

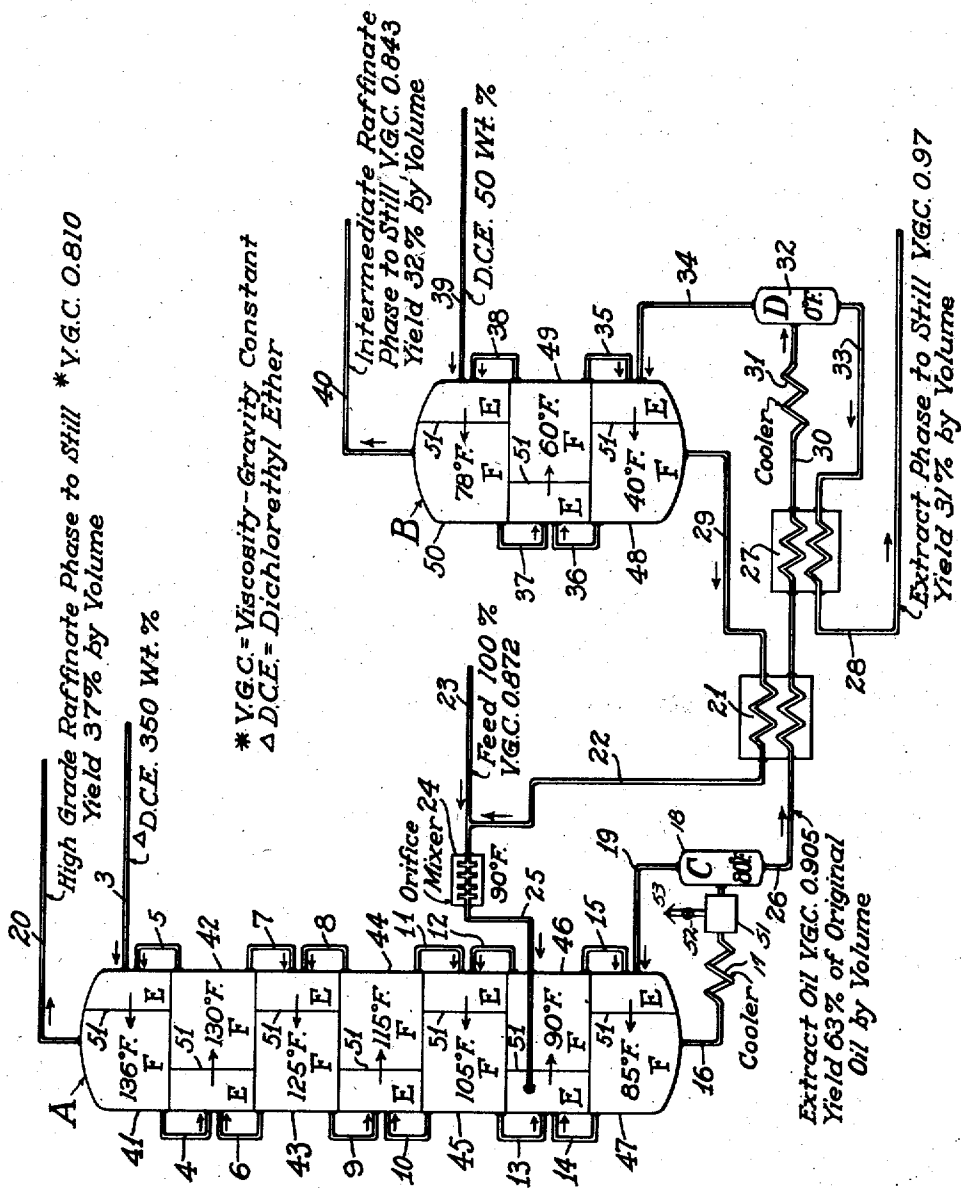
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D. R. MERRILL

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SOLVENT EXTRACTION OF OIL

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INVENTOR
 David R. Merrill
 BY *Philip Subkow*
 ATTORNEY.

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SOLVENT EXTRACTION OF OIL

David R. Merrill, Long Beach, Calif., assignor to
Union Oil Company of California, Los Angeles,
Calif., a corporation of California

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20 Claims. (Cl. 196—13)

This invention relates to the fractionation of petroleum hydrocarbons by the use of solvents.

Most crude oils are complex mixtures of hydrocarbons and contain varying proportions of paraffin, naphthene, aromatic and unsaturated hydrocarbons. In the production of lubricating oil for internal combustion motors it is desirable to produce a finished oil that exhibits a low temperature viscosity susceptibility, i. e., one which shows a minimum change in physical characteristics for a given change in temperature. The hydrocarbons of highest hydrogen to carbon ratio are usually waxes, which because of their high melting point are not suitable for ordinary lubrication. The hydrocarbons of next highest hydrogen ratio are the so-called "paraffinic lubricating oils" from paraffin base crude. The paraffinic oils are characterized by exhibiting a relatively low temperature viscosity susceptibility, whereas, the aromatic and highly unsaturated hydrocarbons are characterized by exhibiting a relatively high temperature viscosity susceptibility.

In many crude oils, such as those produced from the Mid-Continent fields, which are of a mixed base character, and those of the California fields, which are asphaltic in character to varying extent, there are present three distinct types of oils. One group resembles the oils which are present in paraffin base crudes and exhibits a low temperature viscosity susceptibility. A second group is present which exhibits a very high temperature viscosity susceptibility and a third group is present which has a temperature viscosity susceptibility intermediate between the group having the low temperature viscosity susceptibility and the group having the high temperature viscosity susceptibility.

Recently a number of solvents, such as aniline, nitro-benzene, furfural, B B' dichlorethyl ether, methyl cellosolve, cellosolve acetate and sulphur dioxide, have been employed to separate a hydrocarbon mixture into its respective paraffinic and non-paraffinic constituents. If a hydrocarbon mixture is mixed with one of the foregoing solvents under the proper conditions of temperature, the unsaturated aromatic hydrocarbons in the mixture tend to be dissolved, and, furthermore, if this mixture of undissolved fractions and solvent containing the dissolved fractions is allowed to settle, the relatively light insoluble oil fractions rise to the top and form an upper liquid phase and the solvent and dissolved fractions which are relatively heavy settle out and form a lower liquid phase. The undissolved fraction which is more paraffinic in character is often

referred to as the raffinate, whereas, the fraction dissolved in the solvent is known as the extract, and may consist to a considerable extent of either unsaturated or aromatic hydrocarbons or a mixture of these hydrocarbons. For convenience the raffinate fraction, or the fraction which is insoluble in the solvent, is called "paraffinic oil" and the fraction which dissolves in the solvent is called "non-paraffinic oil".

In the conventional method of employing solvents to separate paraffinic and non-paraffinic fractions two oil fractions are produced; a raffinate fraction, or the portion insoluble in the solvent and an extract fraction, or the oil fraction which is soluble in the solvent. Where oils are extracted which are mixed base in character, or asphaltic in character and which contain the intermediate group of hydrocarbons mentioned above, this group is either recovered in the raffinate or it is lost in the extract because modern methods of refining with solvents will not permit these middle fractions to be produced as a separate entity. It is undesirable to permit this middle oil to be recovered as a raffinate along with the paraffinic fractions because the presence of these middle oils tends to increase the temperature viscosity susceptibility of the raffinate. Furthermore, it is undesirable to permit these middle oils to be recovered in the extract since the intermediate oils are valuable lubricating oils for purposes where temperature viscosity susceptibility is of minor importance. The extract is usually employed for fuel or for cracking purposes or for the production of solvents which are aromatic in character. These middle oils, therefore, act as contaminants. The most desirable cracking stocks are composed mainly of hydrocarbons which are aromatic in character and which are capable of producing fuels having high anti-knock value. Furthermore, where the extract is to be employed for a stock for producing highly aromatic solvents, it is undesirable to have present fractions which are intermediate between the aromatic and paraffinic groups.

I have discovered that it is possible to separate these middle oil fractions present in the crude oils as a separate fraction by means of solvent extraction. By separating these middle oils as a separate fraction I am able to produce a paraffinic oil having a relatively low temperature viscosity susceptibility which is not contaminated with fractions of a relatively high temperature viscosity susceptibility and/or an extract which is highly aromatic in character.

In any system of solvent extraction it is highly

desirable to employ a minimum quantity of solvent to obtain a maximum degree of refinement. This can only be carried out providing proper conditions of extraction have been determined.

5 successive extraction of a hydrocarbon mixture with a selective solvent at one temperature is only capable of producing a raffinate which is of limited paraffinicity. The first one or two treatments of the oil with a solvent at one definite temperature will result in production of relatively high yields of extract, but thereafter the solvent becomes relatively ineffective and will not remove from the oil the remaining undesirable fractions present but the material extracted is of substantially 10 the same composition as that remaining. Furthermore, it is undesirable to separate at relatively low temperatures because of the large quantity of solvent which is necessary to dissolve the non-paraffinic fractions present in the hydrocarbon mixture. Where high temperatures are employed in separating paraffinic and non-paraffinic fractions great care must be exercised in order that the temperature employed is below that at which the oil and solvent are completely miscible. 20 The desirable method of separating paraffinic and non-paraffinic fractions by solvent extraction is to extract the oil in stages operating at a temperature close to the point of complete miscibility between the oil and the solvent. Such a system of extraction results in the maximum yield of refined oil with a minimum quantity of solvent. By successively extracting a hydrocarbon mixture at successively higher temperatures with a selective solvent it is possible to obtain a maximum degree of refining with a minimum amount of solvent. 30 As has been pointed out before, successive extraction of a hydrocarbon mixture at one temperature with the same solvent is open to criticism because after the first one or two extractions the solvent becomes relatively ineffective and is incapable of removing fractions which are present which are undesirable. However, where the extraction is carried out in stages operating at successively higher temperatures this fault is not present. 40 The extraction at successively higher temperatures compensates for the increasingly limited ability of the solvent to remove the undesirable fractions present. At the higher temperatures the solvent power for the undesirable fractions remaining in the oil becomes greater and they are thereby removed from the mixture. 50

In separating a hydrocarbon mixture with a selective solvent, such as dichlorethyl ether, near the temperature of complete miscibility it is possible, as has been described before, to produce a raffinate which is highly paraffinic in character and which exhibits a low temperature viscosity susceptibility and an extract which contains all of the non-paraffinic fractions together with the middle oils. After the extract phase is withdrawn from the extraction system, it is cooled to a temperature considerably below the temperature of the first extraction. At this low temperature a second raffinate is produced which has temperature viscosity susceptibility characteristics of the intermediate oil present in the hydrocarbon mixture and an extract is produced from the second extraction at a lowered temperature which is highly non-paraffinic in character. In producing 70 the high grade raffinate from the first extraction and the second raffinate by rejection from the extract first recovered from the primary extraction it is necessary that temperatures be employed which are very close to the point of complete miscibility of the solvent and oil. I have found that 75

it is desirable to operate within 20° F. of the temperature of complete miscibility. These three grades of oil are best produced by the process shown in the figure.

It is, therefore, an object of my invention to extract oil with a selective solvent and to produce a first grade raffinate, a second grade raffinate and an extract. 5

It is another object of the invention to extract oil with a selective solvent near the temperature of complete miscibility between the oil and the solvent and to separate a raffinate fraction and a fraction dissolved in the selective solvent at this temperature. 10

It is another object of the invention to counter-currently extract oil with a selective solvent at successively higher temperatures. 15

It is another object of the invention to extract oil in a plurality of stages with a selective solvent at a temperature in each extraction stage about 20° F. lower than the temperature of complete miscibility between the oil and the solvent. 20

It is still another object of the invention to counter-currently extract oil with a selective solvent in a plurality of stages in which the temperature of extraction in each extraction stage is about 20° F. lower than the temperature of complete miscibility between the oil and the solvent. 25

My process will be more thoroughly understood by referring to the drawing. Referring more particularly to the drawing, the apparatus comprises two extraction columns A and B. These extraction columns are divided into a plurality of extraction stages, 41, 42, 43, 44, 45, 46, 47, 48, 49, and 50. Each of these extraction stages is divided into an agitating zone E and a settling zone F. After the solvent and oil have been thoroughly agitated in the agitating zone E they pass through the partition 51 in the direction indicated by the arrow into the settling zone F. Each of these extraction stages is provided with means for introducing oil and solvent into the agitating zone E and means for withdrawing raffinate and solvent containing dissolved fractions from the settling zone F. From the upper part of the column A raffinate is withdrawn through line 20 into the upper part of the column and selective solvent is introduced into line 3. From the lower zone of the column A extract and dissolved fractions are withdrawn 50 through line 16, cooled in cooler 17, settled in separator C and that portion of the extract phase insoluble at the lowered temperature and forming the upper layer in cooler C is returned through line 19 into the agitating zone of extraction stage 47. The solvent and dissolved fractions forming the lower layer in cooler C are withdrawn through line 26 and pass through heat exchangers 21 and 27 to cooler 31 where the temperature of the solvent and dissolved fractions is lowered to a point where a further quantity of oil is separated as an insoluble fraction at this lowered temperature. The cooled mass then passes from cooler 31 into separator D where the heavy solvent containing the remaining dissolved fractions settles to the bottom of separator D and is removed through line 33, heat exchanger 27 and line 28. The insoluble oil fractions in separator D forming the upper layer are removed through line 34 and introduced into the agitating or mixing zone E of stage 48 in extraction column B where it meets solvent and dissolved fractions introduced through line 35. Fresh solvent is introduced through line 39 and countercurrently extracts the fractions introduced through line 34 75

in extracting stages 48, 49, and 50. From stage 50 there is removed an intermediate raffinate through line 40. The solvent and dissolved fractions removed through line 29 from extracting stage 48 pass through line 22 into feed line 23 and are mixed in the orifice mixer in line 23. This mixture then passes through line 25 into stage 46. Thus it is seen that the oil introduced into feed line 23 is split into three fractions, i. e., first grade raffinate withdrawn from line 20, a second grade raffinate withdrawn through line 40, which I have designated on the drawing as an intermediate raffinate, and a final extract which is withdrawn from line 28 alone with solvent. The three fractions withdrawn from the respective lines 20, 40, and 28 are distilled to remove their respective content of solvent.

From the drawing it will be seen that the process is essentially a method of countercurrently extracting oil in a plurality of stages operating at successively higher temperatures. The oil to be extracted is introduced into an intermediate extraction zone and the raffinate produced in this zone is successively extracted at successively higher temperatures and, preferably, at a point near the temperature of complete miscibility between the oil and the solvent. The extract phase withdrawn from the settling zone of the stage in which the oil is introduced, i. e., stage 46, is passed to an extraction stage operating at a lower temperature than stage 46 where it is contacted with fractions which have been removed from stage 47 by cooling the extract phase withdrawn from stage 47 and obtaining a fraction insoluble at this lowered temperature. This insoluble fraction is passed back through line 19 and introduced into the agitating zone E of extraction stage 47 along with the solvent and dissolved fractions withdrawn from stage 46 through line 15.

While I have shown that the solvent and dissolved fractions introduced into the agitating zone E of stage 47 can be washed or rectified with insoluble fractions obtained from cooler C through line 19 I do not propose to limit myself by the use of fractions for washing purposes or for rectification which have been obtained by cooling a selective solvent containing dissolved fractions. Other oils may be introduced through line 19 into agitating zone E to wash or rectify the solvent and dissolved fractions introduced through line 15. For example, I may partially evaporate a selective solvent from the extract phase withdrawn through line 16, introduce the mass containing the remaining selective solvent in oil fractions into cooler C where an oil fraction will separate as an upper layer and can be removed through line 19 and introduced into the agitating zone E of stage 47. This fraction which is obtained by partially evaporating a solvent from the extract phase withdrawn from line 16 will have the same function as fractions introduced through line 19 obtained by cooling the extract phase as described above. I may also use other oils to wash or rectify the extract phase introduced through line 15 into stage 47, for example, liquid normally gaseous hydrocarbons, such as liquid propane, or I may use petroleum naphtha. These materials are introduced through line 19 and mixed with the extract phase introduced through line 15 in the same fashion as described above for mixing these extract phases with the fractions obtained by cooling or partial evaporation of the selective

solvent from an extract phase containing solvent and dissolved fractions.

The oils introduced through line 19 into the agitating zone E of stage 47, as described above, are termed wash oils and are employed to remove valuable constituents of the low solubility paraffinic type from the extract phase. These wash oils, to accomplish such removal of valuable constituents from the extract phase, should be leaner in paraffinic constituents than the oil feed to the column as explained above. Preferably, the types of wash oil are: 1. A fraction separated from the extract phase by cooling or partial evaporation of the solvent; 2. A portion of the whole extract recovered by evaporation of the solvent from the extract phase; 3. A suitable oil fraction from a different stage or operation provided only it is leaner in desirable fractions than the feed to the column and will not contaminate the various extraction products; or 4. A diluent miscible with oil, such as propane or naphtha, which will reduce the viscosity of the oil phase and which has a greater affinity than the selective solvent for the paraffinic fractions in the exact phase or which lowers the solvent power of the selective solvent in the extract phase and causes the most paraffinic constituents present to be forced out of solution from the extract phase.

It is, therefore an object of this invention to contact an extract phase comprising a selective solvent and dissolved fractions with a wash oil capable of removing from the extract phase those fractions present which are most paraffinic in character.

As a specific example of the method of carrying out my process, an oil feed having a viscosity gravity constant of .872 is introduced through line 23 where it meets solvent and dissolved fractions recovered from stage 48 through line 49 and line 22. This mixture passes to the orifice mixer operating at 90° F. After thorough mixing the mass then passes through line 25 into the agitating zone E of stage 46. Dichlorethyl ether (350 weight per cent based on the feed charge) is introduced through line 3 into the agitating zone E of stage 41 operating at a temperature of about 136° F. The oil introduced into stage 46 is agitated with solvent and dissolved fractions introduced through line 13 from the settling zone of stage 45 along with the oil fractions introduced from stage 47 through line 14. After thorough mixing in the agitating zone E of stage 46 the mass then passes into settling zone F of stage 46 where it is allowed to settle. The raffinate fraction of the upper layer in settling zone F of stage 46 is withdrawn through line 12 and introduced into the agitating zone of stage 45 operating at about 105° F. where it meets solvent and dissolved fractions recovered from the settling zone F of stage 44 withdrawn through line 11. After thorough mixing in the agitating zone E the mass passes into settling zone F of stage 45 where the heavy extract phase is withdrawn through line 13 as described above and the light raffinate fraction constituting the upper layer is withdrawn through line 10 and introduced into the agitating zone E of stage 44 operating at 115° F. where it is mixed with solvent and dissolved fractions withdrawn from stage 43 through line 9 after which it passes into the settling zone F of stage 44. The solvent and dissolved fractions in settling zone F of stage 44 are removed through line 11 as described above and the raffinate fraction of the upper insoluble layer in this settling zone is

withdrawn through line 8 and introduced into the agitating zone E of stage 43 operating at 125° F. where it is mixed with solvent and dissolved fractions recovered from settling zone F of stage 42 through line 7. The mixture in agitating zone E of stage 43 passes into settling zone F of stage 43 where the extract and dissolved fractions are removed through line 9 and the raffinate fraction is removed through line 6 into agitating zone E of stage 42 operating at 130° F. where it is mixed with solvent and dissolved fractions recovered from stage 41 through line 4. After thorough mixing in agitating zone E of stage 42 it passes into the settling zone F of stage 42 where the solvent and dissolved fractions settle to the bottom and are removed through line 7 while the light raffinate fraction is withdrawn through line 5 and introduced into the agitating zone E of stage 41 along with fresh solvent introduced through line 3. This stage operates at a temperature of about 136° F. After thorough mixing in agitating zone E of stage 41 the agitated mass passes through the opening in partition 51, indicated by the arrow, into the settling zone F of stage 41 where the solvent and dissolved fractions are removed through line 4 and the high grade first raffinate is withdrawn through line 20.

The solvent and dissolved fractions in settling stage 46 are withdrawn through line 15 and introduced into the agitating zone E of stage 47 where they are mixed with fractions obtained by cooling the extract phase of stage 47 to a temperature of about 80° F. and then allowing the insoluble oil fractions at this lowered temperature to be withdrawn as an upper layer from cooler C through line 19 as described above. When selective solvents are employed which are normally gaseous at ordinary temperatures and pressures, the cooling may be obtained by vaporizing a portion of the solvent from the extract phase as explained above. The extract phase entering 51 is cooled by opening valve 52 and permitting a portion of the solvent to vaporize through line 53. The agitated mass in zone E of stage 47, operating at about 85° F., then passes into settling zone F of stage 47 and the raffinate oil fractions in this stage are withdrawn through line 14 and introduced into agitating zone E of stage 46.

The solvent and dissolved fractions in cooler C are withdrawn through line 26 into cooler 31 where the temperature is lowered to about 0° F. At this temperature a further quantity of the more paraffinic fractions in this extract phase are forced out of solution. The chilled mass then passes to separator D where the solvent containing the remaining dissolved fractions is withdrawn through line 33. The insoluble oil fractions in separator D forming the upper layer are withdrawn through line 34 and introduced into the agitating zone E of stage 48 operating at about 40° F. where these oil fractions are mixed with solvent and dissolved fractions withdrawn from stage 49 through line 35. After thorough mixing the mass in agitating zone E of stage 48 passes into the settling zone of this stage. From the upper part of this settling zone there is withdrawn a raffinate phase through line 36 which is introduced into a stage 49 operating at about 60° F. From the lower part of the settling zone F of stage 49 solvent and dissolved fractions are removed through lines 29 and 22 and introduced into the feed line 23 as described above. The solvent and dissolved fractions from the settling zone F of stage 50 are removed

through line 37 and mixed with the oil introduced into the mixing zone E of stage 49 with the oil introduced through line 36 at a temperature of about 60° F. From settling zone F of stage 49 solvent and dissolved fractions are withdrawn through line 35 and a raffinate is withdrawn through line 38 and introduced into agitating zone E of stage 50 where it is mixed with dichlorethyl ether at a temperature of about 78° F. The amount of dichlorethyl ether introduced through line 39 will be about 50% by weight based upon the oil charged to this stage. From the settling zone of stage 50 there is withdrawn an intermediate raffinate from line 40.

When the process is carried out according to the manner just described and the temperatures in each successive extraction stage are maintained at the values indicated and the quantities of oil and solvent introduced into columns A and B are maintained at the volumes shown on the drawing and just previously described, I am able to obtain from an oil having a viscosity gravity constant of .872 a high grade raffinate having viscosity gravity constant of .810 representing 37% of the original oil charged to the extraction process, an intermediate raffinate having viscosity gravity constant of .843 representing 32% of the oil charged to the process and an extract having viscosity gravity constant of .97 and representing 31% of the oil charged to the process.

It is to be understood that the temperatures which I have employed above are merely illustrative of one set of conditions which may be employed in the process. These temperatures obviously depend upon characteristics of the oil which is introduced into the process and the characteristics of the solvent used to separate the paraffinic from the non-paraffinic fractions. In many cases it may be unnecessary to employ as many stages as shown. Furthermore, it may be found that a wider temperature range will be more advantageous than the range which I have just described, or in some cases it may be found necessary to employ even a narrower range in order to obtain the optimum results. These variations are within the knowledge of those skilled in the art.

The term "viscosity gravity constant" is a means of expressing the temperature viscosity susceptibility of an oil, that is, the change in viscosity with a change in temperature. This constant is described in the Journal of Industrial and Engineering Chemistry, vol. 20, page 641 of 1928 by Hill and Coates. A high value represents a high degree of naphthenicity or a high temperature viscosity susceptibility while low values indicate relatively greater paraffinicity or a lower temperature viscosity susceptibility. Lubricating oils from natural crudes range from .903 for an extreme Gulf Coast type to .807 for an extreme Pennsylvania type.

I claim:

1. A process for the separation of paraffinic and non-paraffinic fractions from an oil containing the same comprising extracting said oil with a selective solvent, separating a raffinate insoluble in said solvent, separating an extract dissolved in said solvent, commingling the extract dissolved in said solvent with a wash oil comprising an insoluble fraction separated from said selective solvent solution of oil by cooling the solution and allowing said insoluble fraction to separate from said selective solvent solution.

2. A process for the solvent extraction of oil which comprises commingling said oil with a

selective solvent to separate a raffinate insoluble in said solvent from extract phase comprising said solvent and oil soluble therein, removing said raffinate from said extract phase, separating said extract phase into an oil fraction insoluble therein and a further extract phase comprising said solvent and oil fractions remaining dissolved therein, removing said last mentioned insoluble oil fraction from said last mentioned extract phase, separating said extract phase comprising said solvent and oil fractions remaining dissolved therein into a second oil fraction insoluble therein and an extract phase, commingling said last mentioned insoluble fraction with a selective solvent to separate a raffinate from an extract phase and returning said last mentioned extract phase to said first mentioned extraction.

3. A process for the separation of oil into fractions relatively more paraffinic in character and relatively less paraffinic in character than the original oil which comprises commingling said oil with a selective solvent in an extraction system and thereby forming a raffinate phase comprising the more paraffinic oil fractions and an extract phase comprising oil fractions dissolved in the selective solvent, separating said phases, recovering an oil fraction from said extract phase which is more paraffinic in character than the remaining oil fractions dissolved in the selective solvent and returning said oil fraction recovered from said extract phase to said extraction system.

4. A process according to claim 3 in which the oil fraction is recovered from the extract phase by cooling the latter.

5. A process according to claim 3 in which the selective solvent employed is normally gaseous at ordinary temperature and pressure and the oil fraction is recovered from the extract phase by vaporizing a portion of the selective solvent under reduced pressure and thereby cooling the extract phase to cause separation of said oil fraction.

6. A process for the separation of oil into fractions in an extraction system with a selective solvent which comprises introducing said oil into the extraction system, introducing a selective solvent into said extraction system, withdrawing a final raffinate from said extraction system, withdrawing an extract phase from said extraction system, recovering an oil fraction from said extract phase which is more paraffinic in character than the remaining oil fraction dissolved in the extract phase and returning said oil fraction to said extraction system at a point intermediate the points of introduction of oil and withdrawal of the extract phase of said system.

7. A process according to claim 6 in which the oil fraction is recovered from the extract phase by cooling the latter.

8. A process according to claim 6 in which the selective solvent is normally gaseous at ordinary temperature and pressure and the oil fraction is separated from the extract phase by vaporizing a portion of the selective solvent under reduced pressure to cool the extract phase.

9. A process for the separation of oil into fractions which comprises introducing oil and selective solvent into an extraction system and thereby forming a final raffinate phase comprising the more paraffinic fractions of the oil and an extract phase comprising oil fractions dissolved in the selective solvent, separating said phases, cooling the extract phase and thereby separating an intermediate raffinate and contacting the

extract phase in said extraction system with said intermediate raffinate.

10. A process for the separation of oil into fractions with a selective solvent which comprises introducing said oil and selective solvent into a primary extraction stage and thereby forming a raffinate phase and an extract phase, separating said phases, removing the raffinate phase from said primary extraction stage, passing the extract phase from said primary extraction stage to a secondary extraction stage, introducing raffinate from said secondary stage into said primary stage, separately removing extract phase from said secondary stage, cooling the extract phase removed from said secondary stage and thereby forming an intermediate raffinate phase and a final extract phase, separating said intermediate raffinate phase from said final extract phase, introducing said intermediate raffinate phase into said secondary extraction stage, and commingling said extract phase and intermediate raffinate phase in said secondary stage and thereby forming a raffinate phase in said secondary stage.

11. A process for the separation of oil into fractions with a selective solvent which comprises introducing selective solvent into a primary extraction stage, introducing said oil into a secondary extraction stage, introducing raffinate from the secondary extraction stage into the primary extraction stage, removing raffinate from the primary extraction stage, introducing extract phase from the primary stage into the secondary stage, introducing raffinate from a tertiary stage into said secondary stage, introducing extract phase from the secondary stage into the tertiary stage, withdrawing an extract phase from said tertiary extraction stage, cooling the extract phase withdrawn from said tertiary extraction stage and thereby separating an oil fraction insoluble in the extract phase at the lowered temperature, recovering said insoluble oil fraction, passing the insoluble oil fraction recovered from the extract phase by cooling the latter to the tertiary extraction stage and commingling said insoluble oil fraction with the extract phase in said tertiary extraction stage and thereby forming a raffinate in said tertiary stage.

12. A process according to claim 11 in which the primary, secondary and tertiary extraction stages are operated at progressively lower temperatures.

13. A process according to claim 10 in which the primary extraction stage is operated at a higher temperature than the secondary stage.

14. A process for the separation of oil into fractions with a selective solvent which comprises introducing the selective solvent into a primary extraction stage, introducing said oil into a secondary extraction stage, passing raffinate from the secondary extraction stage to the primary extraction stage, extracting the raffinate passed to said primary extraction stage with the selective solvent and thereby forming a raffinate and an extract phase in said primary extraction stage, passing the extract phase formed in said primary extraction stage to said secondary extraction stage, extracting the oil introduced into said secondary stage with the extract phase introduced from the primary stage into said secondary stage and thereby forming a raffinate and extract phase in said secondary extraction stage, passing the extract phase formed in said secondary extraction stage to a tertiary extraction

stage, passing raffinate phase from said tertiary extraction stage to said secondary extraction stage, withdrawing extract phase from said tertiary extraction stage, cooling the extract phase withdrawn from said tertiary stage and thereby forming an oil fraction insoluble in said extract phase, recovering said insoluble oil fraction, passing said insoluble oil fraction to said tertiary extraction stage, contacting the extract phase present in said tertiary extraction stage with said insoluble oil fraction and thereby forming a raffinate phase and an extract phase in said tertiary extraction stage.

15. A process according to claim 14 in which the primary stage is operated at a higher temperature than the secondary stage.

16. A process according to claim 14 in which the primary, secondary and tertiary stages are operated at successively lower temperatures and the temperature employed to separate the insoluble oil fraction from the tertiary extract phase is lower than the temperature employed in said tertiary extraction stage.

17. A process for the separation of oil into fractions with a selective solvent in an extraction system which comprises contacting said oil and said selective solvent in said extraction system

and thereby forming a raffinate phase and an extract phase, separating said phases, separating said extract phase into a phase containing the relatively more paraffinic oil fractions of said extract phase and a phase containing the relatively less paraffinic oil fractions of said extract phase and contacting the extract phase in said extraction system with said phase containing the relatively more paraffinic oil fractions recovered from said extract phase.

18. A process as claimed in claim 17 in which the extract phase is separated into a phase containing the relatively more paraffinic oil fractions and a phase containing the relatively less paraffinic oil fractions by cooling said extract phase.

19. A process according to claim 6 in which the selective solvent is one of the members selected from the group consisting of sulphur dioxide, furfural, B B' dichlorethyl ether, nitrobenzine and aniline.

20. A process according to claim 9 in which the selective solvent is one of the members selected from the group consisting of sulphur dioxide, furfural, B B' dichlorethyl ether, nitrobenzine and aniline.

DAVID R. MERRILL.

CERTIFICATE OF CORRECTION.

Patent No. 2,043,389,

June 9, 1936.

DAVID R. MERRILL,

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 25, for the word "exact" read extract; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of February, A. D. 1937.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.

stage, passing raffinate phase from said tertiary extraction stage to said secondary extraction stage, withdrawing extract phase from said tertiary extraction stage, cooling the extract phase withdrawn from said tertiary stage and thereby forming an oil fraction insoluble in said extract phase, recovering said insoluble oil fraction, passing said insoluble oil fraction to said tertiary extraction stage, contacting the extract phase present in said tertiary extraction stage with said insoluble oil fraction and thereby forming a raffinate phase and an extract phase in said tertiary extraction stage.

15. A process according to claim 14 in which the primary stage is operated at a higher temperature than the secondary stage.

16. A process according to claim 14 in which the primary, secondary and tertiary stages are operated at successively lower temperatures and the temperature employed to separate the insoluble oil fraction from the tertiary extract phase is lower than the temperature employed in said tertiary extraction stage.

17. A process for the separation of oil into fractions with a selective solvent in an extraction system which comprises contacting said oil and said selective solvent in said extraction system

and thereby forming a raffinate phase and an extract phase, separating said phases, separating said extract phase into a phase containing the relatively more paraffinic oil fractions of said extract phase and a phase containing the relatively less paraffinic oil fractions of said extract phase and contacting the extract phase in said extraction system with said phase containing the relatively more paraffinic oil fractions recovered from said extract phase.

18. A process as claimed in claim 17 in which the extract phase is separated into a phase containing the relatively more paraffinic oil fractions and a phase containing the relatively less paraffinic oil fractions by cooling said extract phase.

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