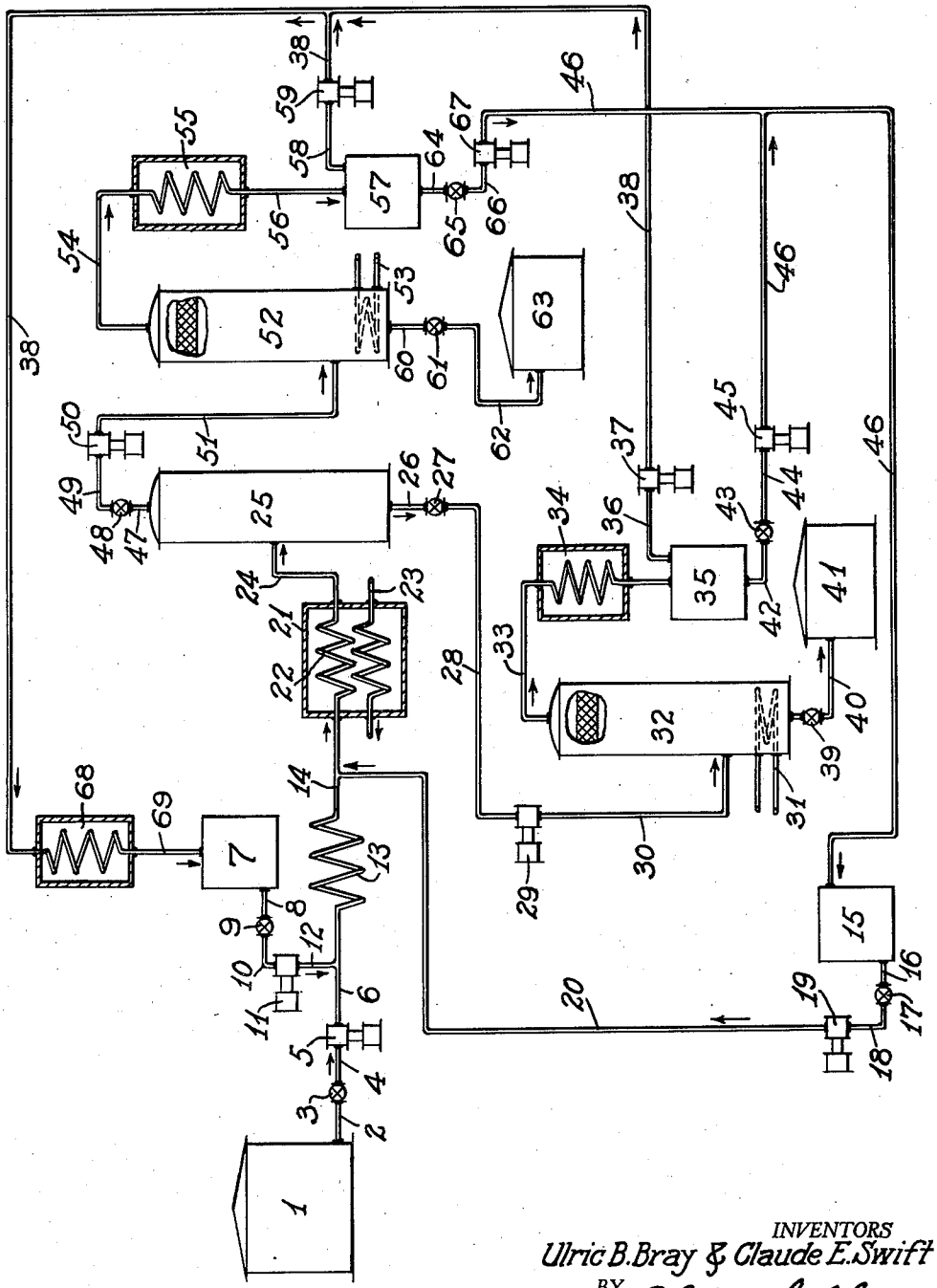
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PROCESS FOR PRODUCTION OF LUBRICATING OIL

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PROCESS FOR PRODUCTION OF LUBRICATING OIL

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6 Claims. (Cl. 196—13)

This application is a continuation in part of the application of Ulric B. Bray and Claude E. Swift, Serial No. 594,605, filed February 23, 1932, for a Process for producing lubricating oil.

As is generally known, most crude oils are mixtures of hydrocarbons of varying physical characteristics. Some of the oils present in crude oil exhibit a high temperature viscosity susceptibility, and others present a low temperature viscosity susceptibility, i. e., those oils present which show a high change in viscosity with a given change in temperature are said to have a high temperature viscosity susceptibility, and those oils present which show a relatively low change in viscosity with a given change in temperature are said to have a low temperature viscosity susceptibility.

In the production of lubricating oil from hydrocarbon mixtures, it is desirous to obtain a final product which exhibits a low temperature viscosity susceptibility. This is especially true where the product is to be used in internal combustion motors where it is desired to maintain a high degree of viscosity through the temperature range at which the motor operates. As these heavy lubricating oil components of crude oil which exhibit a low temperature viscosity susceptibility are the most desirable as lubricants, a number of methods have been devised to separate this class of hydrocarbons from hydrocarbon mixtures containing the same. One of the means which is generally used for separating the oils present which exhibit a low temperature viscosity susceptibility and are paraffinic in character, from the oils present which exhibit a high temperature viscosity susceptibility, and are non-paraffinic in character, is solvent extraction. Certain solvents have the power of selectively dissolving the non-paraffinic hydrocarbons present in a hydrocarbon mixture. This solution of non-paraffinic hydrocarbons may then be separated from the undissolved paraffinic hydrocarbons by ordinary gravity separation. Many of the solvents which are employed as solvents for the non-paraffinic hydrocarbons have a relatively high specific gravity, as compared to the oil undergoing extraction. Therefore, the oils which are soluble in these solvents produce solutions which are relatively heavy, and which readily separate from the undissolved paraffinic oils. As examples of solvents which exhibit a selective solvent power for the non-paraffinic hydrocarbon, we find liquid sulphur dioxide, furfural, aniline, nitrobenzene, methyl formate, B B' dichlorethyl ether, phenyl acetate, methyl thiocyanate; and selenium oxychloride. The hydrocarbon oil mixture is commingled with these respective solvents or mixtures thereof, under proper conditions of temperature and pressure, and the non-paraffinic hydrocarbons are dissolved therein. The mixture of undissolved paraffinic oil and non-paraffinic oil dissolved in these respective solvents is allowed to settle and the solvent containing the dissolved non-paraffinic fractions forms a lower liquid phase, while the undissolved paraffinic oils form the upper liquid phase. These liquid phases are then separated by ordinary decantation methods and distilled to remove their respective solvent content. That portion of the hydrocarbon mixture which is soluble in the solvent is usually referred to as the extract and the portion which is insoluble in the solvent is usually referred to as the raffinate.

In the extraction of many hydrocarbon mixtures with the foregoing solvents difficulty is ofttimes experienced in obtaining a satisfactory separation of the paraffin oil or raffinate phase from the non-paraffinic oil dissolved in the solvent or extract phase. Accordingly we have found it desirable to carry out the extraction of such a hydrocarbon mixture in the presence of a low boiling non-viscous, normally gaseous hydrocarbon. This is the subject matter of applications filed by Ulric B. Bray and Claude E. Swift, bearing Serial Numbers 555,018 and 594,605, filed August 4, 1931 and February 23, 1932, respectively. In these applications we pointed out that it was desirable to carry out the extraction of a hydrocarbon oil mixture with a selective solvent in the presence of liquid propane. By liquid propane, we mean a fraction which is recovered by the rectification of natural gasoline. Such a fraction is a liquid under about 125 pounds per square inch pressure, and 70° F. and consists mainly of propane with varying minor amounts of such hydrocarbons as methane, ethane, and butane. In carrying out our process we first dissolve the hydrocarbon mixture in the normally gaseous hydrocarbon under conditions of temperature and pressure sufficient to maintain the normally gaseous hydrocarbon diluent in the liquid phase. After forming a solution of the hydrocarbon mixture in the normally gaseous liquid diluent, we then subject this solu-

tion to extraction with selective solvents such as sulphur dioxide, aniline, nitrobenzene, methyl formate, phenyl acetate, methyl thiocyanate, or selenium oxychloride. The extracted mass is then allowed to settle. The relatively heavy solution of non-paraffinic hydrocarbons dissolved in the extract phase settles out and forms a lower layer, while the relatively light paraffinic fractions dissolved in the light hydrocarbon diluent, forms the upper phase. These two phases are then separated by ordinary decantation means and distilled to remove their respective solvent content. If necessary, the valuable paraffinic fractions may then be treated by conventional means such as with acid, alkali, and/or clay, to produce a finished oil.

In the separation of the paraffinic from non-paraffinic hydrocarbons contained in the lubricating oil fractions of a hydrocarbon mixture, we have found the use of nitrobenzol in the presence of liquid propane highly desirable. This solvent in the presence of liquid propane produces a paraffinic fraction which exhibits the low temperature viscosity susceptibility, a low Conradson carbon value, and a high color. After the hydrocarbon mixture dissolved in liquid propane has been extracted with nitrobenzol, clay treatment of the raffinate is usually sufficient to produce a finished oil having a very high color. In carrying out our process, the oil is first dissolved in the liquid propane in a proportion of about one part of oil to one to three parts of liquid propane. This is carried out under ordinary temperature, i. e., a temperature of about 60 to 70° F., and under sufficient pressure to maintain the solvent in the liquid state. Providing the oil contains any asphalt, this material forms a heavy insoluble residue which is easily separated from the propane solution of oil by ordinary decantation means. The propane solution of oil is then extracted with nitrobenzene. Ordinarily two or three parts of nitrobenzene to one part of undiluted oil are sufficient to remove the undesirable non-paraffinic hydrocarbons present in the mixture. The temperature at which the extraction of the oil dissolved in the liquid propane with nitrobenzene is to be carried out, varies somewhat with the type of the oil to be extracted. Usually a temperature between 35 to 75° F. has proven satisfactory. In some cases we find it desirable to dissolve the oil in liquid propane as aforementioned, add nitrobenzene in the proportion of two to three parts of nitrobenzene to one part of oil, heat the mixture to a temperature sufficiently high to attain complete miscibility, cool the mass somewhat below the temperature of complete miscibility, i. e., 10° F. to 30° F., and then separate the paraffinic oil dissolved in liquid propane from the non-paraffinic oil dissolved in nitrobenzene. It is to be understood that the mixture of solvents and oil cannot be heated to a point of complete miscibility where this temperature is beyond the critical temperature of the liquid propane. However, in most cases we find that the temperature of complete miscibility is considerably below the critical temperature of the light liquid hydrocarbon fractions.

In carrying out our process we may employ stage extraction. The paraffinic oil dissolved in liquid propane may be successively extracted with nitrobenzol until the degree of refining desired has been obtained. These successive extractions may be carried out at the same temperature, at successively increasing temperatures, or successively decreasing temperatures. For example, the oil may first be dissolved in the liquid propane and extracted with nitrobenzene at a temperature of about 35° F. and then the propane solution of paraffinic oils may be re-extracted with nitrobenzene at a temperature of about 60° F. If desirable, the paraffinic oil dissolved in the propane and recovered from the second extraction may be further extracted at increasing temperatures which are below the point of complete miscibility. Such a system of extraction wherein successively higher temperatures are employed results in a raffinate with a high degree of paraffinicity. However, the yield of paraffinic oil is relatively small and in many instances would not prove economical.

In carrying out our process at the same temperature for successive extractions, the oil is dissolved in liquid propane in the proportion of one part of oil to one to three parts of liquid propane and then agitated with about one to three volumes of nitrobenzene per volume of oil at a temperature between 35° to 75° F. The propane solution of paraffinic oil is then re-extracted at the same temperature with an additional quantity of nitrobenzene. These successive extractions may be employed upon the raffinate fraction dissolved in propane as long as a material lowering of the temperature viscosity susceptibility of the raffinate oil is obtained.

The use of liquid propane in the process permits a degree of refining which is not obtainable by the use of pure solvent alone or with such solvents as gasoline, naphtha, or relatively heavy hydrocarbon fractions. The fluidity or viscosity of liquid propane is comparatively lower than that of gasoline, naphtha or the heavy hydrocarbon fractions. Therefore, its presence in the oil undergoing extraction with such a solvent as nitrobenzol aids materially in obtaining the satisfactory separation of the raffinate phase from the extract phase, which is not obtainable by the use of pure solvents or with solvents mixed with relatively heavy petroleum fractions.

When the lubricating oil fractions of a hydrocarbon mixture are extracted with nitrobenzol in the presence of liquid propane those undesirable hydrocarbons present which have a propensity towards the formation of carbon and are responsible for a high Conradson carbon value are removed along with the nitrobenzol and dissolved fractions. These undesirable carbon forming hydrocarbons are more soluble in the nitrobenzol and dissolved non-paraffinic oil fractions than in the liquid propane and dissolved paraffinic fractions. This phenomenon becomes even more pronounced when the liquid propane employed contains appreciable quantities of liquid ethane (i. e. 80% or more of ethane) as liquid ethane has a less solvent power for these carbon forming compounds than liquid propane and, therefore, forces a larger proportion of these undesirable hydrocarbons into the solvent containing the dissolved fractions. When the lubricating oil fractions are extracted with nitrobenzol in the presence of a diluent such as naphtha, gasoline or other relatively heavy hydrocarbon fractions, these undesirable compounds present which are responsible for a high Conradson carbon value are not removed in the nitrobenzol and dissolved fractions. These undesirable compounds are more soluble in the paraffinic oil fractions dissolved in the gasoline, naphtha or relatively heavy hydrocarbon diluent than in the nitrobenzol and dissolved non-paraffinic oil fractions. Therefore, the raffinate oils which are produced by extracting hydrocarbon

mixtures with nitrobenzol in the presence of naphtha, gasoline or other relatively heavy hydrocarbon diluents usually require further refining to remove the carbon forming compounds present which are responsible for high Conradson values.

It is, therefore, an object of our invention to dissolve a hydrocarbon mixture in a normally gaseous hydrocarbon diluent and thereafter extract this solution with nitrobenzol.

It is another object of our invention to dissolve a hydrocarbon mixture in liquid propane and subject this solution to solvent extraction with nitrobenzol.

The accompanying figure is a schematic arrangement of one form of apparatus which we may employ to carry out our process.

Referring more particularly to the drawing, a hydrocarbon mixture, such as the lubricating oil fractions of petroleum, is withdrawn from tank 1 through line 2, valve 3 and line 4 into pump 5 which forces it into line 6 where it meets the stream of liquid propane coming from tank 7 through line 8, valve 9, line 10, pump 11 and line 12. The mixture of propane and oil in line 6 passes into dissolving coil 13 where the mass is agitated sufficiently to effect solution. The solution of oil dissolved in propane emerges from coil 13 into line 14 where it meets a stream of nitrobenzol coming from tank 15 through line 16, valve 17, line 18, pump 19 and line 20. The mixture of oil dissolved in propane and nitrobenzol passes from line 14 into heater 21 where the temperature of the mass is raised to the desired extraction temperature. Any suitable means may be employed to furnish the necessary quantity of heat to increase the oil and solvent to the desired extraction temperature. In the present drawing, steam introduced through line 23 furnishes the desired quantity of heat. Beside furnishing the necessary amount of heat for the extraction, coil 22 in heater 21 also functions as an agitator to insure thorough mixing of the nitrobenzol with the oil dissolved in the propane. The thoroughly agitated mass in heater 21 emerges through line 24 into separator 25 where the relatively heavy solvent and dissolved fractions settle to the bottom forming the lower liquid phase while the propane and paraffinic fractions rise to the top and form an upper liquid phase.

The nitrobenzol and dissolved fractions in separator 25 are withdrawn through line 26, valve 27, line 28, pump 29, line 30 to the flash tower 32. Here the nitrobenzol and dissolved fractions are heated to a temperature sufficiently high to vaporize the nitrobenzol and any liquid propane present. The necessary heat is furnished to this flash tower by closed steam coil 31. The extracted fractions in flash tower 32 which have been freed from their content of propane or nitrobenzol are withdrawn through valve 39 and line 40 into tank 41. The propane and nitrobenzol vapors are removed from flash tower 32 into line 33 to a partial condenser 34 where the nitrobenzol is liquefied and is removed through line 42, valve 43, line 44, pump 45 and line 46 to nitrobenzol storage 15. The uncondensed propane vapors in separator 35 are removed through line 36, compressor 37 and line 38 to condenser 68 where they are liquefied and passed by means of line 69 to propane storage tank 70.

The propane solution of paraffinic oil is removed from separator 25 through line 47, valve 48, line 49, pump 50 and line 51 to flash tower 52 where sufficient heat is introduced by means of steam through coil 53 to vaporize the propane and any nitrobenzol which may be present in the solution. Paraffinic oil free from nitrobenzol and propane is removed from the bottom of flash tower 52 through line 60, valve 61 and line 62 to tank 63.

The propane and nitrobenzol vapors are removed from flash tower 52 to line 54 into partial condenser 55 where the temperature of the vapors is lowered sufficiently to condense the nitrobenzol present. The condensed nitrobenzol and propane vapors pass from condenser 55 through line 56 into separator 57. The condensed nitrobenzol is removed from separator 57 through line 64, valve 65, line 66, pump 67 and line 46 to nitrobenzol storage 15.

The uncondensed propane in separator 57 passes by means of line 58, compressor 59 through line 38 to condenser 68 where it is liquefied and passes by means of line 69 to propane storage tank 7.

In the foregoing description the propane solution of oil and nitrobenzol is heated and agitated in coil 22 after which it passes into separator 25. As a modification of this method of extraction, we may heat the propane solution of oil separately from the nitrobenzol and introduce the propane solution of oil into the lower zone of an extraction column and the nitrobenzol into the upper zone of an extraction column and allow the relatively light propane solution of oil to be countercurrently extracted with a relatively heavy nitrobenzol.

In some instances it may be further desirable to heat the solution of oil dissolved in propane and nitrobenzol in coil 22 to a temperature sufficiently high to effect complete miscibility of the solvent and oil. When this method of extraction is employed, it then becomes necessary to cool the heated mass to a temperature somewhat below their complete temperature of miscibility in order to force the paraffinic oil fractions out of solution before the mass enters separator 25. This is accomplished by inserting a cooler in line 24, which is not shown.

As a specific example of the method of carrying out our process a dewaxed Kettleman Hills long residuum was dissolved in liquid propane in the proportion of one volume of oil to three volumes of liquid propane. The propane solution of oil was then extracted three successive times with nitrobenzol at 35° to 40° F. using a volume of nitrobenzol for each successive extraction equal to the original volume of oil placed into the extraction equipment. After the three successive extractions were made at 35°–40° F. the temperature of the remaining oil dissolved in liquid propane was extracted three successive times with nitrobenzol at 65° to 70° F. The quantity of nitrobenzol employed for each of the three extractions at 65° to 70° F. was equal in volume to the original volume of oil placed in the extraction apparatus.

The following table gives a comparison between the physical characteristics of the original unextracted Kettleman Hills dewaxed stock; the physical characteristics of the raffinate produced after three successive extractions of the stock with nitrobenzol at 35° to 40° F. followed by three successive extractions at 65° to 70° F. in the manner described above except without the presence of propane; and, the physical characteristics of the raffinate after three successive extractions of the stock at 35° to 40° F. followed

by three successive extractions at 65° to 70° F. in the presence of liquid propane as described above:

Sample	Gravity degrees A. P. I. at 60° F.	Conradson carbon value percent	Color N. P. A.	Viscosity Saybolt Universal at 100° F.	Viscosity Saybolt Universal at 150° F.	Viscosity Saybolt Universal at 210° F.	Gravity/viscosity constant
Dewaxed Kettleman Hills long residuum	18.6	2.52	Opaque.	----------	407	105	0.876
Raffinate produced by extraction of dewaxed Kettleman Hills long residuum with nitrobenzol alone	29.4	0.21	Opaque.	1057	272	95	0.796
Raffinate produced by extraction of dewaxed Kettleman Hills long residuum dissolved in propane with nitrobenzol	29.3	0.11	7	449	135	62	0.806

The Conradson carbon value described in the foregoing table is the test which has been recommended by the American Society of Testing Materials for the determination of the carbon forming properties of a lubricating oil and is known as the American Society of Testing Materials Method of Test D-189-30.

The color values given in the foregoing table are those of the National Petroleum Association.

The gravity-viscosity constant referred to in the table is defined by Hill and Coats in the Journal of Industrial and Engineering Chemistry, volume 20, page 641 (1928). This constant represents the paraffinicity or naphthenicity of a given oil. A high value indicates a high degree of naphthenicity while low values indicate relatively greater paraffinicity. Lubricating oils from natural crudes range from .903 (for an extreme Gulf type) to .807 for an extreme Pennsylvania type or even beyond.

As a further modification, we may partially extract the oil with nitrobenzol in the presence of liquid propane, remove the propane from the raffinate so obtained and then re-extract this raffinate with nitrobenzol without the presence of propane. Accordingly, the stock to be treated is dissolved in liquid propane in the proportion of one volume of stock to about three volumes of liquid propane. The solution of the stock in the liquid propane is readily accomplished by commingling the stock and liquid propane at a temperature of about 70° F. and 125 pounds per square inch pressure. The propane solution of stock is then extracted with nitrobenzol after which the raffinate or remaining oil dissolved in liquid propane is distilled to remove the propane. The raffinate from which the propane has been removed is then re-extracted with nitrobenzol and a lubricating oil is produced having highly desirable physical characteristics. The temperature of extraction with nitrobenzol will vary somewhat with the composition of the stock, however, we find a range between 35° F. to 45° F. satisfactory for carrying out the extraction of the oil dissolved in propane and a temperature of 60° to 75° F. satisfactory for carrying out the extraction of the raffinate fraction recovered after the removal of the propane as described above.

It is, therefore, an object of our invention to dissolve a hydrocarbon mixture, containing paraffinic and non-paraffinic hydrocarbons in liquid propane, extract the hydrocarbon mixture dissolved in liquid propane at a relatively low temperature with liquid propane, separate a raffinate oil containing propane, remove the propane from this raffinate oil and re-extract the raffinate oil with nitrobenzol at a relatively high temperature.

It is sometimes found desirable to dissolve the hydrocarbon mixture containing paraffinic and non-paraffinic oil in liquid propane, extract the propane solution of oil first with a selective solvent such as liquid sulphur dioxide to remove the most non-paraffinic oil from the solution, after which the remaining oil dissolved in the liquid propane may be re-extracted with nitrobenzol. The sulphur dioxide removes from the propane solution of oil those constituents present which have the highest gravity-viscosity constants or which exhibit the highest temperature viscosity susceptibilities and which tend to reduce the effectiveness of the nitrobenzol to produce a sharp separation between the paraffinic and non-paraffinic hydrocarbons. In employing the modified extraction process just described we have found it desirable to carry out the extraction with liquid sulphur dioxide at a temperature of about 10° F. after which the extraction of the remaining oil dissolved in the liquid propane may be re-extracted with nitrobenzol at a temperature between 35° F. and 75° F.

The foregoing example is not to be taken as limiting, but merely illustrative of one mode of carrying out our invention as many variations can be made by a man skilled in the art within the scope of the following claims.

We claim:

1. A process for the fractionation of hydrocarbon oil mixtures containing paraffinic and non-paraffinic oil constituents which comprises commingling said oil with a light hydrocarbon diluent and a selective solvent, forming a raffinate oil phase comprising paraffinic oil constituents and a portion of the non-paraffinic oil constituents dissolved in the light hydrocarbon diluent and an extract phase comprising non-paraffinic oil constituents dissolved in the selective solvent, separating said phases, removing the diluent from the raffinate phase, re-extracting the diluent-free raffinate oil phase with a selective solvent, forming a second raffinate oil phase and a second extract phase comprising non-paraffinic oil fractions dissolved in the selective solvent and separating said second formed phases.

2. A process according to claim 1 in which the light hydrocarbon diluent is a liquefied normally gaseous hydrocarbon.

3. A process according to claim 1 in which the light hydrocarbon diluent is liquid propane.

4. A process according to claim 1 in which the selective solvent is one of the members of the group consisting of sulphur dioxide, nitrobenzene furfural, aniline and dichlorethyl ether.

5. A process according to claim 1 in which the light hydrocarbon diluent is a liquefied normally gaseous hydrocarbon and the selective solvent is one of the members selected from the group consisting of sulphur dioxide, nitrobenzene, furfural, aniline and dichlorethyl ether.

6. A process according to claim 1 in which the second extraction is performed at a higher temperature than the temperature prevailing during the first extraction.

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