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METHOD FOR DEWAXING OILS

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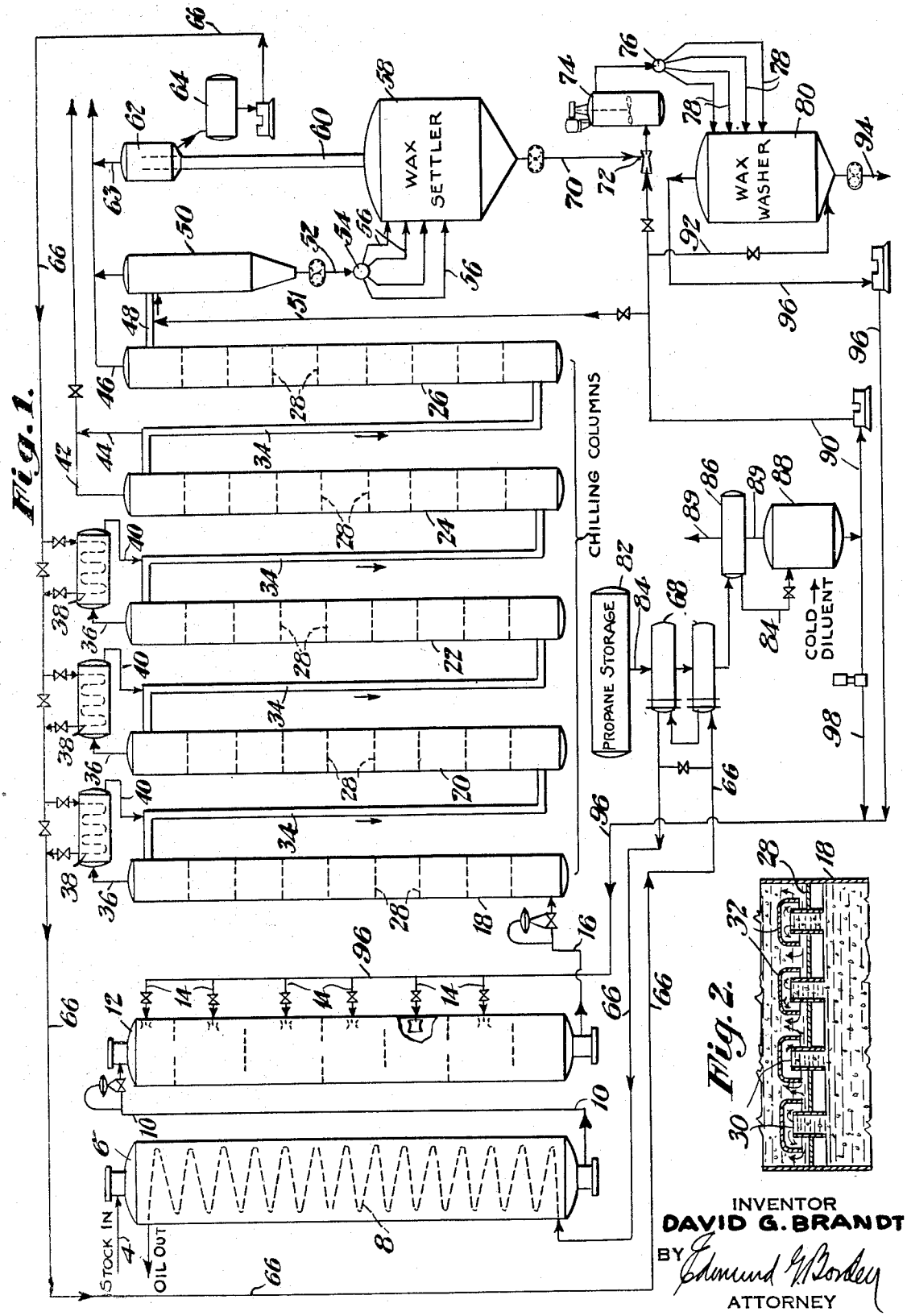


Fig. 1.

Fig. 2.

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METHOD FOR DEWAXING OILS

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12 Claims. (Cl. 196—18)

This invention relates to a process for dewaxing petroleum oils and more particularly to a dewaxing process in which a liquid normally gaseous hydrocarbon is used as a diluent and chilling medium in the dewaxing of petroleum lubricating oil stocks.

In general, the process of the present invention constitutes an improvement upon the process disclosed in applicant's prior applications, Serial No. 670,066, filed May 9, 1933, for "Art of dewaxing oils," and Serial No. 207,231, filed May 11, 1938, for "Process and apparatus for dewaxing petroleum oils."

The first-mentioned application discloses a dewaxing process in which the oil stock is diluted with propane, passed through two indirect heat exchange towers and then successively through a series of vertical chilling chambers in which progressively lower pressures are maintained and lower temperatures secured by vaporizing portions of the diluent which may be propane. The chilled stock containing the precipitated wax is removed from the last chilling chamber of the series and distributed onto the trays in a multiple-tray wax settler. This wax settler is disclosed as being provided with a central rotary shaft with sweeps mounted thereon for moving settled wax on the trays to the center of the chamber where it passes downwardly through central openings in the trays. The wax-free oil passes around the periphery of the trays and upward in the chamber to the top, from which it is discharged and used for the preliminary cooling of the mixture to be dewaxed. The settler is a vertical jacketed chamber chilled by the evaporation of propane in the jacket. Liquid propane is also cooled and introduced into the vertical chilling chambers along with the mixture being conducted from one chamber to another in the series.

Application Serial No. 207,231 discloses a dewaxing operation in which the oil stock diluted with propane is passed through a preliminary cooling chamber and cooled by indirect heat exchange down to about the pour point of the diluted stock, after which it is conducted into the top of an enlarged vertical chilling chamber in which vaporization is prevented and in which the wax content of the oil desired to be removed from the stock is precipitated by mixing extremely cold propane, or propane wax washings, or both, with the diluted oil stock in the chilling chamber as it passes downwardly through the chamber. The cold medium introduced into the vertical chilling chamber is supplied at a plurality of vertically spaced points into more or less separate chilling zones or compartments determined by baffle plates at spaced levels in the chamber. The chilling medium is jetted into the side of the vertical chilling chamber in such a manner as to cause a local circulation to bring about substantial mixing and equilibrium.

An important feature of the disclosure of application Serial No. 207,231, is the handling of the chilled diluted oil stock containing the precipitated wax in a settling operation. The extremely cold mixture is passed into a settling chamber in which the wax is settled out and passed as a slurry into a wax washing chamber and settler, where the wax is washed with a cold propane mixture. From this wax washing chamber the wax is again conducted into a mixer where it is mixed with a substantial proportion of cold propane and then passed into a second wax washer and settler. The solution from the latter settler which is very cold, is mixed with the wax slurry from the original wax settling chamber and passed therewith into the first wax washing chamber. The cold dilute solution or wash liquid removed from the first wax washing and settling chamber is used in the vertical chilling chamber for effecting the precipitation of wax. In this capacity the wax wash liquid may be augmented by cold liquid propane. The wax settler and wax settler and washing chambers are of the same construction as the wax settler of application Serial No. 670,066.

While the improved process of the present invention includes the use of some of the features described above, the primary object of the invention is to provide a dewaxing process in which the wax precipitation is effected in a series of zones at progressively lower pressures by a combination of different chilling processes.

Briefly stated, the improved process of the present invention includes the steps of dissolving the oil stock to be dewaxed in a liquefied normally gaseous hydrocarbon which is liquid at dewaxing temperatures, such for example as propane, cooling the mixture to a temperature slightly above that of wax precipitation by indirect heat exchange with cold wax-free oil solution obtained in the process, further cooling the mixture to a low temperature, for example 20° F., by mixing therewith cold diluent or cold wax washings composed mainly of the diluent used in the operation, and thereafter passing the resulting mixture containing the proper proportion of diluent through a series of zones maintained at progressively lower pressures and temperatures

in which the zones are arranged in such a way that a liquid head of the oil mixture is utilized in the series of zones for effecting the progressive pressure reduction.

The oil mixture containing precipitated wax is removed from the final chilling zone of the series and passed into a settling chamber provided with a plurality of trays. In the portion of the chilling operation in which the pressure reduction is effected and vaporization of a portion of the diluent is permitted, the resulting vapors are subjected to partial condensation at a number of points, and the resulting condensate as well as the remaining diluent vapors at each point are mixed with the oil mixture passing on through the series of chilling zones.

The problem of progressively chilling a mixture of oil and propane diluent by the evaporation of a portion of the diluent at successively lower temperatures and pressures was accomplished in accordance with the disclosure of applicant's 1933 application referred to above, by the use of pressure reducing valves in transfer lines between a plurality of chilling chambers maintained at predetermined pressures. The present invention provides an improvement by which a more gradual temperature and pressure reduction is obtained, this being accomplished by using the back pressure obtained from a hydrostatic head of the oil mixture being chilled to effect progressive pressure reduction and chilling of the oil mixture by progressively vaporizing portions of the diluent. In this connection, it has been found that while a tall column of diluted oil mixture provides a hydrostatic head of liquid, the utilization of the back pressure from such a column in the progressive chilling of an oil mixture by the evaporation of a part of the diluent is not a simple one, because under stabilized conditions, vaporization and the resulting chilling takes place only in the upper layer of the column of liquid. Now, since it is impossible to maintain a column body of liquid in a tower with the upper portion of the body colder than the lower portion, the cold oil mixture produced at the top of the body will flow by difference in specific gravity to the bottom of the tower.

It is apparent therefore that in a stabilized operation where a tall column of oil mixture is maintained in a tower with continuous introduction of oil mixture at the bottom of the tower, and continuous removal of vaporized diluent and chilled oil mixture from the top of the tower, the column of oil mixture in the tower will be at approximately uniform temperature with vaporization and resulting cooling taking place only at the top of the tower. It is furthermore apparent that in such an operation, there would be a constant thermosiphonic circulation of the cold oil mixture from the upper part of the tower to the lower part of the tower which would keep the whole body of oil mixture in the tower at approximately the same temperature (the same as in the heating of the bottom of a domestic water tank). Under such conditions the relatively warmer oil mixture being introduced into the bottom of the tower would be cooled by the body in the tower so that vaporization of diluent in the lower part of the body would not take place.

This outline of the problem of utilizing the hydrostatic pressure of a column of liquid in a chilling operation is supported by the further fact observed in present dewaxing processes where a substantial body of oil in a chamber is chilled by evaporation of diluent, that after a stable operation has been established, vaporization and resulting chilling takes place only in the upper layer of the body of oil. In starting up a chilling operation in which an oil mixture is introduced into the bottom of a tower, and chilling effected therein at reduced pressure by vaporization of diluent, the portion of the oil mixture first to enter the bottom of the tower will be chilled to the equilibrium temperature according to the pressure contained in the tower by vaporization of diluent. In continuing the introduction of oil mixture, as the body of liquid accumulates in the tower, it will continue to be at this same equilibrium temperature because of the thermosiphonic circulation within the body. But under such conditions, the diluent in the mixture entering the cold body of oil mixture in the bottom of the tower will not be vaporized immediately, but the whole mixture as it enters will be cooled by the body of oil, and vaporization will take place only in the upper layer of the oil body where the pressure is the lowest. Therefore, as the liquid level rises in the tower, the area of vaporization will also rise and remain in the upper layer of the body of oil mixture.

In accordance with the process of the present invention, the use of a hydrostatic head of liquid to effect the progressive vaporization and cooling of a diluted oil mixture has been made possible by dividing up a column or plurality of columns of the diluted oil (sufficient to provide the desired hydrostatic back pressure), into relatively small zones or units and arranging them in such a way as to effectively avoid the conditions and results pointed out above which are encountered in attempting to make use of the hydrostatic back pressure of a tall column or columns of liquid. These individual units or zones are established in the tower or towers by dividing up the vertical height of the tower with horizontal trays which act to insulate the different zones from each other and which also act as check valves to permit the upward flow of liquid and vapor and prevent the downward flow of liquid in the tower. The process of the present invention also involves other features including a combination of chilling operations which has been found to be particularly adapted for the production of wax crystals which are readily settled or otherwise removed from the diluted oil mixture.

The advantages of the improved process of the present invention will be apparent to those skilled in the art from the following more detailed description thereof taken in connection with the accompanying drawing, in which:

Fig. 1 is a diagrammatic flow sheet showing an apparatus arrangement which is particularly adapted for carrying out the improved process. In this figure certain elements of the apparatus are shown in elevation.

Fig. 2 is an enlarged broken section of one of the chilling columns showing the tray structure employed.

The petroleum oil stock to be dewaxed and which may be an overhead wax distillate or a long residuum or other oil stock, containing wax components to be removed, is diluted with from about 30% to 50% of a liquid normally gaseous hydrocarbon and brought into solution therein. While a number of such diluents are available propane will be used as an example in describing the process. The resulting mixture which will be under a considerable pressure sufficient to keep the propane in the liquid state, is introduced into the

apparatus through a line 4, and passed downwardly through an enlarged indirect heat exchange chamber or tower 6 where it passes in heat exchange with a relatively cool fluid, such as the cold dewaxed oil produced by the process, which is conducted through a heat exchange coil 8. The solution of oil stock passing downwardly through the chamber 6 is preferably cooled therein to a temperature slightly above that at which the wax would start to precipitate, so that no wax will be deposited on the coil 8 or the walls of the chamber 6. The temperature to which the solution of oil stock is cooled in chamber 6 may for example be approximately 50° F.

The resulting cooled solution is conducted from the bottom of the chamber 6 through a pressure valve controlled line 10 into the upper portion of a vertical chilling tower or chamber 12 wherein the oil stock passes through a series of chilling compartments separated only by baffle plates, so that the oil stock passes in succession through the compartments. The valve in the line 10 is used to maintain a back pressure in chamber 6 sufficient to prevent vaporization of the diluent, although this valve may be omitted. The oil solution introduced into the chamber 12 is preferably chilled to progressively lower temperatures as it passes downward through the compartments by introducing an increment of a cold chilling medium from a plurality of valved intake pipes 14 distributed along the chamber. The chilling agent injected from each of the pipes 14 is preferably introduced into the side of the chamber through an injection type of nozzle which prevents shock chilling by creating a flow of oil mixture passed the nozzle and by producing a gentle eddying action in the oil mixture in each compartment of the chamber. This insures thorough mixing of the injected cold chilling agent with the oil solution and prevents substantial shock chilling of the oil, so that by the time the oil is passed through the chamber substantial chilling and wax precipitation has been effected. The extent of the dilution in the chamber 12 should be carefully controlled so as not to get the mixture so dilute that good crystallization cannot be obtained. Therefore in the chamber 12, extent of dilution should control rather than extent of temperature reduction. In general however, it is preferred to chill the oil mixture to a temperature of only about 20° F. in the chamber 12, if the mixture can take the dilution and give proper wax crystallization.

The oil mixture reaching the bottom of the chamber 12 is withdrawn through a pressure valve controlled line 16 and introduced into the lower portion of a vertical chilling column 18 which is the first of a series of similar columns 18, 20, 22, 24 and 26, used for effecting the further chilling of the oil mixture. The valve in line 16 is preferably arranged to maintain a back pressure in the chamber 12 sufficient to prevent vaporization of the diluent. The pressure necessary to maintain the diluent in liquid phase in the chamber 6 may be for example about 240 lbs. per square inch abs., while that necessary for the same purpose in the chamber 12 may only be about 95 lbs. per square inch. (All pressures used in describing the process of the present invention are absolute.)

The vertical columns 18 to 26 are divided into a plurality of vertically spaced compartments or zones, all of which are intended to be substantially filled with liquid and which are separated by trays 28 of the bubbler type shown in enlarged detail in Fig. 2. In each of the columns 18 to 26, the compartments between the bubbler trays 28 are substantially filled with liquid which in every instance flows upwardly through the tray above by means of riser tubes 30 which extend above and below the tray proper, the upper extensions being covered with bubble caps 32 in the usual manner. The various compartments are effectively insulated from each other by means of the gas layer maintained under each tray 28 by the portions of the riser tubes 30 which extend below the tray plate.

The series of chilling columns 18 to 26 are connected by relatively large overflow pipes 34 so that the liquid mixture reaching the top of each column, except the last, overflows into the pipe 34 and is conducted into the lower portion of the next column of the series.

The chilling carried on in the tower 12 is preferably controlled so that the oil solution is chilled to a temperature of about 20° F. or below as it is discharged through the line 16 into the bottom of the column 18. Under these conditions and the arrangement of columns 18 to 26, a pressure of about 52 lbs. per square inch would be found in the upper part of the column 18, the oil solution being brought to a temperature of about 10° F. in passing upwardly through the column. The mixture introduced into the lowermost compartment of column 18 will be chilled slightly because of the vaporization of propane permitted at the valve in line 16 and in the compartment. Some vaporization and cooling will take place in each of the compartments at successively higher levels in the column 18, since the pressure will be gradually lower at higher levels because of the reduced head of liquid.

An examination of the relationships of the series of columns 18 to 26 will show that together they provide the same pressure conditions as would be obtainable from a single very tall column of liquid having a hydrostatic pressure of approximately 50 lbs. per square inch, the pressure in the top of the last column being about 10 lbs. per square inch. Under these conditions the pressure in the top of column 20 is approximately 40 lbs. per square inch, that in the top of column 22 about 28 lbs. per square inch, and that in the top of column 24 about 18 lbs. per square inch. The height of each column should be about 40 feet to provide the pressure drops indicated above for a solution of oil and propane containing about two parts propane to one part of residuum type oil by weight.

In column 18, as well as in each of the other columns of the series, the vapors formed by partial evaporation of the propane pass upwardly through the column and the trays 28, and keep the bodies of liquid in the compartments in motion so that the body in each compartment is at approximately a constant temperature level in spite of the fact that liquid is constantly entering and leaving. From what has been said above, it will be apparent that the liquid bodies maintained in each of the compartments of the columns 18 to 26 will each develop a substantially constant temperature in spite of the hydrostatic head of liquid in each compartment and in spite of the fact that both liquid and vapor enter the bottom of each body. The liquid and vapor passing into the lower portion of each body after equilibrium has been established in the system will be warmer than the body and will therefore tend to rise through the compartment and keep the wax in suspension.

There is a very small temperature differential

between adjacent bodies but since each successive body is at a lower pressure, the vapor will pass on through and actually increase in volume. The adjacent bodies in any one of the columns 18 to 26 are kept separate and insulated from each by the particular structure and functioning of the traps 28. Vapor or gas is always present under the caps 32 so that liquid cannot pass around the caps and enter the upper ends of the risers 30. The diameter of the columns 18 to 26 may be as great as 3½ feet or more, so that the cross sectional area of the columns, as well as the volume of each compartment, is relatively great compared to the rate of flow of oil mixture through the columns. This arrangement provides an operation in which the body of liquid in each compartment has a constant gentle motion and develops a slightly lower temperature than the next preceding body.

A portion of the propane vapors reaching the top of columns 18, 20 and 22, pass through vapor lines 36 into condensers 38 in which it is condensed at substantially the pressure existing in the upper part of the respective columns. In each instance this reduces the volume of vapor passing into columns 20, 22 and 24 respectively and avoids intense agitation. The condensates from condensers 38 pass through lines 40 into the upper portion of the large conduits 34, so that they mix with the oil-wax-propane mixture passing from one column to the next in series, as shown. Some propane vapor in the top of columns 18, 20, and 22 will pass directly into the conduits 34, which are not maintained filled with liquid or permitted to become filled solid with liquid. The presence of propane vapor passing downwardly through these conduits (which are of relatively large size) into the bottom of the next succeeding column, will prevent the accumulation of a liquid column in the conduits 34 and give a pressure in the bottom of one column which is essentially the same as that at the top of the next preceding column.

A portion of the propane vapor evolved in column 24 is removed through lines 42 and 44 and sent to a compressor and condenser for returning it to the supply system for the process, but some propane vapor is continuously passed from column 24 to the bottom of column 26 through conduit 34, as in the case of the preceding columns. Since in the example described, a pressure of ten lbs. per square inch abs. is maintained at the top of column 26, a suction is applied to this column through a line 46 and the propane vapor removed is compressed, condensed, and sent to the propane storage and supply system referred to hereinafter by means not shown.

Under the conditions of the example described above for the series of chilling columns 18 to 26, the temperature of the oil mixture at the top of column 20 will be approximately minus 2° F., at the top of column 22 approximately minus 16° F., at the top of column 24 approximately minus 34° F., and at the top of column 26 approximately minus 60° F. At this last temperature the mixture of oil, wax and propane is conducted through a line 48 into the upper part of an accumulator 50 from which the wax-oil-propane mixture is pumped to a settler. The accumulator chamber 50 is vented to the suction line 46 as shown. The oil-wax mixture introduced in the chamber 50 should contain the proper proportion of diluent for the settling operation, and accordingly any additional cold propane for this purpose may be introduced into the line 48 through a valved line 51. The oil-wax mixture to be settled is withdrawn continuously through a line 52 and conveyed by means of a pump therein into a rotary valve mechanism 54 from which the mixture is alternately distributed through a plurality of lines 56 at different levels into a multiple-tray settling chamber 58 of the type shown in the drawings of the applicant's pending application Serial No. 670,066, filed May 9 ,1933.

The settling chamber shown in that application is a jacketed chamber in the jacket of which liquid propane is vaporized to maintain low tempertures, the chamber itself being provided with a plurality of vertically spaced trays which slope toward the center of the chamber and which have central openings for the passage of settled wax. The trays are also of such a size that a free space is left between their outer edges and the inside wall of the settler chamber for the upward passage of separated oil solution. Provision is made for introducing oil mixture containing the solid wax particles at a point above each tray, except the upper tray, and near the center of the chamber, so that the space between adjacent trays comprises a more or less individual settling zone. The settling chamber is also provided with sweeps above each tray for moving settled wax toward the center opening in each tray. Separated wax-free oil solution is discharged from the top of the settling chamber while the settled wax slurry is removed from the bottom of the chamber by means of a gear pump or other suitable means.

In the present instance, it is intended that the oil mixture be introduced from one of the lines 56 periodically at a point above a tray therefor so that for the four lines 56 as shown there should be at least four trays with an additional one above the highest point of introduction. The valve 54 is operated to supply the oil mixture through only one of the lines 56 at a time so that the settling zones between trays in the settler 58 will have a definite period of time during which no oil mixture will be supplied.

The settling chamber 58 is provided with a relatively large diameter vertical oil discharge line 60 which overflows into a chamber 62, the line 60 being sufficiently tall to provide a substantial hydrostatic head of liquid in the chamber 58, thus preventing vaporization of propane therein. The chamber 62 is connected through a line 63 with the suction line 46, to maintain pressure equilibrium with chambers 26 and 50. The separated cold oil solution free of wax is conducted from the chamber 62 into a surge tank 64 from which the cold solution is passed through a line 66 by means of a pump therein through the condensers 38 in the order shown, in any desired proportions to effect the partial condensation of propane from the columns 18, 20, and 22. The line 66 is provided with suitable valves and connecting lines as shown for supplying the desired cooling solution for the condensers 38. After the cold oil solution passes the condensers 38, it is conducted through additional heat exchangers 68 for cooling liquid propane and then through the coil 8 in tower 6. The oil solution discharged from the coil 8 may be subjected to any desired further treatment including the removal of the propane.

The wax slurry produced in the settling chamber 58 is removed through a line 70 by means of a gear pump therein, mixed with extremely cold liquid propane in a nozzle 72, and passed through a mechanical mixer 74, into an apparatus arrangement similar to that shown and described in application Serial No. 207,231. The wax slurry

(in nozzle 72 and mixer 74) is substantially diluted with cold propane, and the resulting mixture passed to a rotary valve 76, of the same type as the valve 54, from which the mixture is distributed through a plurality of lines 78 to a wax settling chamber 80 which may be, and preferably is, of the same construction, and operated in the same manner as the chamber 58.

The cold propane used for mixing with the wax slurry in the nozzle 72 and mixer 74 may be obtained by conducting liquid propane from a plant storage 82 which may receive propane from the lines 42 and 46, by passing it through a line 84 in which is mounted the heat exchangers 68 and a further heat exchanger 86, and then through a pressure reducing valve in the line 84 into a propane chilling chamber 88 in which extremely cold propane is produced by partial evaporation. The propane vapor evolved in the chamber 88 is removed by suction through a line 89 by a pump (not shown), passed through heat exchanger 86, and discharged into line 42 or 46 for compression. The extremely cold liquid propane is supplied to the nozzle 72 from chamber 88 through a valved line 90 by a pump mounted therein. Cold propane is also supplied to the line 51, and directly to the bottom of the settling chamber 80 through a valved line 92 for washing the settled wax. The settled and washed wax slurry is removed from the chamber 80 through a line 94 which is provided with a gear pump, while the very cold propane solution containing a relatively small proportion of oil is removed from the top of the chamber 80 through a line 96 and forced by means of a pump therein into the supply lines 14 for the chamber 12.

The chamber 80 is preferably jacketed and operated at a very low temperature (for example as low as minus 60° F.) so that the liquid wash material removed through the line 96 is extremely cold, and is therefore very suitable for cooling and diluting the oil solution in the chamber 12. While in any given instance sufficient cooling medium for the chamber 12 may be supplied by the wax washings from chamber 80, additional cold propane at the desired temperature may be supplied from the chamber 88 through a line 98 by means of a pump therein, the line 98 connecting directly into the line 96 leading to the branch lines 14.

In the operation of the series of chilling columns 18 to 26, the pressure may be varied to some extent in each column by varying the density of the solution, but in each instance the pressure reduction secured at any point in the series of columns 18 to 26 depends on the total column of liquid beyond the point and the density of liquid, which in turn depends on the proportion of gas or vapor in the liquid which may exist as bubbles of diluent passing upwardly through the columns.

Furthermore the series of chilling columns 18 to 26 is controlled to regulate the proportion of propane vapor passed from one column to the other. One means of accomplishing this is shown in connection with columns 18 to 24, and comprises the control of condensation effected by the condensers 38. In actual operation, these condensers may be automatically controlled to provide for a definite flow of vapor through the lines 34, and such control may involve the automatic supply of cooling medium from the line 66 in conjunction with the volume of vapor flowing in the lines 34. The vaporization in the columns 18 to 26 is controlled to some extent by pressure reduction and extent of cooling, but in any case the vaporization should only be gradual and the amount of vapor passed through the liquid bodies in the different columns only sufficient to provide a gentle bubbling action. Intense agitation and high velocities are to be avoided, and the proportion of vapor passed through the bodies may be regulated by venting vapor from any compartment or column.

The operation of the chamber 12 also has an influence on the operation of the series of columns 18 to 26, so that in any particular apparatus and proposed procedure the extent of cooling effected in the chamber 12 should be regulated in accordance with the range of temperature reduction to be effected in the columns 18 to 26, inclusive.

While the invention has been described above in connection with a more or less specific example in which the columns 18 to 26 are approximately 40 feet high, it will be apparent that the number of columns may be decreased or increased, and that their height may be changed without departing from the spirit and scope of the invention. Various other modifications may be made in the operation in accordance with the scope of the accompanying claims.

Furthermore, it is to be understood that in describing the process of the present invention, the temperatures, pressures and other conditions are merely used in connection with a specific example. Other normally gaseous hydrocarbon diluents may be employed instead of propane and two or more diluents of different boiling point may be used at the same time, one of which may substantially remain in the liquid state while the other may be vaporized and partially condensed as the operation proceeds in the series of columns 18 to 26.

Having thus described the invention, what is claimed as new is:

1. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquefied normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures, the improvement which comprises chilling the solution by passing it through a series of interconnected large zones held at progressively lower pressures by the hydrostatic head of the mixture in the succeeding zones, in each of which a substantial body of the oil-diluent mixture is maintained, vaporizing portions of the diluent in each zone and thereby chilling the mixture of oil and diluent therein, and passing vaporized diluent from each zone upwardly through succeeding zones in intimate contact with the oil mixture therein to effect agitation thereof.

2. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquefied normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures, the improvement which comprises chilling the solution initially held under a substantial pressure to a low temperature by passing the solution through a series of freely communicating large zones at progressively lower pressures maintained by the hydrostatic head of the mixture in the succeeding zones, maintaining a substantial body of the oil-diluent mixture in each zone, vaporizing portions of the diluent in each zone because of the reduced pressure therein and thereby chilling the mixture of oil and diluent in each zone, and passing vaporized diluent in vapor form from each zone upwardly through the

next succeeding zone of the series in intimate contact with the oil mixture therein to effect agitation thereof.

3. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquefied normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures, the improvement which comprises chilling the solution to a low temperature by passing the solution through a series of interconnected large zones which are held at progressively lower pressures by the hydrostatic head of liquid in the succeeding zones, maintaining a substantial body of the oil-diluent mixture in each zone, permitting portions of the diluent in each zone to vaporize and thereby chill the mixture of oil and diluent therein, and passing vaporized diluent from each zone into the bottom of the next succeeding zone of the series whereby a back pressure is created by the series of bodies of oil mixture.

4. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquid normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures, and in which the resulting solution is chilled to crystallize the wax content of the oil to be removed therefrom, the solution being made at a substantial superatmospheric pressure, the improvement which comprises effecting at least a part of the chilling operation in a continuous manner by passing a continuous stream of the oil solution into and through a series of interconnected relatively large chilling zones each containing a substantial body of the oil solution or mixture and which are maintained at progressively higher pressures in a direction opposite to that of the flow of oil solution through said zones by having the zones arranged in such a way as to provide a hydrostatic head of liquid in the series of zones, maintaining a relatively low pressure on the final zone of the series and providing a sufficient hydrostatic head of liquid in the zones in relation to the temperatures therein to permit vaporization of only a small portion of the diluent in each zone to thereby effect the desired chilling operation, passing diluent vapors from each zone into the lower part of the next zone of the series, separately condensing a portion of the diluent vaporized in a plurality of the zones, and passing each condensate with the oil mixture advancing to the next zone of the series.

5. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquid normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures, and in which the resulting solution is chilled to crystallize the wax content of the oil to be removed therefrom, the solution being made at a substantial superatmospheric pressure, the improvement which comprises effecting at least a part of the chilling operation in a continuous manner by passing a continuous stream of the oil solution into and through a series of interconnected relatively large chilling zones each containing a substantial body of the oil solution or mixture and which are maintained at progressively higher pressures in a direction opposite to that of the flow of oil solution through said zones by the hydrostatic head of liquid in the series of zones, vaporizing a portion of the diluent in each zone and passing at least a portion thereof in vapor form into the body in the next succeeding zone, maintaining a relatively low pressure on the final zone of the series and providing a sufficient hydrostatic head of liquid in the zones adapted to permit vaporization of only a small proportion of the diluent in each zone to thereby effect the desired chilling operation, condensing a portion of the diluent vaporized in some of the zones, and passing the resulting condensate into the next zone of the series.

6. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquid normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures and in which the resulting solution is chilled to crystallize the wax content of the oil to be removed therefrom, the solution being made at a substantial superatmospheric pressure, the improvement which comprises effecting at least a part of the chilling operation in a continuous manner by passing a continuous stream of the oil solution into and from zone to zone through a series of bodies of the oil solution in a series of zones which are maintained at progressively higher pressures in a direction countercurrent to the flow of oil solution from zone to zone, the pressures being maintained by using the series of bodies of oil solution to provide a hydrostatic head of liquid in the series of zones, maintaining a relatively low pressure on the final zone of the series and providing a sufficient hydfostatic head of liquid in the series of zones adapted to permit only a gradual vaporization of portions of the diluent in the series of zones, to thereby effect the desired chilling operation, and passing a continuous stream of the vaporized diluent through the series of zones in the direction of oil solution flow, the vapors being introduced directly into the lower portion of the body of oil solution in one zone from the preceding zone.

7. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquid normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures and in which the resulting solution is chilled to crystallize the wax content of the oil to be removed therefrom, the solution being made at a substantial superatmospheric pressure, the improvement which comprises effecting at least a part of the chilling operation in a continuous manner by passing a continuous stream of the oil solution into and from zone to zone through a series of bodies of the oil solution in a series of zones which are maintained at progressively higher pressure in a direction countercurrent to the flow of oil solution from zone to zone, the pressures being maintained by a hydrostatic head of liquid in the series of zones, maintaining a relatively low pressure on the final zone of the series and providing a sufficient hydrostatic head of liquid in the series of zones adapted to permit only a gradual vaporization of portions of the diluent in the series of zones, to thereby effect the desired chilling operation, condensing a portion of the diluent vaporized in some of the zones, and passing diluent vaporized in each zone in vapor form and condensed diluent into the body of oil solution in the next succeeding zone of the series.

8. A process for dewaxing petroleum oil stocks as defined by claim 7 in which the condensation of a portion of the diluent vaporized in some of the zones is effected by passing diluent vapors from such zones into heat exchange with cold dewaxed oil solution and in which the condensing

operations are controlled so as to avoid condensing all of the diluent vapors from the zones from which vapors are condensed.

9. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquefied normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures, the improvement which comprises chilling the solution by passing it through a series of interconnected large zones which are held at progressively lower pressures by the hydrostatic head of liquid in the succeeding zones, maintaining a substantial body of the oil-diluent mixture in each zone, permitting portions of the diluent in each zone to vaporize and thereby chill the mixture of oil and diluent therein, and intimately distributing diluent vapors from each zone and the oil diluent mixture passed therefrom into the bottom of the next succeeding zone of the series whereby the body of oil-diluent mixture therein is agitated.

10. In an apparatus for dewaxing mineral oils, the improved chilling arrangement for effecting chilling of a solution of mineral oil in a liquid normally gaseous hydrocarbon diluent comprising a series of tall columns each of which are divided vertically into a plurality of compartments, means for introducing the oil solution into the lower portion of the first column of the series, means for conducting oil solution from the upper portion of each column except the last into the lower portion of the next succeeding column of the series, condensing means at the top of the first column of the series for condensing vaporized diluent from that column, means for conducting the resulting condensate from the condenser means into the means for conducting the oil solution from the upper part of the first column to the lower portion of the next column of the series, and means separating the compartments in each column adapted to substantially uniformly distribute the solution and vaporized diluent from a lower compartment into the next higher compartment in each column.

11. In a process for dewaxing petroleum oil stocks in which the stock to be dewaxed is dissolved in and diluted with a liquefied normally gaseous hydrocarbon diluent which is liquid at dewaxing temperatures, and in which the resulting solution is chilled by vaporization of portions of the diluent while passing upwardly through a zone of substantial height containing a vertical series of bodies of oil-diluent mixture in separate compartments, the solution being subjected to progressively lower pressures as it flows upwardly through the series of bodies by reason of the decreasing hydrostatic head of liquid in the zone, the improvement which comprises passing all of the diluent vapors formed in said zone upwardly through the oil-diluent mixture therein from the points of vapor formation, whereby all vapors formed are contacted with the portions of the oil-diluent mixture above the points of vapor formation therein, and intimately distributing the diluent vapor from each compartment into the body of oil-diluent mixture in the next higher compartment of the zone.

12. The process as defined by claim 9 in which a portion of the vapors in each zone is condensed and in which the amount of diluent vapor conducted from one zone into the next is controlled by regulating the amount of vapor condensation effected in said condensing operation.

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