nitrobenzene	Ratio of solvent to oil	Extraction temperature	Viscosity index	Percent yield of raffinate	True color
				°F.			
I	50	50	3:1	50	90	65.1	179
II		100	3:1	50			
III	100		3:1	50	89	66.8	350

It is apparent from the above data that the combination of cresylic acid and nitrobenzene produces a raffinate with a better color than either of the single solvents.

The following table illustrates the results obtained from the mixed solvent extraction of Mid-Continent 50 lubricating distillate having a viscosity of 114 seconds Saybolt at 210° F., viscosity index of 56.5, true color of 1100, and an A. P. I. gravity of 21.6:

Table III

Example	Solvents: Percent dinitrobenzene	Solvents: Percent di (2-chlorethyl) ether	Ratio of solvent to oil	Extraction temperature	Viscosity index	Percent yield of raffinate	True color
				°F.			
I	25	75	3:1	81	87.4	68.8	181
II	25	75	3:1	79	89.4	61.9	177

Another embodiment of this invention relates to the use of an admixture of solvents in combination with liquid propane or other similar low-boiling hydrocarbon diluents for the extraction of non-paraffinic constituents from mineral oil distillates or residuums. The oil and liquid propane may be mixed together and then extracted with the mixture of solvents. If desired, gaseous

propane may be dissolved in the oil and the mixture then extracted with the combination of solvents. The oil may be first mixed with propane and then flashed in order to cool the oil, thereby precipitating the asphaltic material and then extracting with the admixture of solvents. It should be understood that a substantial proportion of the propane remains in the oil after the flashing operation. This last modification is generally known as deasphalting combined with solvent extraction. Other modifications of our invention will be apparent when considered with the schematic arrangement of the apparatus set forth hereinafter. However, it should be understood that other types of extraction apparatus may be used for extracting oils with the herein mentioned mixture of solvents.

Referring more particularly to the schematic drawing in Figure II, which illustrates a continuous method of extracting oil, a lubricating oil containing paraffinic and non-paraffinic constituents is passed from the reservoir 10 by the valved conduit 11 and pump 12 to the mixer 13 where it is mixed with liquid propane coming from tank 14 through the valved conduit 15 and pump 16. The solvent, an admixture of di (2-chlorethyl) ether and cresylic acid, is also introduced into the mixer 13 from tank 17 by the valved conduit 18 and pump 19. The mixture of liquid propane, oil, and admixture of solvents passes from the mixer 13 to the combined mixer and heater 20, where the components are further mixed and heated to a desired temperature, such as the miscibility temperature. Any suitable heating means such as the steam coils 21 may be used to heat the oil and solvent to the desired temperature or miscibility temperature. Generally this temperature is below 150° F. In this particular example we prefer a temperature of >135° F. The temperature of oil, propane, and admixture of solvents is then reduced by introduction into the cooler 22 where a portion of the propane is vaporized in order to cool the mixture to about the extraction temperature. The vaporized propane passes through the valved conduit 23 to the compressor 24 and thence to conduit 25, where it is passed to the condenser 26 and liquefied. The liquefied propane is then returned to the storage tank 14 for reuse.

The cooled solution of oil, propane, and solvents is then introduced into the extractor 27 by the pump 22*a* which is operated in response to the fluid-level device 23*a*. The fluid-level device maintains a vapor space in the top part of the cooler 22 so that a portion of the propane can be flashed. The mixture in the extractor 27 is allowed to separate into an upper raffinate layer and a lower extract layer. The solvents and dissolved fraction settle to the bottom of the separator while the propane and paraffinic oil or raffinate rises to the top part of the separator.

The mixture of di (2-chlorethyl) ether, cresylic acid, and dissolved non-paraffinic constituents or naphthenic constituents in the lower part of the extractor 27 is withdrawn through the valved conduit 28 by the pump 29 and passed to the tower 30 where the two solvents and dissolved naphthenic constituents are heated to a temperature sufficiently high to evaporate the two solvents and any liquid propane which may be present. Suitable heating means such as the steam coils 31 may be used to distil the solvents and diluent from the extracted fraction. Also gases such as propane or steam may be introduced into the bottom part of the tower 30 by the perforated pipe 31*a* to strip the last trace of solvents from the extract. Baffle plates 32 may also be placed in the tower 30 to aid the removal of the solvents. The extract in tower 30 may be continuously withdrawn through the valved conduit 33 and passed to the storage tank 34. The distilled di (2-chlorethyl) ether and cresylic acid and propane pass from the top part of the tower 30 through conduit 35 to the condenser 36 where the solvents are condensed. Obviously, if steam is used to strip the solvents from the extract it will also be condensed by the condenser 36. The mixture of liquefied di (2-chlorethyl) ether, cresylic acid, and propane gas then passes by conduit 37 to the separator 38. The liquid di (2-chlorethyl) ether and cresylic acid, and water if present, are removed from the lower part of the separator through the valved conduit 39 by pump 40 and returned through conduit 41 to the solvent storage tank 17. If water is entrained in the solvents, it may be removed therefrom in tank 17. The gaseous propane is passed from the upper part of the separator 38 through the valved conduit 42 and compressor 43 and returned by conduit 25 to the condenser 26, where it is liquefied and then passed to the propane storage tank 14.

The propane solution of paraffinic oil with a small amount of the two solvents dissolved therein may be continuously removed from the separator 27 by the valved conduit 44, pump 45, and passed to the tower 46, where the mixture is heated to a temperature sufficiently high to vaporize the propane. Any other suitable heating means such as the steam coils 47 may be employed to heat the contents of the tower 46. Steam or propane gas may be introduced into the bottom part of the tower 46 by the perforated pipe 48 to strip the last trace of the di (2-chlorethyl) ether or cresylic acid from the oil. Baffle plates 46*a* may be disposed in the tower 46 to aid the removal of the solvent and diluent from the paraffinic oil. The paraffinic oil or raffinate, free from propane and the solvents, is passed from the bottom part of the tower 46 through the valved conduit 49 to the storage tank 50. The propane and solvent vapors are removed from the tower 46 through conduit 51 and passed to the condenser 52, where the solvents are condensed. The liquefied solvents and gaseous propane are then passed to the separator 53, where the liquid solvents separate from the gaseous propane. The liquid solvents are then removed from the lower part of the separator 53 by the valved conduit 54 and pump 55 and returned through conduit 41 to the storage tank 17. The gaseous propane is removed from the upper part of the separator 53 through the valved conduit 56 by the compressor 57 and returned to the condenser 26, where it is condensed. The liquefied propane is then returned to the storage tank 14 and again reused in the process.

It is apparent that many modifications of the hereinbefore described process can be made without departing from the scope of the invention; for example, the propane solution of oil may be heated separately from the solvents and several mixers may be used to thoroughly contact the solvents with the oil and propane. Instead of using the propane cooler 22, cooling coils may be used in the extractor 27. Also instead of using equal proportions of di (2-chlorethyl) ether

and cresylic acid, any of the proportions represented by the curves in Figure I may be used. It should also be appreciated that different mixtures of oil, propane and solvents may be used; for example, from 1 to 5 volumes of the mixed solvent may be used for each volume of oil and from 1 to 5 volumes of propane may be used for each volume of oil.

If one extraction of the oil with the mixed solvents is not sufficient to produce an oil having the particular color and viscosity index desired, the raffinate may be recycled through the process. It should also be understood that the process illustrated by Figure II may be carried out without the use of propane at all. The diluent is desirable because it permits the use of high extraction temperatures and hastens phase separation.

The admixture of solvents may also be used to extract oils by first dissolving the oil in one of the solvents and then contacting the solution with a second solvent. For example, the oil may be dissolved in cresylic acid by heating and then contacted with di(2-chlorethyl) ether. The resulting mixture is then permitted to separate into a raffinate fraction and an extract fraction.

This application is a continuation in part of our co-pending application Serial 637,978, filed October 15, 1932, and our copending application Serial 605,814, filed April 18, 1932.

While we have described our invention with reference to particular examples, it should be understood that such examples are not given as limitations as to the scope of the invention and that other alternative methods may be used without departing from the scope of the invention.

We claim:

1. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and a substantial proportion of a solvent selected from the group consisting of cresylic acid, nitrobenzene, phenol, aniline, chlorophenol and chloroaniline, to form two liquid layers, separating said layers and removing the solvents therefrom.

2. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and from 70 to 30% by volume of a solvent selected from the group consisting of cresylic acid, nitrobenzene, phenol, aniline, chlorophenol and chloroaniline, to form two liquid layers, separating said layers and removing the solvents therefrom.

3. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and cresylic acid, to form two liquid layers, separating said layers and removing the solvents therefrom.

4. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and from 70 to 30% by volume of cresylic acid, to form two liquid layers, separating said layers and removing the solvents therefrom.

5. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and nitrobenzene, to form two liquid layers, separating said layers and removing the solvents therefrom.

6. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and from 70 to 30% by volume of nitrobenzene, to form two liquid layers, separating said layers and removing the solvents therefrom.

7. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and phenol, to form two liquid layers, separating said layers and removing the solvents therefrom.

8. In a process for producing lubricating oil having a high viscosity index and a low true color from a mineral oil containing naphthenic and paraffinic constituents, the steps comprising extracting the mineral oil with a mixed solvent which contains di(2-chlorethyl) ether and from 70 to 30% by volume of phenol, to form two liquid layers, separating said layers and removing the solvents therefrom.

ARTHUR B. BROWN.
FRED F. DIWOKY.