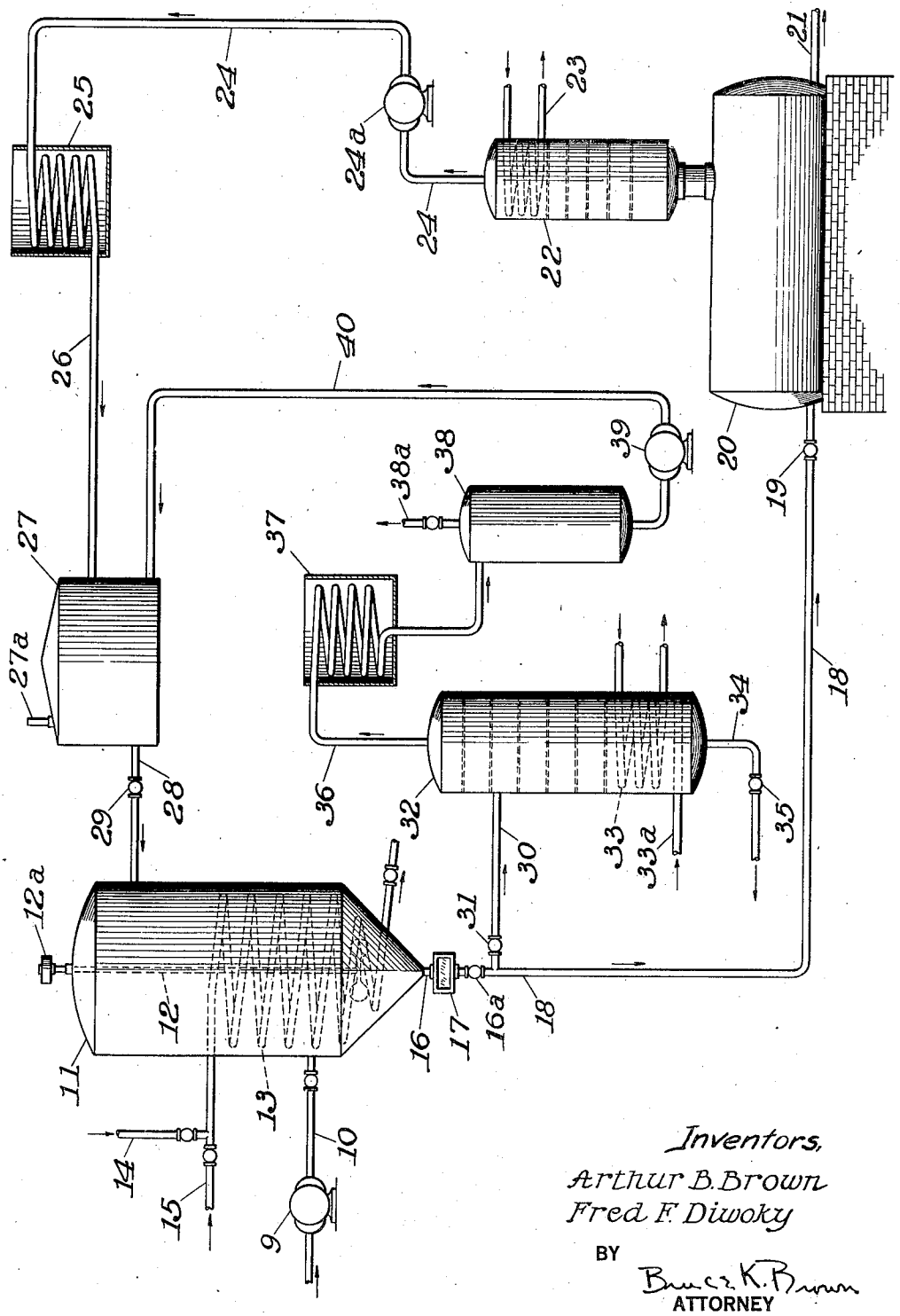
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SOLVENT EXTRACTION OF OILS

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Inventors,
Arthur B. Brown
Fred F. Diwoky

BY
Bruce K. Brown
ATTORNEY

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SOLVENT EXTRACTION OF OILS

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

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This invention relates to a process for extracting hydrocarbon oils with organic solvents and it pertains more particularly to the use of oxygenated-halogen organic solvents for extracting hydrocarbon oils such as naphthas and lubricating oils.

The general object of our invention is to provide a process for extracting naphthenic, aromatic and unsaturated hydrocarbons from hydrocarbon oils.

One application of our invention provides an improved process for treating light hydrocarbon distillates, such as kerosene, and burning oils whereby the naphthenic hydrocarbons, sulfur compounds and other objectionable substances can be removed. Our extraction process is used to replace the acid treatment generally applied to light hydrocarbon distillates. We may also employ our process for extracting the naphthenic and unsaturated hydrocarbons from gasoline and naphtha and thereby obtain a fraction of compounds that have improved anti-knock properties.

A more specific object of our invention is to provide a process for extracting objectionable substances from lubricating oils whereby the oils have improved viscosity characteristics, for example, such as is shown by the viscosity index. A further specific object is to provide an improved process for treating mixed base petroleum lubricating oils without the nuisance and expense 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 towards sludge formation when exposed to oxidizing conditions. Other objects will be apparent as the detailed description of our invention proceeds.

The expression "viscosity index", as used herein, refers specifically to the index defined by Dean & Davis in Chemical and Metallurgical Engineering, volume 36, page 618 (1929). The viscosity index of a lubricating oil is an indication of its composition or type, that is, whether it is a paraffin base or naphthenic base oil. Paraffin base oils are arbitrarily assigned a viscosity index of 100. Naphthenic base oils are assigned a viscosity index of 0 and mixed base oils lie between these extremes. When our invention is applied to mixed base lubricating oils the object is to obtain from these lubricating oils a maximum yield of paraffin oils (with a high viscosity index)—without the nuisance or cost of acid treating and without appreciable destruction of the naphthenic and unsaturated constituents of the oil.

We have discovered that oxygenated-halogen organic compounds such as halogenated esters, for example ethyl chloracetate; and chlorethyl acetate, have remarkable properties for the extraction of undesirable substances, such as naphthenic and aromatic compounds, from hydrocarbon oils such as naphthas and mixed base lubricating oils. In describing one of the preferred embodiments of our invention we will illustrate in detail the use of ethyl chloracetate as a solvent for extracting the naphthenic, aromatic and unsaturated compounds from a mixed base lubricating oil. It should be understood that compounds selected from the above classes and equivalent classes of compounds may be used in the following example without departing from the scope of our invention.

In the accompanying drawing which forms a part of this specification we have diagrammatically shown an elevational plan view of an apparatus which is suitable for carrying out our process. Our invention is applicable to the treatment of any mixed base mineral oil, but in our preferred embodiment, illustrating the extraction of a mixed base lubricating oil, we will describe the treatment of a heavy untreated lubricating distillate having a viscosity of about 102 seconds Saybolt at 210° F. and gravity of about 21.3 A. P. I. and a Dean & Davis viscosity index of about 58. We will also disclose the use of a batch process wherein equal amounts of the solvent and oil are mixed and separated in successive steps. But it is apparent that we may also use a continuous process and extract the oil with a solvent countercurrently.

The mixed base lubricating oil may be introduced by the pipe 10 into extractor 11 which is provided with suitable agitating means, such as the stirrer 12. A pulley 12a is provided on the stirrer so that it may be driven by a belt of some suitable means. A closed coil 13 is provided on the inside of the extractor, said coil being provided with connections whereby it may be heated with steam from the valved pipe 14 or cooled with water, brine or suitable refrigerants from the valved pipe 15. The base of the extractor is preferably conical and it terminates in a discharge pipe 16 which preferably has a glass window 17 therein so that the liquids flowing through the pipe may be seen.

After the extraction, which will be later described, the solvent and naphthenic extract are withdrawn through pipe 18 and valve 19 to the

still 20, the extract being removed from the still through the pipe 21. The solvent is removed from the extract by distillation and passes up through the fractionating tower 22, around the reflux coils 23, through the pipe 24 to the condenser 25 and thence through pipe 26 to the storage tank 27 from which it may be introduced into the extractor by means of pipe 28 in amounts regulated by valve 29. Suitable venting device 27a is provided on storage tank 27. The vacuum pump 24a, which is connected in the line 24, may be used to reduce the pressure in still 20, thereby enabling the solvent to be distilled at lower temperatures than would be necessary if the distillation were performed at atmospheric pressure. In the preferred operation of our process, the vacuum pump 24a is usually placed in the line 26, or at some point beyond the condenser. It is particularly desirable to use vacuum distillation when high boiling solvents, that decompose on heating, are used for the extraction.

The residual oil or raffinate is withdrawn through pipe 30 and valve 31 and passed to the stripping tower 32 which is provided with heating coil 33 in the base thereof and a perforated pipe 33a for supplying a stripping gas such as steam or other inert gaseous materials. The oil, freed from the solvent, is withdrawn through pipe 34 and valve 35. The chlorinated ester or solvent is removed from the stripper by pipe 36, condensed in condenser 37, separated from the stripping medium in separator 38, and then returned by pump 39 and pipe 40 to the storage tank 27. A valved vent 38a is placed on the top part of the separator to remove the stripping medium.

We introduce equal parts of untreated viscous oil, hereinabove described, and ethyl chloracetate into extractor 11. If desired we may use two or three volumes of ethyl chloracetate to each volume of oil. We then introduce steam into coils 13 to raise the temperature high enough to obtain complete miscibility between the oil and chlorinated ester. In this particular example we will use a temperature of about 90° F., but the temperature used in our processes of extraction may vary considerably with different oils, the preferred range being between 50 and 200° F. During the first step, the oil and solvent may be thoroughly mixed by the agitator 12. In fact, if the agitation or mixing is sufficiently complete, the temperature need not be raised to effect complete miscibility. It is very important, however, to obtain thorough contact of oil with solvent. After the solvent has been thoroughly mixed with the oil we cool the mixture to decrease the amount of oil dissolved with the extract. Cooling may be effected by passing cold water, brine or other fluids through coil 13, the agitation being preferably continued during the cooling step. It appears that the temperature at which the mixture is cooled has a marked effect upon the yield of the paraffin type oil and the selectivity of the solvent. The yield of oil increases as the temperature of the mixture undergoing separation decreases. From about 35 to 95° F. this is closely proportional in magnitude to the temperature change. At higher temperatures the decrease in yield is more rapid than the increase in temperature.

After cooling, the oil and solvent are allowed to separate which separation may require from one half hour to four or five hours at temperatures of from 100° F. to 35° F. and we prefer to use the lower temperature and the longer period of separation. In some cases it is desirable to use temperatures as low as 0° F. or lower. If the oil has not been dewaxed the upper layer may solidify to a mush on cooling, the lower layer being practically wax free and fluid. Usually, both the oil and solvent will be in the liquid state and we therefore close valve 16a when the oil layer or the raffinate appears in the sight glass 17. By closing valve 19 and opening valves 16a and 31 we can pass the residual oil or raffinate into the stripping column 32 as hereinabove described. Or we may extract the raffinate a second time or as many times as desired to effect the degree of refining required. In this case we may employ the subsequent extracts for initially treating new batches of raw oil in the manner herein described. Also with highly volatile solvents the extraction may be performed under pressure in such processes, the pump 9 may be used to force the solvent into the extractor 11. The extraction may be performed at any pressure, but preferably at a pressure within the range of 1 to 50 lbs. per square inch.

The operating temperatures of still 20, column 22 and stripper 33, the number of fractionating plates in towers 22 and 32, the amount of reflux in coils 23, etc., may be determined by anyone skilled in the art, and since they form no part of the present invention, they will not be described in detail. In fact, we may draw the oil from the top of the extractor by suitable draw-off pipes and we may also use the extractor itself as a steam still for separating the chlorinated ester or solvent from the extract; a suitable vapor take-off pipe and condenser being provided between the extractor and the solvent storage tank 27. Other expedients will be apparent to those skilled in the art.

Other halogenated esters may be used as solvents for extracting mixed base hydrocarbon oils and naphthas, and these halogenated esters may be used in substantially the same manner as described hereinabove. The halogenated esters given below are representative of the classes of esters suitable for our invention. Some of the halogenated esters set forth may boil above or below the boiling point of ethyl chloracetate, and the miscibility of these solvents with the oil to be extracted can be regulated by increasing or decreasing the temperature at which the oil is extracted. The selection of a proper temperature can be easily determined by those skilled in the art. Most of the halogenated esters suitable for our invention have the general formula $R—CO_2—R_1$ wherein R and R_1 represent organic residues, one or both of which may be chlorinated. Also R_1 may represent a hydrogen atom. Also some of the chlorinated esters have the general formula

$$R_2\begin{matrix}-CO_2R_3\\-CO_2R_4\end{matrix}$$

wherein R_2 represents an alkylene residue, R_3 and R_4 represent organic residues, and any one combination or all three of said residues may be chlorinated. Examples of the chlorinated esters suitable for our invention are methyl chloroformate, chloromethyl acetate, methyl chloracetate, methyl trichloracetate, ethyl chloroformate, 2-chlorethyl formate, 2-trichlorethyl formate, 3-chloropropyl formate, 2-chlorethyl acetate, ethyl chloracetate, 2-dichlorethyl acetate, ethyl dichloracetate, alkyl trichloracetates, 3-chloropropyl acetate, 2-chlorethyl propionate, ethyl 2-chloropropionate, trichlorisopropyl acetate, 2-di-

chlorethyl chloracetate, 3-chloracetoacetic ester, chlorethyl benzoate, dichloromethyl benzoate, chlorethyl lactate, methyl beta-chloropropionate, ethyl beta-chloropropionate, 2-chlorethyl beta-chloropropionate, and the like. Where the ester contains a chloralkyl group, we prefer to have the chlorine situated on a carbon atom at least one atom removed from the carboxyl group.

It should be understood that the compounds set forth hereinabove are representative of the general classes of organic compounds suitable for our invention and that other chlorinated derivatives, homologues, analogues and isologues may be used as solvents for extracting mineral oils. The above compounds may be used in the anhydrous form, chemically pure form or commercial form. We have found that the commercial purity is generally satisfactory. If desired, we may use mixtures of the above compounds for extracting hydrocarbon oils and the ratio of solvents used in the mixture may be varied to suit the particular needs. For example, we may use equal proportions of two solvents or we may use two or three volumes of one solvent to each volume of the other solvent. Also one to four volumes of a single or mixed solvent may be used to extract one volume of oil. It should be understood that those skilled in the art can easily select any suitable combination and proportion of solvent that will give satisfactory results.

It should be understood that the mineral oil to be extracted, or the solvents, may be mixed with other diluents or solvents such as propane, butane, propylene, naphtha, acetone, etc., for the purpose of effecting a better solvent. Also these diluents permit a sharper separation of the phases. When the very light diluents are used such as propane and butane, we may evaporate a portion thereof to obtain cooling whenever desired. For example, instead of passing a brine through the coils **13** we may add propane to the oil within the extractor **11** and flash off the propane in order to effect the desired cooling. Chlorinated hydrocarbons such as ethylene-dichloride, trichlorethylene, and the like may be used in combination with the solvents set forth hereinabove.

Instead of using the extraction process as a sole means for treating lubricating oils, it may be supplemented by a preliminary acid treat. The preliminary acid treat may, for instance, be particularly desirable for separating out tarry material which would be undesirable in the extract. We preferably follow the extraction process with a light sulfuric acid treatment to improve color; this may also be followed by a clay treatment either by percolation or contacting with fine clay at somewhat elevated temperatures.

A very important characteristic of the oils produced by our improved extraction process is their ability to resist oxidation and sludge formation. This abnormal freedom from sludge formation, when exposed to oxidation, is preferably due to the removal of certain potential sludge forming ingredients in the oil, and while we do not understand the exact phenomenon, experiments have proven the superior sludge resistant properties of our finished lubricating oils. For instance, an oil which, when acid treated, has a sludging time of 22 hours and a deterioration time of 47 hours has, when extracted in accordance with our invention, a sludging time of more than 60 hours and a deterioration time of more than 125 hours. As stated above, the solvents and process set forth may be used to extract naphthas, kerosene, gasoline and the like for the purpose of removing naphthenic and/or sulfur containing components of said hydrocarbon distillates. When our process is used to extract the anti-knock substances from naphthas and particularly a cracked naphtha, the process is substantially the same as that set forth hereinabove in connection with the extraction of lubricating oils. The solvent is distilled from the extract in still **20** and stripped from the oil in the stripper **32** in the same manner as herein described. The solvent used to extract the naphtha should preferably boil at about or somewhat below the initial boiling point of the naphtha. For example, if the naphtha has an initial boiling point within the range of about 250 to 350° F. (an end boiling point within the range of about 360 to 420° F.), the boiling point of the solvent should be somewhat below the initial boiling point of said naphtha.

As a modification of our process of extracting naphthas, we may extract naphthas with solvents that boil above the end boiling point of the naphtha. For example, if the naphtha has an end boiling point within the range of 200 to 340° F., we may use a solvent that boils above the end point of said naphtha. In this modification of our invention it is apparent that the extract must be distilled from the solvent in still **20**. Similarly, the raffinate is distilled from the solvent in the stripper **32**. In this modification we disconnect the conduit **26** from the storage tank **27** and divert it to a tank, not shown, to collect the extract. Similarly, conduit **40** is disconnected from tank **27** and diverted to a tank, not shown, to collect the raffinate. The solvent is removed from conduits **21** and **34** and returned to the tank **27** for further use in the extraction of naphthas. We prefer to use vacuum distillation on still **20** for removing the extract from the solvent.

As a second modification of our process we may use solvents that boil within the boiling range of the naphtha. In this case we cannot satisfactorily separate the solvent and extract or solvent and raffinate by distillation. However, other methods may be used for separating the solvent from the extract and raffinate. For example, a 50 to 75% methyl or ethyl alcohol solution may be added to the mixture of oil and solvent to aid the separation or other water-like solvents may be used for this purpose.

The extracts obtained from naphtha and other low boiling hydrocarbons have high anti-knock properties and these extracts may be added to motor fuels in order to enhance the anti-knock value of said motor fuel.

We do not limit ourselves to any theory or explanation of why the compounds set forth above are suitable extracting agents, but experiments have shown that the above general classes of compounds have unique properties for extracting hydrocarbon oils and the results obtained are of an entirely different order from the results obtained by other well known solvents.

Many modifications of our invention will be apparent to those skilled in the art. For instance, we may heat a mixture of lubricating oils and solvent to a miscibility temperature (say 150° F.) and then instead of making a single separation we may separate the oil in consecutive steps as the temperature is lowered (say 135° F., 80° F., and 35° F.), taking a raffinate cut at each temperature which may be further extracted if desired. The final separation temperature may be below the pour point of the oil layer. Counter-

current extraction may also be used to great advantage in our process.

While we have described the preferred embodiments of our invention it should be understood that we do not limit ourselves to any of the details hereinabove set forth, except as defined by the following claims which should be construed as broadly as the prior art will permit.

We claim:

1. The method of treating hydrocarbon oils containing paraffinic and naphthenic compounds, which comprises extracting the unsaturated compounds from said oil with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents a trichlorinated aliphatic residue and R_1 represents a hydrogen atom or an alkyl radical.

2. The method of preparing lubricating oils which have a high viscosity index and which are stable against sludge formation, which comprises extracting the oil with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents a chlorinated aliphatic residue and R_1 represents a chlorinated aliphatic radical.

3. The process of preparing lubricating oil having a high viscosity index, which comprises extracting the oil with an organic solvent containing not more than five carbon atoms and having the general formula $R—CO_2—R_1$ wherein R represents a chlorinated aliphatic residue and R_1 represents a chlorinated alkyl radical or an alkyl radical.

4. The method of preparing lubricating oils which have a high viscosity index, which comprises mixing a mixed base lubricating oil with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents a trichlorinated aliphatic residue and R_1 represents a hydrogen atom or an alkyl radical, heating the mixture of oil and solvent to obtain substantial miscibility, cooling the oil and solvent until separation of the solvent and dissolved compounds from the remainder of the oil occurs, and separating the solvent together with the dissolved compounds from the treated oil.

5. The method of preparing lubricating oils which have a high viscosity index, which comprises mixing a mixed base lubricating oil with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents a chlorinated aliphatic residue containing not more than two carbon atoms and R_1 represents an alkyl radical or a chlorinated alkyl radical containing not more than three carbon atoms, heating and agitating the oil and solvent to obtain miscibility, cooling the oil and solvent until separation of the solvent and dissolved compounds from the remainder of the oil occurs, and separating the solvent together with the dissolved compound from the treated oil.

6. The method of extracting unsaturated and naphthenic hydrocarbons from a mineral oil distillate, which comprises mixing the oil with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents a chlorinated aliphatic residue and R_1 represents an alkyl radical or a chlorinated alkyl radical, cooling the mixture of oil and solvent until the solvent and dissolved unsaturated and naphthenic hydrocarbons separate from the remainder of the oil, and separating the solvent cake with the dissolved hydrocarbons from the treated oil.

7. The method of extracting naphthenic hydrocarbons from a mineral hydrocarbon oil distillate, which comprises mixing the oil with a chlorinated ester of an aliphatic acid, said ester containing not more than five carbon atoms, cooling the mixture of oil and solvent until the solvent and dissolved naphthenic hydrocarbons separate from the remainder of the oil, and separating the solvent together with the dissolved naphthenic compounds from the treated oil.

8. The method of extracting naphthenic and unsaturated compounds from a hydrocarbon oil distillate, which comprises mixing the oil with a chlorinated-alkyl ester of an aliphatic acid, cooling the mixture of oil and solvent until the solvent and dissolved hydrocarbons separate from the remainder of the oil, and separating the solvent together with the dissolved compounds from the treated oil.

9. The method of extracting unsaturated and naphthenic hydrocarbons from a mineral oil distillate, which comprises mixing the oil with an alkyl ester of a chlorinated aliphatic acid, said ester containing not more than five carbon atoms, cooling the mixture of the oil and solvent until the solvent and dissolved hydrocarbons separate from the remainder of the oil, and separating the solvent together with the dissolved hydrocarbons from the treated oil.

10. The process of extracting unsaturated hydrocarbons from petroleum naphtha, which comprises mixing the naphtha with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents an alkyl residue or a chlorinated alkyl residue and R_1 represents a hydrogen atom or a chlorinated alkyl radical, cooling the mixture of naphtha and solvent until the solvent and dissolved unsaturated hydrocarbons separate from the remainder of the naphtha, and separating the solvent together with the dissolved unsaturated compounds from the treated naphtha.

11. The process of extracting unsaturated hydrocarbons from petroleum naphtha, which comprises mixing the naphtha with a chlorinated alkyl ester of an aliphatic acid, said ester containing not more than five carbon atoms, cooling the mixture of naphtha and solvent until the solvent and dissolved hydrocarbons separate from the remainder of the naphtha, and separating the solvent together with the dissolved hydrocarbons from the treated naphtha.

12. The process of preparing lubricating oil having a high viscosity index, which comprises extracting the oil with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents an organic residue and R_1 represents a chlorinated alkyl radical.

13. The method of preparing lubricating oil having a high viscosity index and substantially free from sludge forming constituents, which comprises mixing a mixed base lubricating oil with an organic solvent having the general formula $R—CO_2—R_1$ wherein R represents an alkyl group or a phenyl group and R_1 represents a chlorinated alkyl group containing not more than three carbon atoms, heating the mixture of oil and solvent to obtain substantial miscibility, cooling the oil and solvent until separation of the solvent and dissolved compounds from the remainder of the oil occurs, and separating the solvent together with the dissolved compounds from the treated oil.

14. The method of preparing lubricating oils which have a high viscosity index and are free from sludge forming constituents, which comprises mixing a lubricating oil with a chlorinated-

alkyl ester of a low molecular weight aliphatic acid, heating the mixture of oil and chlorinated ester to obtain substantial miscibility, cooling the mixture of oil and chlorinated ester until the chlorinated ester and dissolved constituents separate from the remainder of the oil, and separating the chlorinated ester together with the dissolved constituents from the treated oil.

15. The method of preparing lubricating oils having a high viscosity index and substantially free from sludge forming constituents, which comprises mixing a lubricating oil with an alkyl ester of a chlorinated low molecular weight aliphatic acid, heating the mixture of the oil and chlorinated ester to obtain substantial miscibility, cooling the oil and chlorinated ester until separation of the chlorinated ester and dissolved constituents from the remainder of the oil occurs, and separating the chlorinated ester together with the dissolved constituents from the treated oil.

ARTHUR B. BROWN.
FRED F. DIWOKY.