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PROCESS OF TREATING OILS

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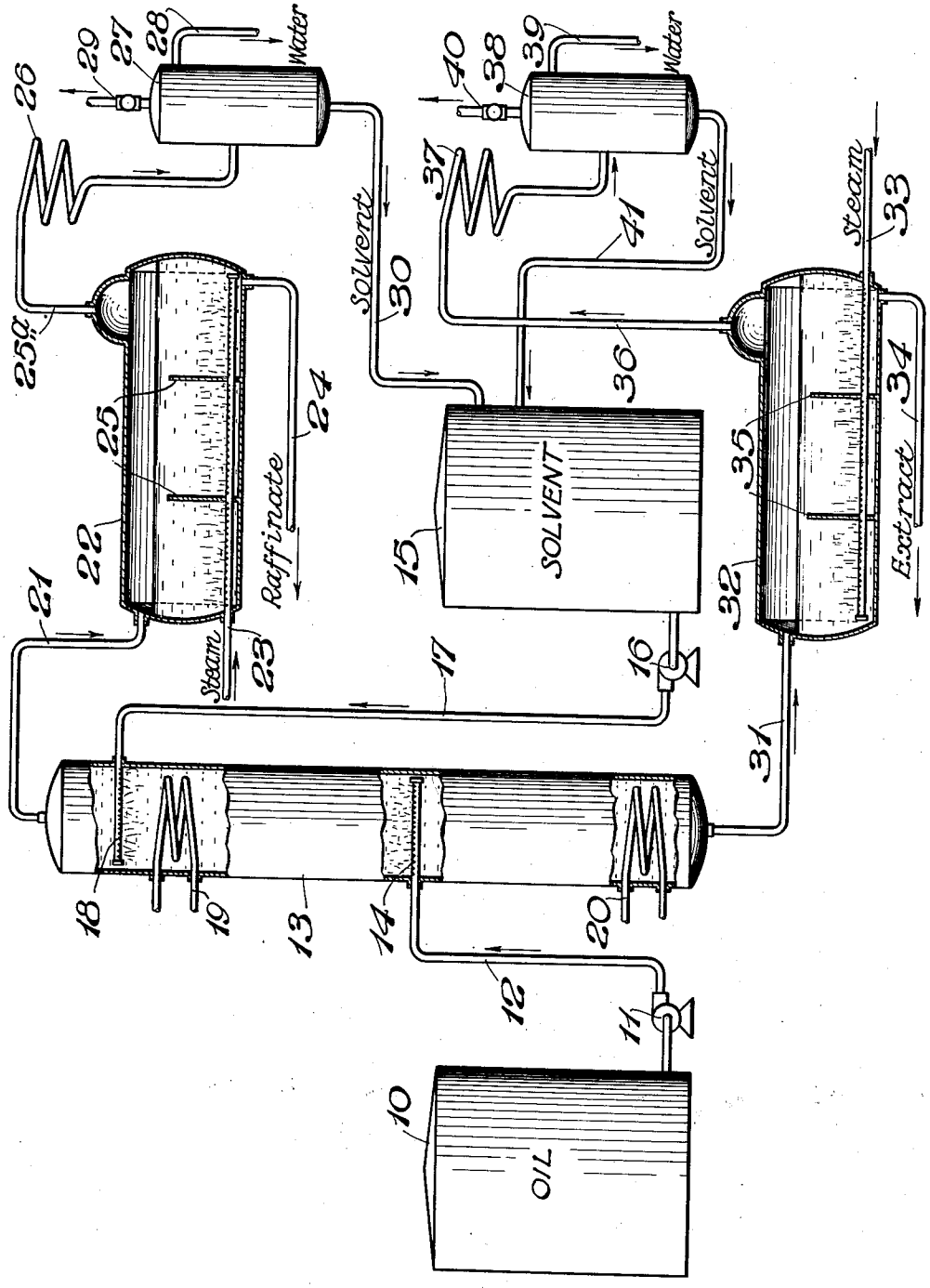

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PROCESS OF TREATING OILS

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4 Claims. (Cl. 196—13)

This invention relates to the extraction of mineral lubricating oils with organic solvents or mixtures of solvents for the purpose of preparing highly paraffinic oils with excellent color.

Petroleum is essentially an admixture of hydrocarbons comprising several groups or homologous series of compounds such as paraffins, hydroaromatics, aromatics, polymethylenes, 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, 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. The mixed base oils such as those from Oklahoma and the Mid-Continent areas are in general intermediate 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 would show paraffinic characteristics; whereas the lubricating oils derived from Winkler 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 similar to 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; this is 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 improved solvents for extracting the naphthenic constituents or non-paraffinic constituents from hydrocarbon lubricating oils so that the resulting oils will have improved viscosity temperature 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.

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. At the same time lubricating oils prepared by our process have a minimum tendency toward sludge formation when exposed to oxidizing conditions consistent with the increased yield obtained. Also the solvent we employ removes more color from the oil than is the case with most other solvents used to remove naphthenic constituents.

A particular object of this invention pertains to the use of monochloro phenols and particularly ortho- and para-chlorophenol or mixtures of these two chlorophenols for extracting naphthenic or non-paraffinic constituents from mineral oil. These solvents may be employed at ordinary temperatures, giving good phase separation without necessity of resorting to refrigeration.

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 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.

In accordance with one feature of the invention we have discovered that ortho-, meta-, and para-monochlorophenols or admixtures of monochlorophenols, for example, an admixture of ortho- and para-chlorophenol have remarkable solvent properties when used to extract the non-paraffinic or sludge forming constituents from mineral oils. The commercial grades of these chlorophenols may also be used, for example, the product obtained by chlorination of phenol or by the partial hydrolysis of dichlorobenzenes by known methods. The proportions of the ortho- and para-chlorophenols in the admixtures may vary over a wide range but generally from 25 to 50% of ortho-chlorophenol and 70 to 40% of para-chlorophenol is used. Also as much as 15% of phenol may be present in combination with the admixture of ortho- and para-chlorophenols, for example, a solvent comprising about 30 to 33%

ortho-chlorophenol, about 65 to 57% para-chlorophenol and about 5 to 10% phenol may be used. These monochlorophenols and admixtures of monochlorophenols have the remarkable property of removing the color bodies from mineral oils. Without limiting the foregoing description of the solvents which may be used, the following examples of combined solvents may be employed:

	Per cent
Para-chlorophenol	43
Ortho-chlorophenol	47
and	
Phenol	10
Para-chlorophenol	50
and	
Ortho-chlorophenol	50
Ortho-chlorophenol	31
Para-chlorophenol	53
and	
Phenol	16
Ortho-chlorophenol	33
and	
Para-chlorophenol	67

In our copending application 605,814, filed April 18, 1932, of which the present application is a division, we have described a process whereby solvents such as the aliphatic ketones may be used in combination with the monochlorophenols. Examples of these ketones are acetone, methyl ethyl ketone, diethyl ketone, di-isopropyl ketone, methyl butyl ketone, and mixtures of the above ketones.

Briefly, the invention is performed by mixing the mineral oil and chlorophenols at a temperature where substantially complete miscibility is obtained and cooling the mixture until phase separation occurs. The temperature at which miscibility is obtained is termed "miscibility temperature" and the temperature at which phase separation is effected is termed the "extraction temperature". It should be understood that the oil and chlorophenols may be mixed and then heated to any desired temperature, or the oil and chlorophenol may be mixed at room temperatures and then permitted to separate into a raffinate and extract phase. The monochlorophenols and particularly the admixture of ortho- and para-chlorophenols have the highly desirable property of effecting good phase separation at temperatures ranging from 30 to 80° F. This eliminates artificial cooling. The upper layer consists mainly of the paraffinic hydrocarbons and a small amount of solvent and is referred to as the "raffinate phase". The highly paraffinic oil is referred to as the raffinate. The major part of the solvent and the dissolved non-paraffinic or sludge forming constituents separate in the lower phase and are referred to as the extract phase. The non-paraffinic oil is referred to as 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 and it is particularly suitable for lubricating oils. If desired, the raffinate may be given a further light refining treatment with clay, sulfuric acid, or alkali. The solvent is ordinarily recovered from the extract and raffinate by distillation and reused.

It is also possible to extract the naphthenic, non-paraffinic and/or sludge forming constituents from mineral oils with these mono-chlorophenols when used in the presence of a non-viscous, normally gaseous liquid hydrocarbon such as propane, ethane, butane, pentane and the like. The term "propane" is meant to include the light petroleum fraction which is gaseous under normal conditions of temperature and pressure, and which is liquid at temperatures below 70° F. and 125 lbs. pressure per sq. in. Propane may be obtained from the cracking of hydrocarbon oils, rectification of natural gasoline and the like, and it usually contains a small quantity of hydrocarbon such as methane, ethane, isobutane and butane. The purer grade of propane may also be used. These non-viscous, normally gaseous liquid hydrocarbons are sometimes referred to as diluents. When mineral oils are extracted with an admixture of propane and monochlorophenol, the refined oil or raffinate is characterized by having a high viscosity index, a very light color, and a low Conradson carbon value. Diluents such as light petroleum naphthas may also be used in the place of propane. The non-viscous, normally gaseous liquid hydrocarbons aid in bringing about a sharp phase separation. They may also be used as a refrigerant to cool the mixture of oil and solvent by releasing pressure and permitting the liquefied gas to expand directly from the mixture. However, it is seldom necessary to use artificial cooling with the monochlorophenols because of their ability to effect phase separation at ordinary temperatures.

This invention is particularly applicable to the treatment of any mixed base oil, Pennsylvania oil or residual oil; for example, it may be used to remove the naphthenic or non-paraffinic constituents from oils having a Saybolt viscosity within the range of 200 to 3500 seconds at 100° F. The diluents may be used to reduce the viscosity of an oil to any point within this range of viscosity.

As an example of the method of carrying out one embodiment of this invention, one volume of dewaxed mixed base lubricating oil distillate having a gravity of about 21.6 A. P. I., viscosity of 114 sec. Saybolt at 210° F. and a Dean and Davis viscosity index of 56.5 was extracted with two volumes of para-chlorophenol. The oil and solvent were heated to a miscibility temperature of 180° F. and cooled to an extraction temperature of 73° F. where phase separation occurred. It should be noted that the extraction temperature used was equivalent to about normal room temperature. The following table shows the properties of the raffinate produced by the extraction with para-chlorophenol:

Example I

Solvent	Ratio of oil to solvent	Raffinate		Misc. temp.	Extraction temp.
		Yield	Vis. inde		
		Percent		°F.	°F.
Para-chlorophenol.	1:2	65	91.3	180	73

From the above data it is apparent that para-chlorophenol is very effective as a solvent for extracting the non-paraffinic constituents from a mineral oil. It should be noted that by this one extraction we were able to prepare an oil having a viscosity index of 91.3 and that it was not necessary to use artificial refrigeration to bring about phase separation. The mono-chlorophenols are particularly useful as selective sol-

vents because they effect phase separation at relatively high temperatures. The raffinate described above also had a very low true color.

Another embodiment of this invention relates to the use of admixtures of these mono chlorophenols such as ortho- and para-chlorophenol. In this particular example we used an admixture comprising about one-third ortho-chlorophenol and two-thirds para-chlorophenol. The oil used in this extraction was a dewaxed, mixed base lubricating oil distillate having a gravity of 21.6 A. P. I., true color of about 1100, a viscosity of 114 sec. Saybolt at 210° F. and a viscosity index of 56.5. One volume of this oil was extracted three times with an equal volume of the admixture of mono chlorophenols. The following table shows the conditions under which the oil was extracted and the properties of the raffinate.

Example II

Solvent	Ratio of oil to solvent	No. of extractions	Extraction temperature	Raffinate	
				True color	Viscosity index
Mixture of about one-third ortho-chlorophenol and about two-thirds para-chlorophenol	1:1	3	°F. 32–35	48	96
Same	1:1	3	72–80	36	96.5

From the above data it will be noted that the raffinate had a very high viscosity index and a very low true color. Phase separation can be obtained with the chlorophenols at room temperatures without artificial cooling. The yield of raffinate in each of the above two extractions was between 40 and 50%. It is apparent that the mono chlorophenols have the unique property of greatly improving the color of the oil.

The diagrammatic drawing referred to hereinafter illustrates one type of apparatus which may be used in the process of extracting mineral oils with the novel solvents described hereinbefore. In this illustration of our invention, a continuous countercurrent extraction will be described; however, it should be understood that other methods of procedure may be used, such as batch extraction.

The oil to be extracted is passed from the tank 10 by the pump 11 through conduit 12 to about the central part of an elongated vertical extraction tower 13. A perforated pipe 14 is usually employed to introduce the oil into the tower. After the extraction tower has been substantially filled with the oil to be treated, a solvent such as an admixture of about one-third ortho-chlorophenol and two-thirds para-chlorophenol is passed from the tank 15 by pump 16 through conduit 17 to the upper part of the extraction tower 13. A perforated pipe 18 is generally used to spray the solvent into the tower. The volumetric ratio of solvent to oil entering the tower 13 may vary from about one to four. The same general ratio of oil to solvent may be used when a single solvent like ortho- or para-chlorophenol is employed.

The mono-chlorophenol, being heavier than the oil, descends through the tower 13 and effects a countercurrent extraction of the ascending body of oil. If desired, a closed steam coil 19 may be placed in the extraction tower between the pipes 14 and 18, but nearer pipe 18, for the purpose of heating the oil and solvent in that region and thereby effecting greater miscibility of the oil and solvent. For example, the oil and solvent passing the coil 19 may be heated to a temperature of about 60 to 80° F. Likewise, a similar closed coil 20 may be placed in the lower part of the extraction tower for the circulation of a cooling medium to lower the temperature of the extract, e. g. to 30° F., and thereby bring about the separation of any paraffinic oil which may be otherwise carried out with the extract.

The raffinate fraction is removed from the top part of the tower through conduit 21 and passed to the steam still 22 where the chlorophenols are distilled from the highly paraffinic oils or raffinate. Steam is introduced into the bottom part of the still 22 through the perforated pipe 23. If desired, external heat may also be used to supplement the distillation of the chlorophenols from the oil. The paraffinic oils or raffinate, freed from the dissolved and entrained solvent, are removed from the bottom of the still through conduit 24 located at the end of the still away from the inlet pipe 21. Baffles 25 may be placed in the still for the purpose of effecting a uniform flow of liquid through the still and thereby insuring the removal of the chlorophenols from the oil before said oil or raffinate is removed through pipe 24.

The vaporized chlorophenols and steam removed from the raffinate fraction in still 22 pass through conduit 25*a* to the cooling coils 26 where both are condensed. The liquefied chlorophenols and water pass to the separator 27 where the two liquids are permitted to separate. The water being lighter than the chlorophenols rises to the top part of the separator and passes off through conduit 28. Gases and uncondensed materials may be vented through the valved conduit 29. The condensed chlorophenols are removed from the bottom of the separator 27 through conduit 30 and returned to the solvent storage tank 15.

The solvent and dissolved naphthenic constituents or extract fraction in the lower part of the tower 13 are passed through conduit 31 and introduced into the steam still 32 where the chlorophenols are distilled from the naphthenic constituents or extract without decomposition. Most of the chlorophenols which were used in the extraction of the oil will be found in the extract phase. Steam is introduced into the still 32 through the perforated pipe 33. If desired, external heat may be used to supplement the distillation of the chlorophenols from the naphthenic constituents. The naphthenic fraction of oil, freed of the solvent, is removed from the bottom of the still 32 through conduit 34, located at the end of the still away from the inlet pipe 31. Baffles 35 are placed in the still for the purpose of causing a uniform flow of liquid through the still and thereby insuring the removal of practically all of the chlorophenols from the naphthenic oil or extract before said oil is removed through conduit 34.

The vaporized chloropenhols and water removed from the naphthenic constituents in still 32 are passed through conduit 36 to the cooling coils 37 where both are condensed. The water and liquid chlorophenols pass to the separator 38 where the two liquids are permitted to separate. The water being lighter than the chlorophenols rises to the top part of the separator and passes off through conduit 39. Gases and uncondensed materials may be vented through

the valved conduit 40. The chlorophenols are removed from the bottom part of the separator 38 through conduit 41 and returned to the solvent tank 15. The method of extracting just described may likewise be employed with any of the solvents herein described.

The paraffinic oils prepared by the use of these mono-chlorophenols have a high viscosity index, low true color, and are very resistant to sludge formation. If desired, these paraffinic oils may be given a very light sulfuric acid treatment or clay treatment. In view of the extremely low color and very high paraffinic characteristics of the oils prepared by the chlorophenol extraction, said oils may be used for purposes other than that of lubricating internal combustion engines. As another modification of our process, the oils may be acidified with dilute sulfuric acid or other mineral acids before they are introduced into the extraction tower 13. The presence of a small amount of acid tends to prevent the formation of emulsions. When an acidified oil is used, the raffinate should be neutralized with caustic or some alkaline reagent before it is employed for lubricating purposes.

This application is a division of our copending application Serial No. 605,814, filed April 18, 1932.

While we have described our invention with reference to specific operating conditions, it should be understood that our invention is not limited thereby. The particular features of our invention are set forth by the following claims:

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 countercurrently contacting the oil with an admixture of solvents comprising about 43% para-chloropenol, 47% ortho-chlorophenol, and 10% phenol, cooling the mixture of oil and solvent until separation of an extract phase and raffinate phase occurs, separating said phases from each other, and distilling the solvent from said extract phase and raffinate phase.

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 commingling the mineral oil with an admixture of solvents comprising about 30 to 33% ortho-chlorophenol, 65 to 57% para-chlorophenol and 5 to 10% phenol, cooling the admixture of oil and solvents until separation of an extract phase and raffinate phase occurs, separating said phases from each other, and removing the solvent from each phase.

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 commingling the oil with a solvent comprising an admixture of 25 to 39% ortho-chlorophenol, 70–45% para-chlorophenol and 5–16% phenol, cooling the admixture of oil and solvent to effect the formation of an extract phase and a raffinate phase, separating said phases from each other and separating the admixture of solvents from each phase.

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 commingling the oil with a solvent comprising an admixture of 25 to 50% ortho-chlorophenol, 70 to 40% para-chlorophenol and 5 to 10% phenol, cooling the admixture of oil and solvent to a temperature below 80° F. to effect the formation of an extract phase and a raffinate phase, separating said phases from each other and separating the admixture of solvents from each phase.

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