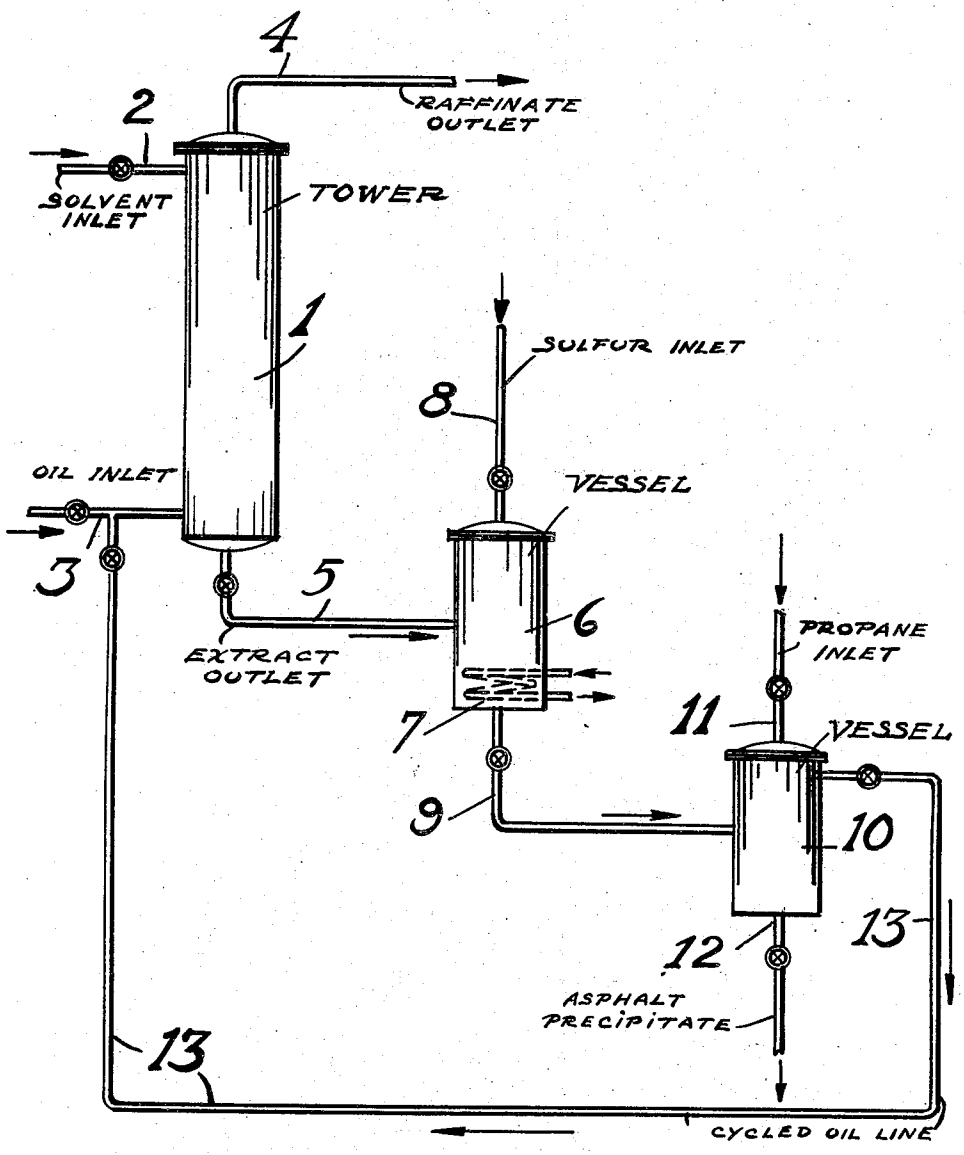
June 20, 1939. K. C. LAUGHLIN 2,163,245

TREATMENT OF SOLVENT EXTRACTS

Filed June 15, 1937



Kenneth C. Laughlin Inventor

By P. L. Young Attorney

Patented June 20, 1939

2,163,245

UNITED STATES PATENT OFFICE

2,163,245

TREATMENT OF SOLVENT EXTRACTS

Kenneth C. Laughlin, Baton Rouge, La., assignor to Standard Oil Development Company, a corporation of Delaware

Application June 15, 1937, Serial No. 148,255

11 Claims. (Cl. 196—13)

This invention relates to the selective solvent extraction of lubricating oils and is more particularly concerned with certain improvements by means of which the yield of high grade, high V. I. oil may be increased.

Certain solvents such as phenol, liquid sulphur dioxide, nitrobenzene, furfural, beta beta dichlorethyl ether, to mention only a few, have the property of selectively dissolving aromatic, unsaturated and naphthenic hydrocarbons from lubricating oils. All of these solvents, however, to a greater or less extent also dissolve small quantities of the desirable paraffinic hydrocarbons and these are carried out in the extract with the undesired portions of the oil. It is, of course, advantageous to recover the paraffinic hydrocarbons from the extract and to recycle them to the solvent extraction treatment so that the maximum possible yield of paraffinic hydrocarbons may be obtained.

The present invention is directed to a new method for recovering the paraffinic or good oil fractions from the extract in a solvent extraction process, and will be fully understood from the following description read with reference to the accompanying drawing which is a semi-diagrammatic view in sectional elevation of one type of apparatus suitable for carrying out the improved process.

Referring to the drawing, numeral 1 designates a conventional countercurrent solvent extraction tower. Numeral 2 designates a line through which selective solvent is introduced into the tower. Numeral 3 designates a line through which oil to be extracted is introduced into the tower. In tower 1 the oil and solvent flow in countercurrent relationship. The raffinate or good oil is removed from the top of the tower through line 4. The extract is removed from the bottom of the tower through line 5. The extract is introduced into a vessel 6 provided with heating means such as a heating coil 7. Other heating means such as the introduction of hot inert gas may also be employed. When the extract in vessel 6 has been heated to about 250° F. sulfur is introduced into the vessel through line 8. The temperature is raised still higher and additional sulfur is added. The mixture is allowed to cook at high temperature for a period of several hours. At the end of this time the cooked extract is withdrawn from vessel 6 through line 9 which may be provided with cooling means (not shown) and the partially cooled mass is then introduced into vessel 10. Propane or other asphalt precipitating solvent is introduced into vessel 10 through line 11. The temperature is lower than that maintained in the sulfur cooking vessel 6 but nevertheless is preferably maintained above about 100° F. The treatment with propane causes the precipitation of dark-colored asphaltic material. This is removed through line 12 and discarded, or valuable asphaltic material may be recovered from it.

The propane soluble material remaining in vessel 10 constitutes the more paraffinic fractions thrown out in the first extract. This is removed from vessel 10 through line 13 and recycled to the extraction tower 1. The propane may first be removed from this cycle oil prior to recycling. This may be done by reduction of pressure and by distillation or any other convenient means.

In the operation of the process the selective solvent used may be any of the well-known selective solvents such as those enumerated above or any others. The quantity of solvent used and the temperature at which the solvent extraction is carried out will naturally depend upon the particular solvent and the type of oil undergoing treatment. In general the quantity of solvent should be at least 100% of the volume of oil and the temperature of treating must of course be below the miscibility temperature of the solvent with the oil.

The quantity of sulfur used for cooking the extract may vary from 5 to 20% or more by weight based on the extract. Free sulfur is preferred but any compound or mixture containing substantial quantities of free sulfur or capable of liberating sulfur may also be used. Selenium or tellurium may be used in place of sulfur but sulfur is preferred for economic reasons. The temperature maintained during the cooking with sulfur is preferably above 250° F. and may be as high as 350 or 400° F. The cooking period may vary from about two hours to five or six hours or more.

In the separation step described above with the use of propane it will be understood that other materials having a preferential solubility for paraffinic fractions as compared with asphalt and unsaturated hydrocarbons may be used. Thus, for example, other liquefied normally gaseous hydrocarbons having between 1 and 4 carbon atoms may be used, such as ethane, butane, ethylene, isobutane, butylene, isobutylene, etc. Higher hydrocarbons such as pentane and hexane can be used but in general these are not as satisfactory as the lower molecular weight hydrocarbons. Water may be used in cases where it is miscible with the selective solvent. For instance, when phenol is the solvent, water

could be used as the precipitant. Methyl or ethyl alcohol, glycerine, ammonia, caustic soda or caustic potash may also be used wherever water could be used. The essential point is that the material used must be miscible with the more paraffinic fractions and at the same time immiscible with the dark-colored asphaltic or resinous bodies.

The following example illustrates the process:

A lubricating fraction derived from Colombian crude is extracted with phenol. The extract obtained in this treatment has the following characteristics.

Gravity, A. P. I.°	12.2
Saybolt viscosity @ 100° F.....seconds..	2870
Saybolt viscosity @ 210° F.....seconds..	89
Viscosity index (calculated)	—73
Viscosity gravity constant	.936

1600 grams of this extract is placed in a flask and heated by bubbling hot inert gas through it to a temperature of 280° F. The gas is shut off and then 5% by weight of sulfur is added. The heating is then continued to a temperature of 350° F. and 5% by weight more sulfur is added. A great deal of hydrogen sulfide is evolved. The mixture is thoroughly agitated by means of a mechanical stirrer and the heating is continued for a period of five hours with a maximum temperature of 385° F. being attained. At the end of the five-hour period, the mixture is very dark colored and viscous and appears to contain suspended solid particles. The characteristics of this product are as follows:

Gravity A. P. I.	7.4°
Saybolt viscosity @ 210° F.....seconds..	360
Saybolt viscosity @ 100° F.....seconds..	62,500
Viscosity index (calculated)	—123
Viscosity gravity constant	.952

This product is introduced into a bomb and four volumes of propane are added. The temperature is maintained at 120° F. The insoluble asphaltic material is removed from the bomb and is found to constitute 25% of the mass. This asphalt has the following characteristics:

Specific gravity @ 77° F.	1.127
Softening point.....degrees F..	209
Penetration @ 77° F.	1
@ 32° F.	½
@ 115° F.	3
Ductility @ 77° F.	Brittle
Solubility in CCl_4.....percent..	99.56
Soluble in CS_2.....do....	99.58
Oliensis	Heterogeneous

The propane soluble material after removal of the propane has the following characteristics:

Gravity, A. P. I.	14.6°
Saybolt viscosity @ 100° F.....seconds..	1655
Saybolt viscosity @ 210° F.....seconds..	79.5
Viscosity index	—4
Viscosity gravity constant	.916

It will be seen that this oil recovered from the phenol extract is substantially better than the entire extract, e. g. its viscosity index is —4 whereas the V. I. of the entire extract is —73. This oil may be recycled to the extraction and may be further improved. The overall yield of raffinate from the solvent extraction treatment is thereby markedly increased.

This invention is not limited by any theories of the mechanism of the reactions nor by any details which have been given merely for purposes of illustration but is limited only in and by the following claims in which it is intended to claim all novelty inherent in the invention:

I claim:

1. Process for recovering valuable oil fractions from extracts obtained in the selective solvent extraction of lubricating oils with solvents of the class which have a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type compounds which comprises digesting the extract with sulfur at a high temperature for a prolonged period, cooling the digested mass to a somewhat lower temperature, adding several volumes of an asphalt precipitating solvent thereto, removing the asphaltic material so caused to separate and recovering oil from the remaining solution.

2. Process according to claim 1 in which the extract is digested with sulfur at a temperature between 250 and 400° F.

3. Process according to claim 1 in which the extract is digested with from 5 to 20% by weight of sulfur.

4. Process according to claim 1 in which the digestion period with sulfur is from 2 to 6 hours.

5. Process for recovering valuable oil fractions from an extract obtained in the selective solvent extraction of lubricating oil with solvents of the class which have a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type compounds which comprises adding to the extract from 5 to 20% by weight of free sulfur, heating the mixture to a temperature between 250° F. and 400° F., maintaining it at this temperature for a period of at least several hours, cooling the mass to a temperature of about 100° F., adding a liquefied normally gaseous hydrocarbon to the partially cooled mass, removing the dark colored material thereby caused to be precipitated and removing the selective solvent and liquefied hydrocarbon from the remaining oil.

6. Process according to claim 5, in which the liquefied normally gaseous hydrocarbon is propane.

7. Process for recovering valuable oil fractions and asphalt from extracts obtained in the selective solvent extraction of lubricating oil with solvents of the class which have a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type compounds, which comprises digesting the extract with sulfur at a temperature above 250° F. and below 400° F. for a prolonged period, cooling the digested mass to a temperature of about 100° F., adding to the partially cooled mass a substance miscible with the more paraffinic fractions but immiscible with the dark colored asphaltic material, removing asphaltic material remaining undissolved, and removing selective solvent and the substance immiscible with asphalt from the remaining oil.

8. Improved process of solvent treating petroleum oils comprising contacting a petroleum oil in a countercurrent treating tower with a solvent of the class which has a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type compounds under conditions to form a raffinate phase and a solvent extract phase, separating the solvent extract phase, digesting the same with sulfur at a high temperature, precipitating asphaltic type materials from relatively more paraffinic type oil by the addition of several volumes of an asphalt precipitating solvent, removing the precipitated asphaltic type materials from the oil and returning said oil to said countercurrent treating tower.

9. Process in accordance with claim 8 in which process 5% to 20% by weight of free sulfur is digested with the solvent extract and in which process the mixture is heated to a temperature in the range from about 250° to 400° F.

10. Improved process for the solvent treatment of petroleum oils comprising treating a petroleum oil in a countercurrent treating tower with a solvent of the class which has a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type compounds under conditions to form a solvent extract phase and a raffinate phase, separating the solvent extract phase, digesting the same with sulfur at elevated temperatures, precipitating asphaltic type materials from the solvent extract by the addition of an asphalt precipitating solvent, separating the precipitated asphalt from the recovered oil and returning the recovered oil to the oil inlet of said countercurrent treating tower.

11. Process in accordance with claim 10 in which said solvent is phenol and in which process from 5% to 20% by weight of free sulfur is digested with the oil at a temperature between 250° and 400° F. for a period from about 2 to 6 hours.

KENNETH C. LAUGHLIN.