Dec. 13, 1938. E. TERRES ET AL 2,140,485

METHOD OF REFINING MINERAL OILS

Filed May 22, 1935

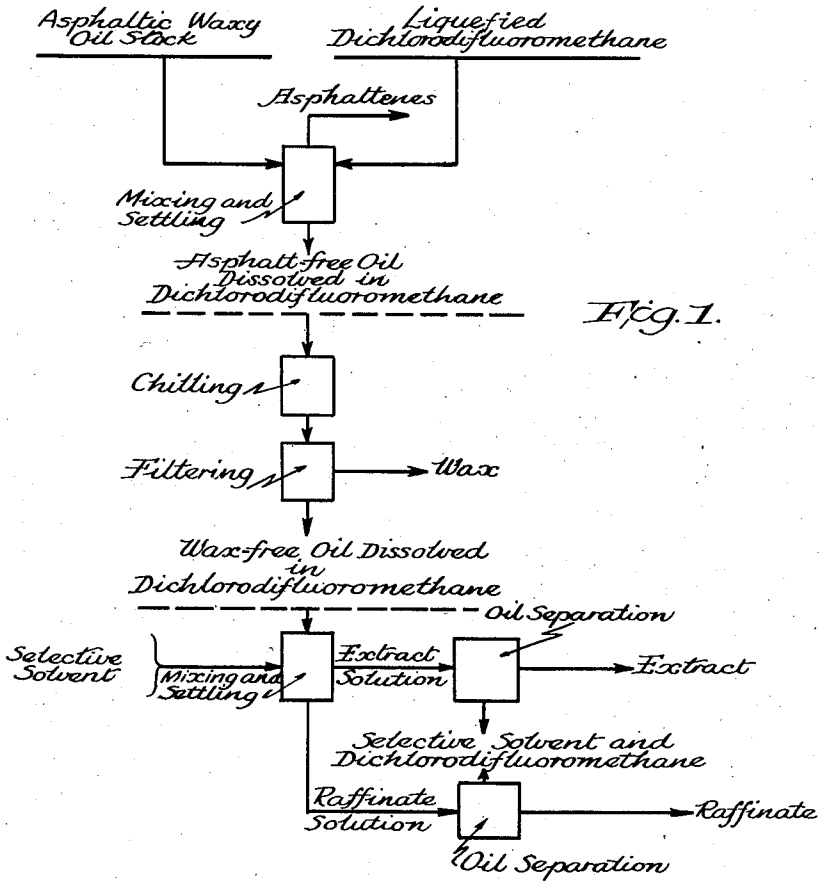
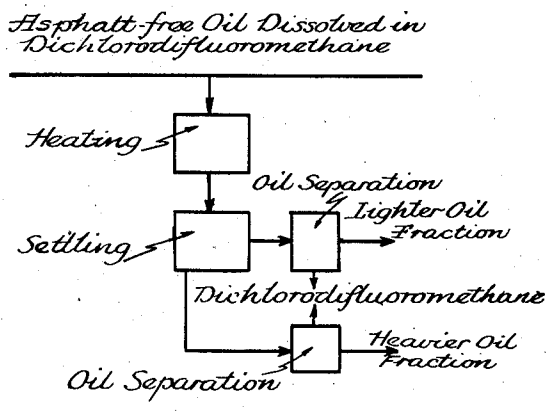


Fig. 1.

Fig. 2.



Inventors
Ernest Terres
Erich Saegebarth.
Joseph Moos
Hans Ramser

By Emery Booth Vanney & Holcombe
Attorneys

Patented Dec. 13, 1938 2,140,485

UNITED STATES PATENT OFFICE

2,140,485

METHOD OF REFINING MINERAL OILS

Ernest Terres, New York, Erich Saegebarth, Long Island City, N. Y., and Joseph Moos, Berlin-Mariendorf, and Hans Ramser, Berlin-Steglitz, Germany, assignors, by mesne assignments, to Edeleanu Gesellschaft, m. b. H., Berlin, Germany, a corporation of Germany

Application May 22, 1935, Serial No. 22,914

8 Claims. (Cl. 196—13)

This invention aims to provide an improved method of refining mineral oils. More particularly, the invention relates to the use of dichlorodifluoromethane as a solvent for treating lubricating oil stocks to produce high quality lubricating oils to meet the needs of modern automobile and airplane motors, although the invention is not limited thereto.

For these uses, lubricating oil stocks require treatment to improve the viscosity and stability characteristics, etc., and, depending on their source, nature and desired quality of the refined oil, are commonly treated under one or more of three headings, namely: deasphaltizing, dewaxing, and extraction or removal of aromatic and unsaturated hydrocarbons.

The use of liquid dichlorodifluoromethane as a dewaxing solvent or diluent is described and claimed in the copending application of one of us, Hans Ramser, Serial No. 572,437, filed October 31, 1931, Patent No. 2,009,454, dated July 30, 1935.

We have discovered that liquid dichlorodifluoromethane can be used very successfully as a deasphaltizing solvent, and that it can also be used to effect a phase separation of hydrocarbon oils at elevated temperatures below its critical temperature (232.6° F.).

The extraction or removal of aromatic and unsaturated hydrocarbons can be effected very advantageously by employing dichlorodifluoromethane in conjunction with other solvents, as will be described hereafter, and such use is part of our invention.

According to our invention, therefore, dichlorodifluoromethane may be employed effectively to accomplish deasphaltizing, dewaxing, and separation or removal of aromatic and unsaturated hydrocarbons.

The use of dichlorodifluoromethane for refining waxy asphaltic lubricating oil stocks is rendered particularly valuable by the fact that, if desired, each type of refining can be conducted separately so as to provide close control and to avoid mixing of the three classes of constituents removed, thereby securing these as initially separated by-products.

Non-asphaltic components of mineral oil are completely dissolved by liquid dichlorodifluoromethane at normal temperatures, whereas asphaltenes are insoluble at all temperatures and separate out as a separate layer from a solution of oil and the solvent. By avoiding low temperatures, there will be no separation of wax; and by avoiding elevated temperatures above a critical point determinable for each stock treated there will be no separation into layers of hydrocarbons normally wholly miscible in the solvent. Thus the asphaltenes can be removed without at the same time causing separation of other components.

In the accompanying drawings, wherein we have shown several embodiments of the invention for purposes of illustration,

Fig. 1 is a flow diagram showing the use of dichlorodifluoromethane in the successive treatment of an asphaltic waxy oil stock for asphalt removal, wax removal, and separation of the oil into a raffinate fraction and an extract fraction by means of a selective solvent;

Fig. 2 is a flow diagram showing the use of dichlorodifluoromethane for dividing an asphalt-free oil into a lighter oil fraction and a heavier oil fraction.

It will be evident to persons skilled in the art that the method steps shown in these flow diagrams may be combined in various different ways and in various different sequences.

The following examples illustrate various types of treatment.

Example 1

This example illustrates the use of the solvent for deasphaltizing.

A Mid-Continent residual oil having an A. P. I. gravity of 20, Saybolt viscosities of 997 at 130° F. and 145 at 210° F., a Conradson carbon residue of 5.6, and a wax content of 10% by volume, was agitated at 130° F. with four volumes of dichlorodifluoromethane in a vessel under pressure sufficient to maintain the solvent in liquid phase. Upon allowing the mixture to stand, two layers were formed. The upper layer consisted of asphaltenes containing some of the solvent in solution, while the lower layer consisted of the bulk of the solvent containing the oil in solution. The layers or phases were separated and the solvent removed therefrom.

The yield of asphalt was 13% by volume and the yield of oil was 87% by volume. The deasphaltized oil had an A. P. I. gravity of 21.9, Saybolt viscosities of 664 at 130° F. and 109 at 210° F., and a carbon residue value of 3.0.

As previously indicated, dichlorodifluoromethane is suitable for dewaxing. When highly asphaltic stocks are to be dewaxed, the stock will ordinarily be deasphaltized first in order to facilitate the mechanical removal of the wax following precipitation thereof, as by filtering, and to permit securing the asphaltenes and wax separated from each other.

In such case the oil is dissolved in the solvent and the asphalt removed, as illustrated in Example 1, and then the oil-solvent solution is chilled to precipitate out the wax.

If desired, as may be the case particularly with oils containing only small quantities of asphaltenes, the separation of asphaltenes and wax may be carried out in one operation by dissolving the stock in the solvent, chilling the mixture to the dewaxing temperature, and filtering. In this case the asphaltenes will be separated with the wax.

Example 2

This example illustrates the use of dichlorodifluoromethane for dewaxing.

A mixed-base lubricating oil of Mid-Continent origin with a pour point of 110° F. was mixed with 2.5 volumes of liquid dichlorodifluoromethane in a pressure vessel. The solution was cooled to −19° F. by applying suction to the vessel to cause evaporation of the solvent, the amount evaporated being replaced by introducing liquid solvent into the vessel, keeping the amount of liquid in the vessel constant. The chilled mixture was then filtered through an ordinary type filter press at −19° F., under a pressure of about 2 lbs. per sq. in. The filtered oil was freed of solvent by evaporation.

The properties of the oil before and after dewaxing were as follows:

	Before dewaxing	After dewaxing
°A. P. I.	24.4	23.1
Viscosity at 210° F.	61	65
Viscosity gravity constant	0.843	0.852
Pour point, °F.	110	−5

Dichlorodifluoromethane possesses a negative temperature coefficient in regard to the solubility of mineral oils therein. Upon heating a solution of asphalt-free oil in the solvent, a point can be reached at which separation into two liquid layers or phases, containing oil of differing properties, occurs. One of the two phases contains the bulk amount of the solvent, having a certain amount of oil in solution, the amount of oil being smaller the higher the temperature. This oil will be lighter than the original oil. The other phase contains the oil which has separated out from the main body of solvent and is saturated with the solvent, and the oil in this phase is heavier than the original oil. Such phase separation will occur at about 212° F. in the case of a heavy cylinder stock. The specific gravity of the solvent, which is 1.5 at −36° F., decreases to 0.83 at 225° F. The position of the two layers may therefore be reversed upon passing a certain temperature, dependent upon the specific gravity of the oil.

Example 3

A 650 steam refined Pennsylvania stock having an A. P. I. gravity of 24.3, a Saybolt viscosity of 231 at 210° F., and a carbon residue of 3.4, was mixed with four volumes of liquid dichlorodifluoromethane and the mixture was heated and agitated to 212° F., under pressure sufficient to maintain the solvent in liquid phase. Upon standing at this temperature, two layers were formed. The upper layer comprised the bulk of the solvent, and contained the fraction of oil which remained dissolved therein. The lower layer consisted of the oil which was undissolved in the solvent at the elevated temperature. The layers were separated and the solvent removed therefrom.

The extraction treatment produced oil fractions having different properties as shown in the following table, which may be compared with the specification of the original oil given above.

	Dissolved oil	Undissolved oil
Yield volume, percent	10.6	89.4
°A. P. I.	27.3	23.6
Viscosity at 130° F.		1790
Viscosity at 210° F.		255
Carbon residue	1.2	4.1

Dichlorodifluoromethane is not entirely miscible with selective solvents such as quinoline, aniline, cresol, phenol, chlorophenol, and others, used for extracting aromatic and unsaturated hydrocarbons and which are characterized by having a selective action as between high and low viscosity-index hydrocarbons. That is, when mixed with such solvents a phase separation will occur. It is therefore possible to use dichlorodifluoromethane in conjunction with these solvents in the way that liquid propane is used, to effect double solvent refining. This procedure is especially advantageous for the treatment of residual oils, which are hard to refine, and is likewise applicable to distillates, as shown by the following examples.

Example 4

One volume of a Mid-Continent residual cylinder stock was agitated with four volumes of dichlorodifluoromethane and one volume of phenol, at 104° F. Upon standing, two layers were formed and these were separated. The raffinate layer, without removal of solvents contained therein, was mixed again with one volume of phenol at 104° F., and upon standing two layers again formed. The solvent was removed from the resulting raffinate layer, and from the two extract phases. The properties of the original stock and of the final raffinate are shown in the table of the next example.

Example 5

One volume of the same Mid-Continent stock referred to in the preceding example was agitated and heated to 140° F. in admixture with four volumes of dichlorodifluoromethane and one volume of parachlorophenol. Upon layer separation, the raffinate layer was treated in the same manner with one volume of parachlorophenol at 140° F., again resulting in a separation into a raffinate layer and an extract layer upon standing. The final raffinate, after solvent removal, had the properties shown in the following table:

	Original oil	Raffinate Example 4	Raffinate Example 5
Yield volume, percent	100	66	54
°A. P. I.	20	24.5	27.5
Viscosity at 130° F.	997	524	320
Viscosity at 210° F.	145	98	77
Carbon residue	5.6		0.67

Example 6

A dewaxed Mid-Continent distillate was mixed and agitated with 3 volumes of dichlorodifluoromethane and 1 volume of aniline, at 104° F. The

layers were allowed to separate and were freed of solvents. The raffinate (refined oil) was contacted with 10% of diatomaceous earth or other color adsorbing material at 450° F. The properties of the untreated oil and of the finished raffinate are shown in the table of the next example.

Example 7

The same distillate employed in the preceding example was treated with 2 volumes of dichlorodifluoromethane and 2 volumes of parachlorophenol, at 113° F. After allowing two layers to form, the layers were separated and the solvents removed by distillation. The properties of the untreated stock and of the raffinate oil are shown in the following table:

	Untreated stock	Raffinate Example 6	Raffinate Example 7
Yield volume, percent	100	90	70
°A. P. I.	23.2	24.9	27.5
Viscosity at 100° F	1287	1054	735
Viscosity at 210° F	91	84.5	74.8
Viscosity index	75	84	94
Carbon residue	1.9	1.1	0.42

Example 8

One volume of the same Mid-Continent distillate, referred to in Examples 6 and 7, was mixed and agitated with two volumes of dichlorodifluoromethane and three volumes of quinoline. The mixture was cooled and at +10° F. a separation into two layers commenced. Cooling was continued to −22° F. to increase the rate of settling out of the layers. After equilibrium was reached the two layers were separated and the solvents removed therefrom. The raffinate oil, which amounted to 68 vol. % of the untreated oil, was finished by contacting with 10% of clay at 450° F. The character of the finished raffinate is shown in the following table:

	Untreated oil	Finished raffinate
°A. P. I.	23.2	28.0
Viscosity at 100° F	1287	728
Viscosity at 210° F	91	74.6
Viscosity index	75	94
Carbon residue	1.9	0.30
A. S. T. M. color		5

The foregoing examples of double solvent extraction of lubricating oils show that the treatment with the selective solvent is rendered highly effective and is benefited by extracting oil which has been dissolved in dichlorodifluoromethane.

From the foregoing description and accompanying flow diagrams it will be evident that in accordance with our invention liquid dichlorodifluoromethane may be used for deasphaltizing, dewaxing, and is of use in extraction or removal of types of hydrocarbon constituents, such as aromatic, unsaturated and unstable components. When oil is dissolved in dichlorodifluoromethane it may then be deasphaltized and dewaxed by appropriate adjustment of temperature; and may be refined by adjusting the temperature to cause a phase separation, or by extracting the solution with phase-forming selective solvents. Thus the presence of the dichlorodifluoromethane is effective in all stages of a complete refining process.

Attention is called to our copending companion application Ser. No. 23,130, filed May 23, 1935, which relates to the use of the broad group of organic fluorine compounds, the use of only one species of which (dichlorodifluoromethane) is expressly described and claimed herein.

What we claim is as follows:

1. A method of refining an asphaltic mineral oil comprising dissolving the oil in dichlorodifluoromethane, removing the undissolved asphalt from the solution at a temperature at which other components of the oil remain dissolved, and extracting the solution with a selective solvent in which the dichlorodifluoromethane is not wholly miscible at a temperature below the critical point of the original solution of oil in dichlorodifluoromethane, to produce an extract phase and a raffinate phase, and separating the two phases.

2. The method of refining an asphaltic waxy mineral oil comprising dissolving the oil in dichlorodifluoromethane, removing the undissolved asphalt at a temperature at which the other components of the oil remain dissolved, chilling the mixture to a low temperature at which the wax separates out, removing the separated wax, and extracting the solution with a selective solvent in which the dichlorodifluoromethane is not wholly miscible at a temperature below the critical point of the original solution of oil in dichlorodifluoromethane, to produce an extract phase and a raffinate phase, and separating the two phases.

3. A method of treating a mineral oil comprising dissolving the oil in dichlorodifluoromethane and heating to a temperature above the critical point of the solution and below 232.6° F. to cause a separating out of initially dissolved components of the oil and the formation of two layers, and dividing out the layers.

4. A method of treating an asphalt-free mineral oil comprising dissolving the oil in dichlorodifluoromethane and heating the solution to a temperature above the critical point thereof and below 232.6° F. to produce two liquid phases, and separating the phases to obtain a relative lighter oil fraction and a relatively heavier oil fraction.

5. A method of treating a mineral oil comprising dissolving the oil in dichlorodifluoromethane and thereafter extracting at a temperature in excess of 100° F. and less than 232.6° F. with a selective solvent which has selective action as between high and low viscosity-index hydrocarbons and in which the dichlorodifluoromethane is not wholly miscible, to produce two liquid phases, and separating the two phases.

6. A method of refining a substantially wax-free mineral oil comprising dissolving the oil in dichlorodifluoromethane and extracting at a temperature above 100° F. and not above 232.6° F. with a selective solvent which has a selective action as between high and low viscosity-index hydrocarbons and in which the dichlorodifluoromethane is not wholly miscible, to produce two liquid phases, and separating the two phases.

7. A method of treating mineral oil comprising dissolving the oil in dichlorodifluoromethane and thereafter extracting at a temperature below 232.6° F. at which contained wax is substantially dissolved with a selective solvent in which the dichlorodifluoromethane is not wholly miscible, to produce an extract phase and a raffinate phase, and separating the two phases.

8. A method of refining an asphaltic mineral oil comprising dissolving the oil in dichlorodifluoromethane at a temperature above 100° F. and not above the critical point of the solution to dis-

solve all except asphaltic components, removing the undissolved residue, heating the solution to a temperature above its critical point and below 232.6° F. to cause separation thereof into two layers, dividing out the layer containing the components dissolved in dichlorodifluoromethane and driving off the latter to produce a lubricating oil fraction having a high viscosity index.

ERNEST TERRES.
ERICH SAEGEBARTH.
JOSEPH MOOS.
HANS RAMSER.