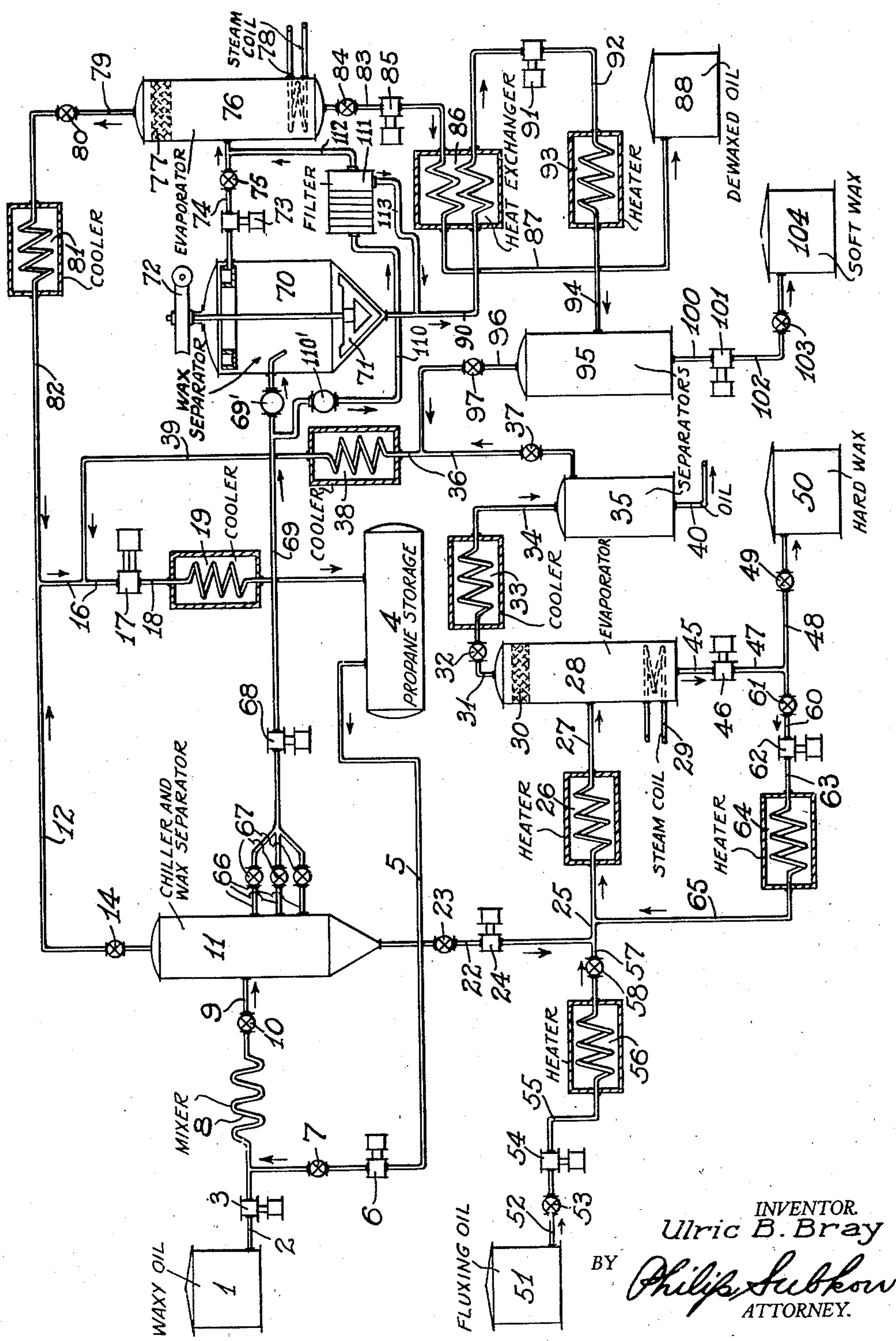
May 5, 1942. U. B. BRAY 2,281,667

METHOD FOR TREATING OILS

Filed July 22, 1933



INVENTOR.
Ulric B. Bray
BY Philip Subkow
ATTORNEY.

Patented May 5, 1942

2,281,667

UNITED STATES PATENT OFFICE

2,281,667

METHOD FOR TREATING OILS

Ulric B. Bray, Palos Verdes Estates, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application July 22, 1933, Serial No. 681,726

3 Claims. (Cl. 196—18)

The present invention relates to a method for separating wax from oils containing the same. More specifically, it relates to a method for separating wax in a plurality of stages and in the presence of a solvent. This invention is a continuation, in part, of my co-pending application Ser. No. 672,433, filed May 23, 1933 now Patent Number 2,041,277.

In the aforementioned co-pending application, I disclosed a plural stage process for the separation of asphalt and wax from oils containing the same to produce lubricating oil. In the first stage of the process, the asphalt and wax containing oil was commingled with a liquefied normally gaseous hydrocarbon solvent, such as liquid propane, under pressure sufficient to maintain the propane in a liquid state. This permitted a hard asphalt to precipitate and settle to the bottom of the decanter depending upon the volumetric ratio of solvent to oil. When using a high volumetric ratio of solvent to oil, the asphalt settling to the bottom of the decanter was a substantially hard or heavy asphalt. The precipitation was carried out at a temperature substantially atmospheric, i. e. about 70° F. to 80° F.

The oil solvent solution was separated or decanted from the precipitated asphalt and was then chilled to a sufficiently low temperature, i. e. —40 to 0° F. by evaporating a portion of the propane under reduced pressure. This effected precipitation of further quantities of asphaltic material which I termed a soft asphalt or pseudo asphaltic material. The refrigeration to the low temperature also caused precipitation of wax from solution. However, due to the longer period of time required to settle the light flocculent wax, the latter remained in suspension in solution of oil and solvent during the period required for settling the heavier asphaltic material. The supernatant solution of oil and solvent containing the suspended precipitated wax was then decanted and transferred to wax settling chambers where longer settling periods were provided to permit the wax to settle from solution.

In the present discussion of my invention by the term "propane" I intend to include such hydrocarbons as are normally vaporous at ordinary temperature and pressure; such hydrocarbons include methane, ethane, propane, butane, iso-butane and mixtures thereof. These normally gaseous hydrocarbon solvents may be obtained by rectification of casinghead gasoline by the so-called stabilizing method now conventional in the natural gasoline industry. They are the overhead fractions obtained. They are liquefied by compression and cooled in the conventional manner and are drawn off into pressure chambers where they are maintained in a liquid state until used. A typical analysis of such a fraction is 6.72% ethane, 72.2% propane, 19.91% butane and 1.17% normal butane. Such a fraction may be maintained in a liquid state at a pressure of 125 lbs. per sq. in. at a temperature of about 75° F. The predominating member in this mixture is propane and hereafter when I use the word "propane" or "liquid propane" I am referring to such a fraction.

In the foregoing process, I observed that the soft asphaltic material settling to the bottom of the decanter and precipitated by refrigerating the solution of solvent and oil to a low temperature contained wax and that this wax was a hard, heavy and granular-like material having physical characteristics substantially unlike the light flocculent wax which remained in suspension in the oil and solvent during the settling of the commingled pseudo asphaltic material and hard wax.

By the present invention, I propose to separate the wax from oils containing the same in a plurality of stages, in particular, in two stages. I have discovered that I may precipitate and recover two different types of wax, that is, a hard wax and a soft wax, if the wax bearing oil such as a paraffinic crude or a residue obtained therefrom or a distillate containing wax, is chilled in the presence of a solvent and the separation from the oil solvent solution is effected in two stages. In one stage of the process, the wax bearing oil is commingled with a liquefied normally gaseous hydrocarbon solvent under pressure sufficient to maintain the solvent in the liquid state and at a temperature of approximately atmospheric, i. e. about 70° F. to 80° F. The mixture is then transferred into a chilling column where the temperature of the mixture is gradually reduced, preferably at a rate not in excess of 4° F. per minute, to a sufficiently low temperature, i. e. about —40° to 0° F. to effect precipitation of substantially all of the wax present in the oil. When the desired low temperature has been attained, the mixture of oil, solvent and precipitated wax is permitted to settle so that wax will settle to the bottom of the chilling column or any decanter in which the mixture is permitted to settle.

I have observed that a portion of the wax precipitated, that is, released from solution by refrigeration, settles rapidly and in a relatively short time, while the remaining portion remains in a cloudy suspension in the solution of solvent and oil and requires considerable time to settle. This is due to the different physical characteristics of the two types of waxes. The first portion of the wax which settles rapidly to the bottom of the decanter is a hard, heavy and solid wax. It is granular and crystalline and has a larger particle size than the wax remaining in suspension. It may be separated from the remaining portion of the wax substantially as a separate fraction by decanting off the supernatant solution of oil, solvent and suspended wax after the mixture has been allowed to settle for a short period of time. In some cases, depending upon the type of oil treated, this wax may be contaminated with light asphalt or pseudo asphaltic material which also precipitates from solution when the oil is chilled to a dewaxing temperature.

The wax remaining suspended in the supernatant solution is soft and slime-like when the temperature has not been reduced sufficiently low but is substantially flocculent when the solution of oil and solvent has been chilled to a sufficiently low temperature, i. e. approximately −40° F. This portion of the wax may be recovered as a separate fraction by decanting and transferring the solution containing the supernatant wax to separate wax settlers and allowing sufficient time for settling. It may also be recovered by filtration, filter pressing or by centrifuging.

To obtain the desired refrigeration of the solution of oil and solvent such as propane and thus effect precipitation of wax, I prefer to gradually reduce the pressure in the chilling column and thus vaporize propane which will gradually chill the oil and precipitate the wax. The ebullition accompanying the vaporization of the propane will agitate the solution of oil, solvent and precipitated wax and thus will prevent substantial amounts of light flocculent wax from settling and mixing with the hard, heavy wax settling to the bottom of the column. The light flocculent wax will remain in suspension in a solution of oil and solvent during the period required for settling the heavier wax. The supernatant solution of oil and remaining solvent containing the suspended flocculent wax may then be transferred to other settling chambers where a longer settling period may be provided. If sufficient propane is not present in the mixture to give good settling of the light flocculent wax, a further quantity may be added to the mixture.

Instead of employing the uniform slow cooling rate of not in excess of 4° F. per minute throughout the entire range of chilling down to −40° F., the propane solution may be chilled more rapidly, i. e., 10° F. per minute until a temperature of approximately 35 to 45° F. is reached provided the remainder of the chilling down to −40° F. is performed at a slow, controlled rate not in excess of substantially 3° F. per minute. The temperature in the neighborhood of 40° F. to which the propane solution may be chilled rapidly corresponds to the point at which wax begins to precipitate from the propane solution.

With the above discussion in mind, it will be perceived that it is an object of my invention to separate wax from oil by means of solvents in a plurality of stages. It is a particular object of my invention to separate wax from wax bearing oils by chilling the oil to precipitate the wax and then separating the precipitated wax in a plurality of stages.

It is a further object of my invention to separate wax from oils by means of solvents in two stages wherein a substantially hard wax is recovered in the first stage and a light, softer wax is recovered in the second stage, both types of wax being precipitated by refrigeration from the solution of oil and solvent.

A further object of my invention resides in commingling a wax bearing oil with a liquefied normally gaseous hydrocarbon solvent such as propane under pressure sufficient to maintain the solvent in a liquid state and at an atmospheric temperature of about 70° F. to 80° F. and then gradually reducing the temperature of the oil solvent solution to approximately −40° F. to 0° F. by lowering the pressure to effect vaporization of a portion of the solvent and thus precipitating wax from solution, then allowing the chilled solution to settle for a short period of time to permit a hard wax to settle from the solution but to retain a softer wax in suspension in the solution, then decanting the solution of oil and remaining solvent containing the suspended wax from the settled hard wax, allowing the suspended wax to settle from solution and then separating the settled wax from the solution of oil and solvent and removing the solvent from the oil.

Other objects and advantages of my invention will be apparent from the following description of my invention taken from the drawing which refers to a schematic arrangement of apparatus for carrying out my invention.

Referring to the drawing, a wax containing oil, such as crude oil or a residue obtained from a paraffinic crude oil or a distillate containing wax, is taken from tank **1** and is drawn into line **2** by pump **3** where it meets a liquefied normally gaseous hydrocarbon solvent, such as liquid propane taken from storage tank **4** via line **5** and pump **6** which forces the liquid propane through valve **7** into line **2**. The amount of propane introduced into line **2** will depend upon the character of the oil and the temperature desired in the subsequent chilling column **11**, that is, sufficient propane must be introduced into the oil to be treated so the desired temperature may be effected in the chilling column by evaporation of propane as will be described hereinafter. Preferably, the amount of propane mixed with the oil should be sufficient so that subsequent to obtaining the desired low temperature in the chilling column, a sufficient quantity of liquid propane will remain in the oil to provide for adequate settling of the precipitated wax from the solution of oil and propane. During wax settling, it is desirable to maintain a ratio of substantially or in excess of four volumes of propane to one volume of the oil which is adequate for good settling of the precipitated wax. This applies to both the chilling column **11** and the settler **70**. If sufficient propane is not present during chilling, make-up propane may be introduced so that the final volumetric ratio of propane to oil subsequent to the completion of the chilling operation will not be substantially below 4 to 1. The make-up propane may be gradually introduced into the chilling column at such rate as to maintain a constant ratio of 4 to 1 in the chilling column **11**.

It will be observed that other solvents may be employed which are capable of dissolving the oil and wax and that the present invention is not limited merely to the use of propane. Thus, other light petroleum fractions as naphtha and casinghead gasoline or mixtures thereof may be used. Other solvents which may be used are alcohol, ether, mixtures of alcohol and ether, acetone, etc.

The mixture of liquid propane and oil containing wax is passed through turbulence or mixing coil **8** into line **9** controlled by pressure reduction valve **10** into a combined decanter and chilling column **11**. If desired, the mixture of oil and propane may be acid treated and neutralized by methods now conventional prior to its introduction into the column **11**. In column **11**, sufficient propane vaporizes to reduce the temperature of the remaining solution of oil and solvent to a sufficiently low temperature which causes wax to precipitate from solution. It is preferable to lower the temperature gradually to the desired temperature, that is, at a rate not in excess of 4° F. per minute. This is accomplished by controlling the pressure in the column **11** by the proper operation of valve **14** on line **12** and compressor **17** which is connected to the column by lines **12** and **16**. The pressure will be gradually lowered in the column **11** to about 0 to 25 lbs. gauge which corresponds to a temperature of approximately −40° F. to 0° F. If desired, the temperature in column **11** may be lowered rapidly, as, for example, at a rate of approximately 10° F. per minute until a temperature of approximately 35 to 45° F. is attained after which the temperature may be lowered gradually to approximately −40° F. to 0° F. at a rate of approximately 2° F. or 3° F. per minute. The propane evaporating in the column **11** will pass out of the top through line **12** controlled by valve **14** and then into line **16** to the suction of compressor **17** where its pressure is raised to approximately 125 to 175 lbs. per sq. in. in order to liquefy the propane vapors by cooling to atmospheric temperature. The compressed vapors are then cooled in cooler **19** where they are liquefied and then run down into propane storage tank **4**.

Due to the fact that sufficient time must be given to gradually chill the oil and solvent passing into the column **11** and to make the process continuous, a plurality of chilling columns **11** may be provided and operated alternately. However, when operating a batch process merely one of such chilling columns will be sufficient. Thus, the introduction of oil and solvent into decanter **11** may be continued until any desired level in the decanter is reached after which the flow into the column **11** may be discontinued and the mixture chilled by controlling the operation of the valve **14** on line **12**. In the chilling column **11**, the refrigeration of the oil and solvent causes the heavy, hard and solid granular wax to precipitate from solution as well as the light flocculent wax but due to the differences in physical state, i. e., presumably crystal structure and particle size of the two types of wax, the former will settle rapidly to the bottom of the chiller before any substantial amounts of the light flocculent wax will settle. This will require from 5 to 30 minutes depending upon the volumetric ratio of propane to oil. In other words, at a relatively high ratio as for example, about eight volumes of propane to one volume of oil, the hard wax will settle from solution in approximately 5 minutes. At lower volumetric ratios of propane to oil, the time required for settling of the hard wax will be proportionately increased. Moreover, the agitation accompanying ebullition by the evaporation of propane will prevent substantial quantities of light flocculent wax to settle. The hard granular wax settling to the bottom of the column **11** is removed by line **22** controlled by valve **23** and pump **24** as a slurry of wax and propane containing some oil. If desired, this mixture may be washed with cold propane to remove the oil constituents present. As the wax present in the mass containing oil and propane recovered from the bottom of the column **11** is in a form which settles rapidly from the chilled propane it can be washed with cold propane and then passed to a settling device to separate the wax from propane solution of oil.

However, as shown in the drawing the material removed from the bottom of decanter **11** is passed via line **22** and **25** to heater **26** and thence through line **27** into evaporator **28**. Superheated steam is circulated through closed coil **29** to supply additional heat and to vaporize propane and light oil present in the mixture. The overhead from evaporator **28** passing through mist extractor **30** is sent through line **31** controlled by valve **32** to cooler **33** and then via line **34** into separator **35**. The uncondensed propane from separator **35** is sent through line **36** controlled by valve **37** to cooler **38** and thence via lines **39** and **16** to the suction of compressor **17** where its pressure is raised and is then sent to cooler **19** where the propane is liquefied and runs down into propane storage tank **4**. Any condensed light oil is withdrawn from the separator **35** through line **40**. The hard wax is taken from the bottom of evaporator **28** via line **45** and pump **46** which forces the hard wax via line **47** and line **48** controlled by valve **49** to storage tank **50**. The hard wax recovered in tank **50** is suitable for use in candle making by blending with stearic acid after refining by methods now conventional for purifying scale wax. This wax is distinguishable from the light flocculent wax remaining in suspension in decanter **11** which is not suitable for use in candle making due to its softness. However, the soft wax may be used as a component of lubricating greases such as those employed for lubricating ball or roller bearings.

If desired, the precipitated wax slurry containing propane settling at the bottom of the wax separator or decanter **11** may be removed via line **22** and commingled with a hot fluxing oil coming from tank **51** via line **52** controlled by valve **53** and pump **54** which forces the fluxing oil through line **55** and heater **56** and thence into line **57** controlled by valve **58** and line **25** where it is commingled with the wax slurry. The fluxing oil may comprise such petroleum fractions as kerosene, gasoline, oil, lubricating oil distillate, or refinery residuum which, when heated and commingled with the wax, will reduce the viscosity of the latter in order to permit it to be readily fluid and easily handled. The fluxing oil may be heated to a temperature of approximately 500° F. prior to commingling it with the wax slurry. If the wax is to be converted into fuel oil, the wax slurry containing the residual propane and oil may be mixed with ordinary refinery residuum at a temperature of 500° F. and the heat required for vaporizing the propane and fluxing the wax is supplied in the form of sensible heat from the preheated residuum. When it is desired to convert the wax to fuel oil, I prefer to use as a fluxing agent a cracked residuum which possesses a pour point depressant. The mixture of wax slurry and fluxing oil may be further heated in **26** and then introduced into evaporator **28** in which the propane and oil is vaporized and passed into line **31**, cooled in **33**, and passed to separator **35** in which unvaporized propane is withdrawn via line 36 and passed to propane storage tank 4 in the manner heretofore described. The condensed oil is removed via line 40. The fuel oil is withdrawn from the bottom of evaporator 28 and passed to storage tank 50 or a portion thereof may be recirculated to line 25 via heater 64 in the manner hereinafter described.

However, if the wax is to be recovered as a crude petrolatum which may then be processed in some desired manner, the wax slurry may be mixed with an initial amount of petrolatum preheated to a temperature of approximately 350° F. and introduced into line 25. The mixture preferably corresponds to the proportions of two volumes of preheated petrolatum to one of wax slurry. The mixture is then passed into the evaporator 28 where propane is vaporized. Heater 26 may be omitted. The crude petrolatum is withdrawn from evaporator 28 at a temperature of approximately 200° F. which is sufficiently high above the melting point of the petrolatum for efficient pumping and handling and is then passed through line 45, pump 46 and line 47, one volume of the material passing into tank 50 and the other two volumes are recirculated into line 25 via line 60, controlled by valve 61 and pump 62 which forces the material through line 63 and heater 64 where the temperature is again raised to 350° F. and then passed into lines 65 and 25. The cyclic circulation through lines 60 and 63, heater 64 and line 65 into lines 25 is carried on continuously.

If desired, the initial amount of preheated petrolatum introduced into line 25 may be substituted by an initial volume of preheated petroleum residuum which is circulated through the apparatus in the manner described above, one volume being passed to tank 50 while the remainder is recirculated and mixed with the wax slurry coming from decanter 11. After a number of such circulations, the material passing into line 45 will be sufficiently free from petroleum residuum and will comprise a crude petrolatum. Consequently, the material cooling in tank 50 and the portion circulated through heater 64 will also comprise a crude petrolatum.

Chilling column 11 is provided with a plurality of side draw-off lines 66 located at any desired position above the bottom outlet employed for withdrawing the hard granular wax slurry. Each of these lines is provided with a valve 67. By proper operation of these valves, the supernatant solution of oil solvent and precipitated flocculent wax will be withdrawn from the column 11 as a solution substantially free from hard wax. The propane, oil and precipitated wax suspended in solution is withdrawn from column 11 via said draw-off lines 66 and pumped by pump 68 via line 69 and valve 69' into the vapor tight wax separator or settler 70. In batch operation only one of these settlers will suffice but to make the process continuous a plurality of these settlers may be provided operated alternately in order to provide for sufficient settling periods. In order to prevent ebullition in the wax separator 70 during the wax settling operation, pressure is imposed upon the solution of oil. This is accomplished by maintaining pressure within the separator by pump 68. As the chilled mass in the wax separator remains in a non-ebullient state, the wax settles out and is collected by vanes 71 operated by pulley 72 connected to a suitable source of power not shown. The time required for settling the flocculent wax in settler 70 will vary from one-half to two hours depending upon the volumetric ratio of propane to oil as described above. If desired, the wax settler 70 may be replaced by a filter through which the solution of oil, solvent and precipitated wax may be passed to separate the suspended wax from the remaining oil and liquid propane. This may be accomplished by passing the chilled mixture via line 110 and valve 110' to filter 111. The filtrate may be passed via line 112 into line 74 while the separated wax may be passed via line 113 into line 90. If desired, a filter aid such as diatomaceous earth, clay, sawdust or wood flour may be mixed with the chilled propane solution of oil containing the precipitated wax and passed through the filter.

As an alternative method of operating continuously, I may effect chilling in column 11 as aforesaid and without providing for any substantial settling in column 11, the entire charge is withdrawn from the bottom into separate settlers connected in series so that the overflow from the first settler constitutes the feed to the second settler. In the first settler, a relatively short settling time is allowed to permit the hard wax to settle and in second settler, a longer settling time is provided. In order to withdraw a substantially homogeneous mixture from the bottom of column 11, I prefer to employ positive agitation in column 11 during the chilling and transferring operation. If desired, a pump may be located at the bottom of column 11 for continuously circulating a portion of the mixture withdrawn back into the column at a higher point while the remainder of the mixture withdrawn is forced through the settling vessels.

The proportions of hard and soft wax recovered will depend upon the stock being dewaxed. For example, approximately one fourth of the total wax recovered from de-asphaltized Kettleman residuum can be obtained as a hard wax and the remainder as a petrolatum by the operation of my process.

The wax free oil dissolved in propane is withdrawn from the separator 70 and pumped by pump 73 through line 74 controlled by valve 75 into heater 76 provided with mist extractor 77 where the propane present is vaporized by the aid of steam circulated through the closed steam coil 78. The vaporized propane passes out from the heater through lines 79 controlled by valve 80. cooled in cooler 81 and then passed through lines 82 and 16 to compressor 17, cooler 19, into storage tank 4. The dewaxed propane free oil passes from heater 76 by means of line 83, controlled by valve 84 to pump 85 which forces the heated oil solution through heat exchanger 86 and then through line 87 into tank 88. If the oil had been previously treated with acid and alkali, it may be treated in its chilled condition prior to the separation of the propane in the evaporator or heater 76.

The precipitated wax slurry settling to the bottom of the wax separator 70 is removed from the separator through line 90 and is passed through heat exchanger 86 where it extracts heat from the dewaxed oil from heater 76. The wax slurry is then pumped by pump 91, into line 92, through heater 93 and line 94, into separator 95. Vaporized propane is passed to the storage tak 4 via line 96 controlled by valve 97 and line 36, cooler 38, lines 39 and 16, compressor 17 and cooler 19. The propane free wax is withdrawn from the separator 95 through line 100 and pumped by pump 101 into line 102 controlled by valve 103 into storage tank 104. If desired, the wax slurry separated from settler 70 may be treated in like manner as that separated from the column 11, that is, it may be commingled with hot fluxing oil and converted into a fuel oil as previously described or the wax slurry may be treated for the production of crude petrolatum in the manner heretofore described.

It is to be understood that the above is merely illustrative of preferred embodiments of my invention of which many variations may be made by those skilled in the art without departing from the spirit thereof.

I claim:

1. In the method of refining petroleum oil containing paraffin waxes, the steps which comprise, mixing the oil with liquefied hydrocarbon gases having a vapor pressure greater than atmospheric at ordinary atmospheric temperature, cooling the mixture to a temperature sufficient to congeal the wax content, passing the cooled mixture through a settling tank to thereby separate high melting wax from the oil mixture by settling, passing the oil mixture from the settling tank, and then separating the remaining portion of the wax content by filtration.

2. In the method of refining petroleum oil containing paraffin waxes, the steps which comprise, mixing the oil with liquefied hydrocarbon gases having a vapor pressure greater than atmospheric at ordinary atmospheric temperature, cooling the mixture to a temperature sufficient to congeal the wax content, passing the cooled mixture through a settling tank to thereby separate wax from the oil mixture by settling, passing the oil mixture from the settling tank, and then separating the remaining portion of the wax content by filtration.

3. A process as in claim 2 in which the liquefied hydrocarbon gases are preponderantly propane.

ULRIC B. BRAY.