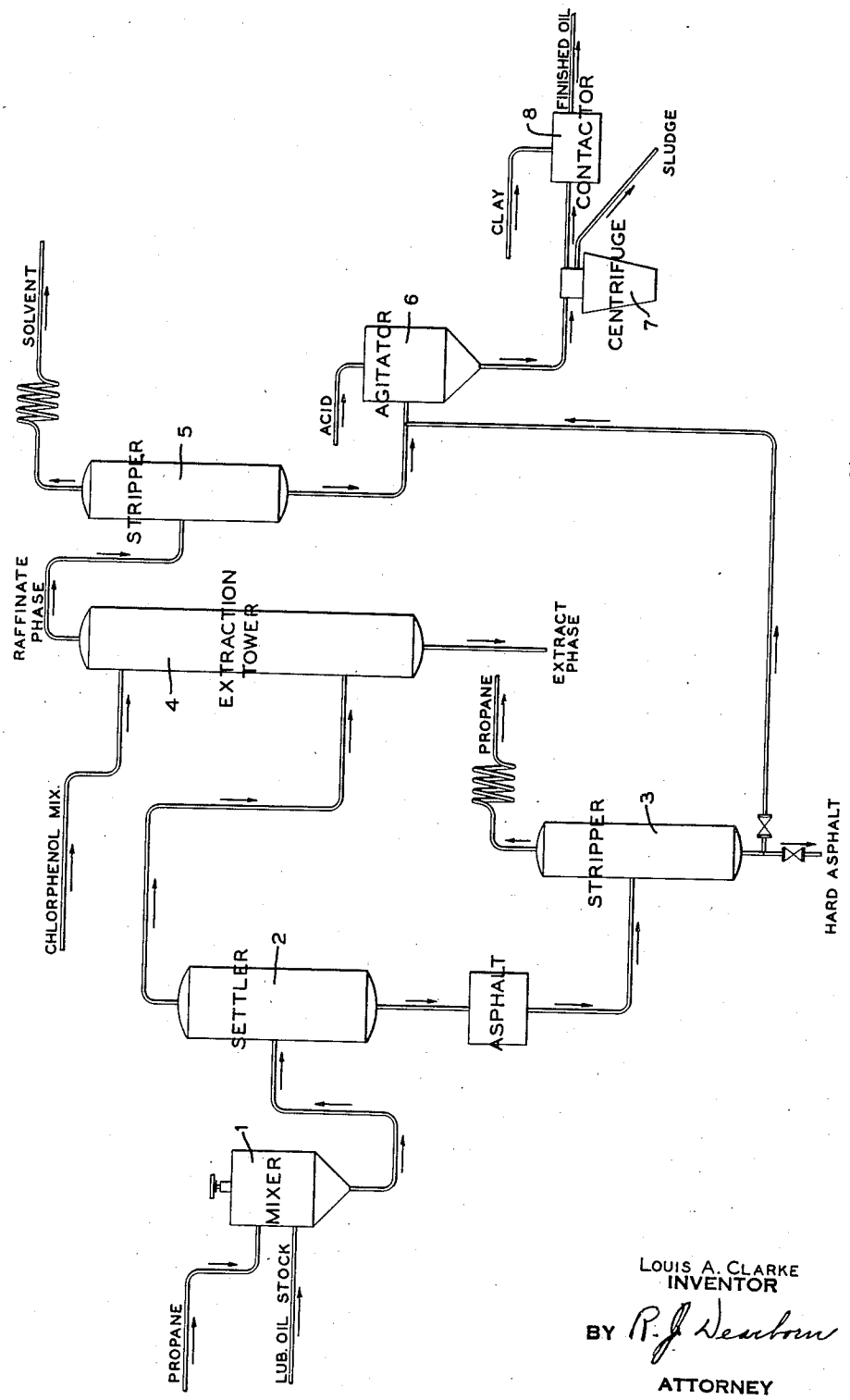
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SOLVENT REFINING OF HYDROCARBON OIL

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SOLVENT REFINING OF HYDROCARBON OIL

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This invention relates to refining hydrocarbon oil by solvent extraction.

The invention contemplates extracting hydrocarbon oil with a solvent obtained by chlorinating crude phenol. The invention contemplates extracting oil with this solvent in the presence of a suitable auxiliary solvent, such as a light petroleum fraction, or a liquefied normally gaseous hydrocarbon, such as propane.

The solvent which I contemplate employing consists of a distillate obtained by distilling to a temperature up to about 220° C. and at atmospheric pressure a mixture resulting from chlorinating crude phenol under conditions such that at least 60% of the phenol has been chlorinated. The distillate so obtained comprises mainly a mixture of ortho and parachlorphenol, and may contain unreacted phenol together with a small amount of dichlorphenol.

Prior to distillation, the chlorinated mixture may be treated with a small amount of alkali sufficient to remove hydrogen chloride formed during the chlorination.

The distillate will have a composition as follows:

Table 1

	Per cent by volume
Phenol	0–40
Parachlorphenol	30–55
Orthochlorphenol	20–50
Dichlorphenol	0–3

If desired, the distillation can be regulated so as to leave the major portion of the dichlorphenol in the residue. The content of unreacted phenol will depend upon the extent to which chlorination has been carried out.

It has been found that a solvent mixture having a composition within the range above specified is suitable for the purpose of this invention. The relative proportions of ortho and paramonochlorphenol in the mixture can be varied to some extent, but it is desirable that substantial proportions of each of these compounds be present and that the parachlorphenol should predominate. Thus, in a mixture of para and orthochlorphenol, the para compound advantageously constitutes about 50 to 75% thereof by volume.

A specific mixture having a composition falling within the range set forth in Table 1 above, and which has been found particularly effective for refining residual lubricating oil stocks, has the following composition:

Table 2

	Per cent by weight
Phenol	15
Orthochlorphenol	31
Parachlorphenol	51
Dichlorphenol	3

A mixture such as this is particularly adapted to the refining of residual lubricating oil stocks, or lubricating oil stocks containing dark-colored constituents and residual carbon-forming bodies. This solvent is particularly efficient in removing these undesired constituents of lubricating oil stock while, at the same time, permitting the obtaining of high yields of refined oil.

For example, in the refining of residual lubricating oil stock, the chlorphenol mixture of my invention is much more efficient in effecting removal of residual carbon-forming bodies and dark-colored constituents than solvent mixtures such as phenol and cresylic acid of the composition usually employed as an extraction solvent for this type of stock.

This is shown by reference to the following examples in which the refining action of the chlorphenol mixture of my invention is compared with a mixture of phenol and cresylic acid containing around 35% of phenol. In each instance, the solvent was employed in conjunction with propane. The residual stock used was a dewaxed paraffin residuum derived from Mid-Continent crude and having the following tests:

Gravity, A. P. I.	18.0
Saybolt Universal viscosity:	
At 100° F.	4336
At 210° F.	161.5
Viscosity index	60
Viscosity gravity constant	.874
Carbon residue, per cent	6.8
Pour, °F.	+20

In the first experiment, the above stock was mixed with propane in the ratio of five parts of propane to one part of stock. The dilute mixture was then subjected to countercurrent extraction with a chlorphenol mixture of the composition shown in Table 2, using one part of chlorphenol mixture to one part of residual stock. The extraction was effected at a temperature of 75° F. at which temperature the stock was separated into extract and raffinate phases. These phases were removed and the solvent stripped therefrom. A separate sample of the same stock was extracted with a mixture of phenol and cresylic acid using the same ratio of solvent mixture to

oil, and the same ratio of propane at the same extraction temperature.

The raffinate oils obtained in each extraction, after removal of the solvents, were found to have the following characteristics:

	Chlorphenol raffinate	Phenol-cresylic acid raffinate
Gravity, A. P. I.	26.7	25.7
Saybolt Universal viscosity—		
At 100° F.	687	739
At 210° F.	70.7	71.9
Viscosity index	88	85
Carbon residue, percent	0.50	0.75
Color Tag Rob	1½	⅝
Yield by volume, percent	60	61

Thus, it will be observed that the volume of raffinate obtained in each case was substantially the same but the raffinate obtained by extraction with the chlorphenol mixture has a somewhat higher viscosity index, a considerably lower residual carbon content, and is of substantially better color.

A second test was made on the same residual stock, with the same solvent mixtures, under the same conditions of propane dilution and extraction temperature, but employing two parts of solvent to one part of residual stock. The raffinate oils obtained in each extraction, after removal of the solvents, were found to have the following characteristics:

	Chlorphenol raffinate	Phenol-cresylic acid raffinate
Gravity, A. P. I.	28.5	28.2
Saybolt Universal viscosity—		
At 100° F.	548	528
At 210° F.	65.4	64.6
Viscosity index	94.5	95
Carbon residue, percent	0.36	0.41
Color Tag Rob	2¼	1
Yield by volume, percent	53	50

In this case, it will be seen that a larger yield of oil of substantially the same viscosity index but having a lower carbon residue and a much better color was obtained by extraction with the chlorphenol mixture.

While residual stocks have been referred to above, it is, of course, contemplated that distillate stocks, such as those having a viscosity of around 75 Saybolt Universal seconds at 210° F. and higher, may be refined to advantage by extraction with the above described chlorphenol mixture. Moreover, extraction with the solvent of this invention permits the production of oils which do not require subsequent treatment with acid and clay. However, subsequent treatment with acid and clay may be employed where it is desired to produce a product having superior characteristics.

Employment of this type of extraction solvent permits extraction at lower temperatures and pressures than with solvents, such as a mixture of phenol and cresylic acid, and yet permits the obtaining of a final product of equal or even better character.

In order to further illustrate the invention, reference will now be made to the following drawing showing a flow diagram of the process as applied to the refining of a lubricating oil stock containing asphaltic constituents.

Lubricating oil stock as, for example, a mixed base residuum, is conducted from a source not shown to a mixer **1** wherein it is mixed with propane, also conducted from a source not shown. In the mixer **1**, the residuum is mixed with propane in the proportion of about one part of residuum to from three to five parts of propane. The mixture may be heated to a temperature of about 70° to 120° F., depending on the wax content of the oil, and at this temperature conducted to a settler **2** wherein precipitation of the hard asphaltic constituents occurs.

It is unnecessary to effect precipitation of the resinous type of asphaltic constituents at this point, since such constituents are extracted from the oil in the subsequent extraction step by the chlorphenol mixture. This, therefore, constitutes an unexpected advantage of the process of this invention since it eliminates the necessity for heating the mixture of propane and oil to a higher temperature in order to precipitate the resinous constituents.

The hard asphaltic constituents precipitated in the settler **2** are withdrawn and conducted to a stripper **3** wherein the propane mixed therewith is removed, leaving the hard asphalt.

The solution remaining in the settler from which the hard asphaltic constituents have been precipitated is withdrawn and conducted to the lower portion of an extraction tower **4**. A chlorphenol mixture of substantially the composition set forth above is introduced to the upper portion of the extraction tower **4** at a temperature of around 70 to 100° F., and in the proportion of from one to two parts of solvent to one part of oil.

The solution of oil and propane is thus brought into countercurrent contact with the chlorphenol solvent mixture, as a result of which extract and raffinate phases are formed. Sufficient pressure is maintained within the extraction tower **4** to keep the propane in the liquefied state. This pressure may range from around 120 to around 180 pounds per square inch.

The extract phase, comprising low viscosity index constituents, as well as soft asphaltic constituents dissolved in the main body of the chlorphenol solvent mixture, is removed from the bottom of the extraction tower **4** and thereafter disposed of in any suitable manner as desired.

The raffinate phase, accumulating in the top of the tower and consisting of high viscosity index oil mixed with some of the chlorphenol mixture and diluted with propane, is drawn off to a stripper **5** wherein the solvent, including propane, is removed.

The solvent-free oil is withdrawn from the stripper **5** and may not require any further treatment. However, where it is desired to further improve the quality, the stripped oil may be conducted to an agitator **6** wherein the oil is treated with sulphuric acid, using about 10 to 25 pounds of 98% sulphuric acid per barrel of oil.

Where emulsion difficulties are encountered in acid-treating, such as in the case of oils having a viscosity index of 100 or over, it is of advantage to add a small amount of hard asphalt to the oil prior to treatment with acid in the agitator **6**. This asphalt advantageously comprises a portion of that removed from the stripper **3**, to which reference has already been made. The addition of this small amount of hard asphalt serves to prevent the formation of emulsions which will not break down readily on standing. Very satisfactory results have been secured with

propane asphalt obtained from Mid-Continent residual fractions.

The mixture is withdrawn from the agitator 6 to a centrifuge 7 by means of which the sludge is removed. The centrifuged oil is then conducted to a contactor 8 wherein it is contacted with clay at a temperature of around 500° F., using about 10 to 25 pounds of clay per barrel of oil.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of solvent refining residual lubricating oil stock containing low and high viscosity index constituents as well as asphaltic constituents to produce extract and raffinate oil, the viscosity index of said stock being about 20 or more lower than that of the raffinate oil produced from it which comprises mixing the oil with propane in such proportion that the hard asphaltic constituents of the oil are precipitated at a temperature of around 70° to 120° F., removing the asphaltic constituents so precipitated, extracting the mixture of propane and oil with a solvent comprising around 15% phenol, 51% parachlorphenol, 31% orthochlorphenol, and 3% dichlorphenol, forming an extract phase comprising low viscosity index constituents dissolved in the bulk of the solvent and a raffinate phase containing relatively high viscosity index constituents mixed with some of the solvent, separating the two phases, removing the solvent therefrom, incorporating in the raffinate oil a small portion of the aforesaid hard asphalt, and subjecting the raffinate oil to treatment with acid in the presence of said added asphalt.

2. The method of solvent refining heavy residual lubricating oil such as derived from mixed base crude petroleum and containing constituents of differing viscosity indices as well as a relatively large proportion of dark-colored and residual carbon-forming bodies to produce extract and raffinate oil, the viscosity index of the untreated oil being about 20 or more lower than that of the raffinate oil produced from it which comprises extracting the stock with a solvent which comprises a phenol mixture containing around 15% phenol, 51% parachlorphenol, 31% orthochlorphenol and 3% dichlorphenol, forming an extract phase comprising low viscosity index constituents together with dark-colored and residual carbon-forming bodies dissolved in the solvent and a raffinate phase containing relatively high viscosity index constituents of light color and of low residual carbon content, separating the two phases, removing the solvent therefrom, and subjecting the raffinate oil to acid treatment in the presence of a small amount of added asphalt, said asphalt being hard, substantially non-resinous and insoluble in liquid propane at a temperature of around 70 to 120° F.

3. The method of solvent refining heavy residual lubricating oil such as derived from mixed base crude petroleum and containing constituents of differing viscosity indices as well as a relatively large proportion of dark-colored and residual carbon-forming bodies to produce extract and raffinate oil, the viscosity index of the untreated oil being about 20 or more lower than that of the raffinate oil produced from it, which comprises extracting the stock in the presence of a liquefied normally gaseous hydrocarbon with a solvent which comprises a phenol mixture containing around 15% phenol, 51% para-chlorphenol, 31% ortho-chlorphenol and 3% dichlorphenol, forming an extract phase comprising low viscosity index constituents together with dark-colored and residual carbon-forming bodies dissolved in the solvent and a raffinate phase containing relatively high viscosity index constituents of light color and of low residual carbon content, separating the two phases, removing the solvent therefrom, and subjecting the raffinate oil to acid treatment in the presence of a small amount of added asphalt, said asphalt being hard, substantially non-resinous and insoluble in liquid propane at a temperature of around 70 to 120° F.

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