Aug. 23, 1938. V. VOORHEES 2,127,708

DEWAXING SYSTEM

Filed June 30, 1934 3 Sheets-Sheet 1

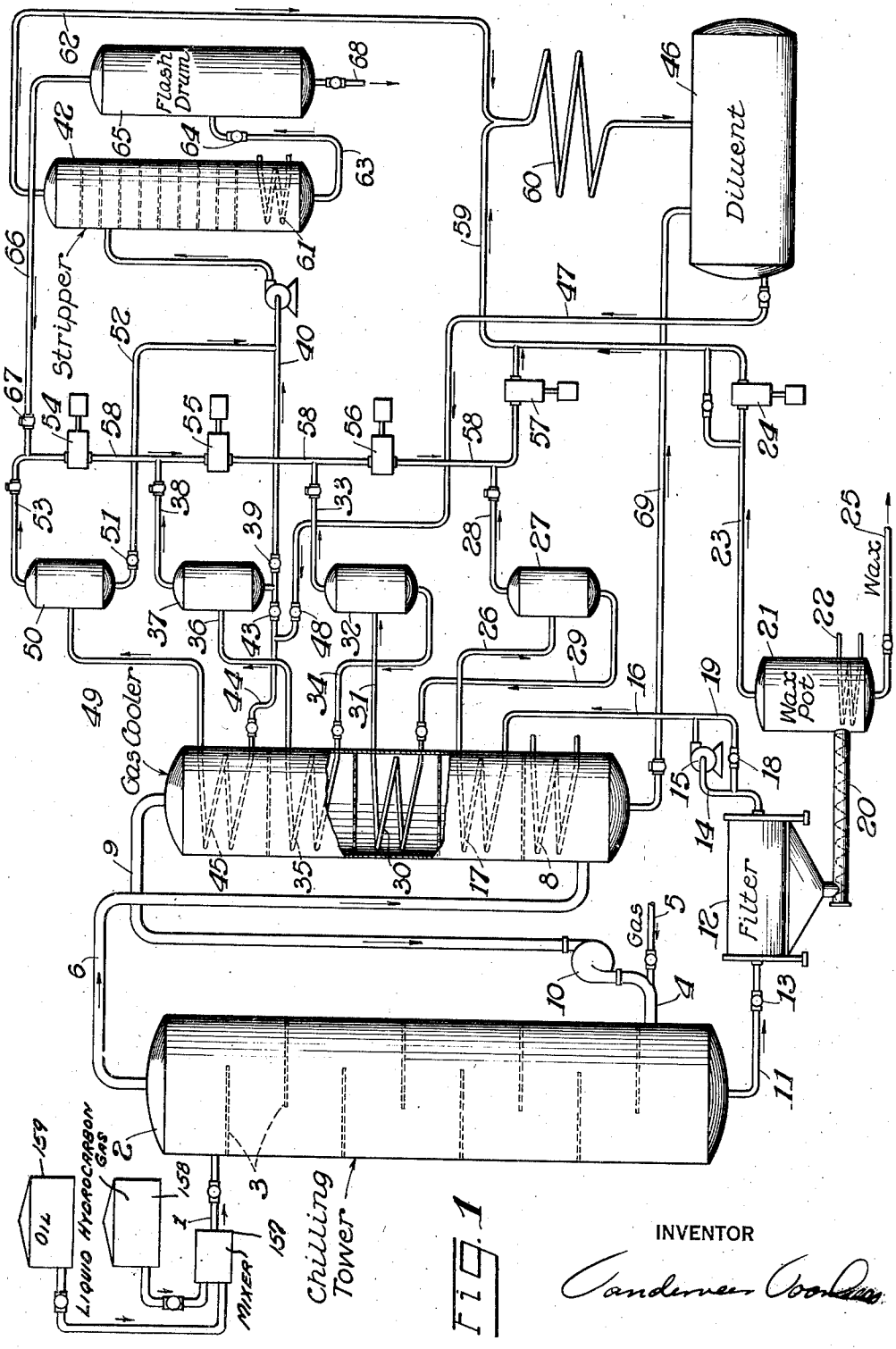



FIG. 1

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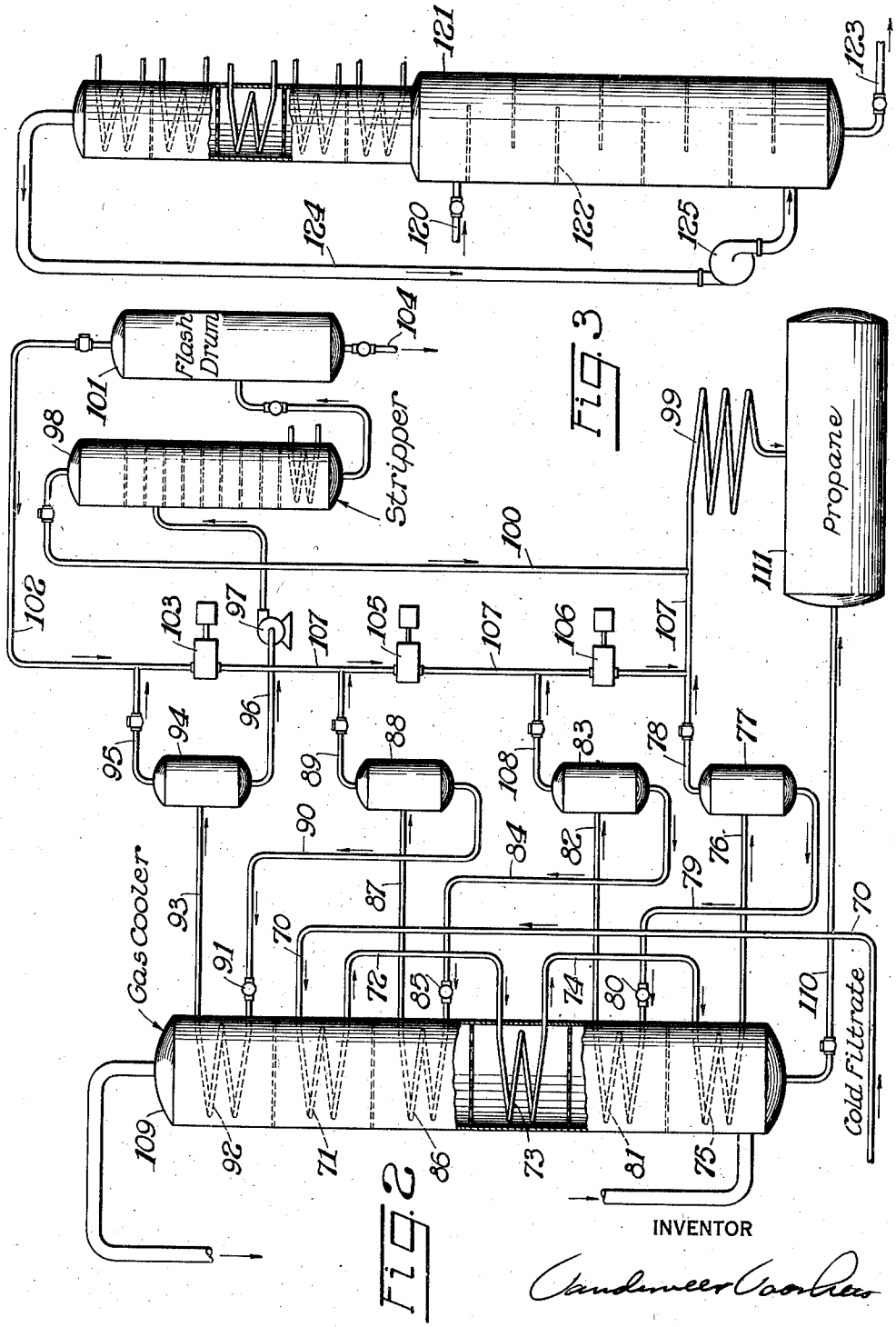



Fig. 3

Fig. 2

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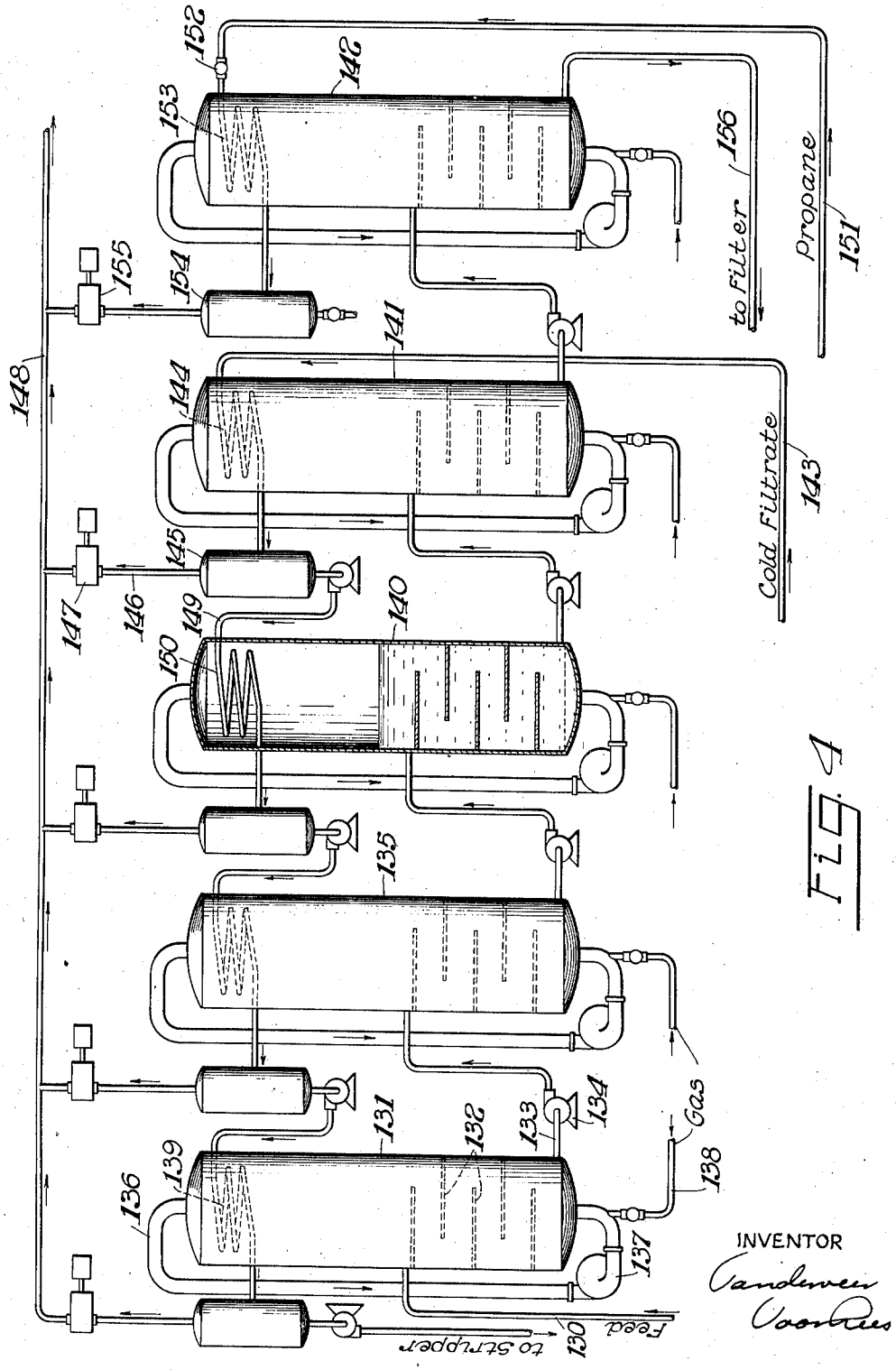



Fig. 4

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# UNITED STATES PATENT OFFICE

2,127,708

## DEWAXING SYSTEM

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12 Claims. (Cl. 196—18)

This invention relates to a process of removing wax from mineral oils and particularly petrolatum and paraffin wax from petroleum lubricating oils. The oils are preferably distillate stocks obtained by the fractional distillation of crude petroleum and they may suitably be fractionated to the desired viscosity required in the finished lubricating oil after removing the wax. The process may also be applied to residual oils containing paraffin and petrolatum, in which case naphthenic and asphaltic material may be separated in the process along with the wax. The process is particularly adapted to the dewaxing of lubricating oil fractions containing amorphous wax which is difficult to remove by ordinary dewaxing processes.

One feature of the invention is the use of liquefied hydrocarbon gases as diluents for the lubricating oil. These gases may suitably be ethane, propane, butane or isobutane and other diluents may be present such as pentane, hexane and heavier hydrocarbons and naphthas. Wax precipitating solvents may also be employed in ccoperation with the liquefied hydrocarbon gases, for example, acetone, ethyl ether, dimethyl ether, sulfur dioxide, benzene, etc. In conducting the process the general method is to dissolve the oil in about one to six volumes of the diluent and cool the solution to a low temperature at which the wax is crystallized and subsequently removed by mechanical means, for example, settling, centrifuging or filtration. Cooling is most suitably accomplished by vaporizing from the solution a portion of the diluent whereby the latent heat of vaporization required by the evaporating diluent is made available for refrigeration. The temperature to which the solution is cooled may suitably be from zero degrees F. to —60° F., although it is preferred to operate at temperatures of—30 to —40° F. which experience has shown is sufficiently low to cause the separation of substantially all the wax contained in the oil. The removal of the wax is also carried out at the low temperature in order to obtain a lubricating oil which will have a minimum pour point.

An important feature of the process is the method by which the vaporization of the liquefied hydrocarbon diluent is effected. In prior processes employing continuous refrigeration by this general method it has been customary to obtain vaporization by releasing the pressure from the solution of oil and diluent. For example, a solution of oil in propane which may be at a pressure of 150 to 200 lbs. per square inch may be discharged through a valve or orifice to a pressure approximately atmospheric, whereupon a large proportion of the propane is flashed off as vapor and the remaining solution is cooled to a temperature of approximately —40° F. This operation has not proved successful for the reason that the sudden or shock chilling accompanied by the high turbulence to which the oil and wax are subjected in the flashing operation results in producing solid wax in an amorphous form which is extremely difficult to separate by any known means such as settling or filtration.

In order to overcome this difficulty in the past it has been the practice to vaporize the propane by gradually reducing the pressure so that shock chilling is avoided. This method of operation is extremely difficult to carry out in a continuous system and therefore it has been the practice to employ batch chilling with all the disadvantages which are well-known to accrue to batch processes.

According to the present invention these difficulties are avoided by evaporating propane from the oil-propane solution at substantially constant pressure. Evaporation is effected by contacting the propane-oil solution or slurry with a current of inert gas into which the propane evaporates and is carried away by the moving gas stream. The propane in the gas stream may be subsequently separated by cooling and condensation and the gas recirculated. By means of this process I am enabled to refrigerate the oil-wax-propane solution at constant pressure, for example, 150 pounds per square inch, reducing the temperature in one operation from ordinary temperature, where the wax is all in solution, to —40° F., for example, where the wax is all crystallized without subjecting the oil and wax to any sudden changes in temperature or undesirable agitation which would result in breaking up the wax crystals and reducing filter rates in subsequent removal of the wax from the oil. The process may be carried out in several ways or modifications, some of which are described in the drawings which accompany and form a part of this specification.

Referring to the drawings, Fig. 1 represents diagrammatically a modification of the process wherein inert gas is circulated through a baffled chilling tower and subsequently through a cooler for removal of propane. The cooling tower obtains part of its refrigeration from the cold filtrate leaving the wax filter. Fig. 2 illustrates another arrangement of employing the refrigeration of the cold filtrate in the gas cooling tower.

Fig. 3 illustrates a combined form of wax slurry chiller and gas refrigerating tower. Fig. 4 illustrates an adaptation of the process to stage operation wherein the wax-oil diluent slurry is passed successively from one stage to the next, each stage being separately cooled by recirculation of an inert gas stream over suitable cooling coils and in contact with the liquid slurry. The process will be more fully understood from a detailed explanation of the drawings.

Referring to Fig. 1, a solution of oil and propane is prepared in mixer 157 by intimately mixing liquid propane drawn from tank 158 and wax-containing lubricating oil drawn from tank 159. The solution, which may contain four volumes of propane and one volume of oil, is introduced by line 1 into chilling tower 2 at a pressure slightly above the vapor pressure of the propane. At 80° F., for example, this will correspond to a pressure of about 140 pounds per square inch gage. At the point of introduction into the tower it is preferred that the temperature be sufficiently high to retain substantially all the wax in solution.

The solution descends through the tower over suitable baffles 3 where it comes into contact with a current of gas which is admitted to the tower by line 4. This gas may be nitrogen, hydrogen, air, flue gas or even methane. It is preferred, however, to employ a gas which is not very soluble in the oil slurry. Additional gas when needed may be supplied to the system by valved line 5.

The inert gas is passed upward through the tower in countercurrent contact with the descending oil slurry leaving the tower by line 6 which leads to gas cooler or exchanger 7. Here the gas flows over a succession of cooling coils, the first of which, coil 8, may be cooled by a supply of cold water. A direct cold water or brine spray may also be used for cooling the gas if desired and adequate means may be provided for keeping separate the water and propane which condenses out of the gas stream. The gas passes out of tower 7 through line 9 and is driven by blower 10 back into the tower 2.

On passing downward through the tower 2 the propane evaporates progressively from the slurry as it comes in contact with gas which is progressively colder and "drier" with respect to propane vapor. When the slurry reaches the bottom of the tower it has been deprived of from one to two volumes of propane and its temperature has been reduced to approximately —40° F. It passes out from the tower by line 11 leading to filter 12 which may suitably be of the continuous rotary drum or leaf type, operating in a closed chamber under pressure. The filter may be operated at substantially the same temperature as the chilling tower 2 or the pressure may be reduced to any desired extent by pressure reducing valve 13. Reduction in pressure at this point will not result in vaporization of propane because the temperature is below the boiling point. The amount of turbulence obtained, therefore, is relatively slight and this may be still further reduced by employing a restricted elongated passage or other device for relieving pressure.

Where the filter is operated at low pressure the filtrate leaving by line 14 is forced by pump 15 through line 16 into cooling coil 17 located in tower 7 previously described. Where the filter 12 is operated at high pressure the pump 15 is not required and may be valved off, the filtrate being led through pressure reducing valve 18 and bypass line 19. Wax which is separated from the oil in filter 12 is discharged through discharge line 20 into wax pot 21, heated by steam coil 22 where the wax is melted and propane is driven off from it through line 23 leading to compressor 24 which may be employed where the pressure in the wax pot is not sufficiently high to effect condensation of the propane vapors in the subsequent propane recovery condenser. Melted wax substantially free from propane is discharged from the wax pot by line 25 and any further propane which it contains may be recovered by flashing at low pressure.

The filtrate containing a large amount of propane after passing through heat exchange coil 17 is led by line 26 to separating drum 27 where any propane vapors are removed by line 28 and the filtrate is passed by line 29 to chilling coil 30, thence by line 31 to separating drum 32 where the vapors are further removed by line 33 and the filtrate is conducted by line 34 to chilling coil 35 and thence by line 36 to separating drum 37. Each chilling coil and separating drum may suitably be operated at progressively lower pressure in order to obtain a progressively lower temperature, as the recirculated cooling gases proceed upwards through the gas cooling tower.

Vapors are removed from separator drum 37 by line 38 and the filtrate may be discharged by valve 39 into line 40 leading to pump 41 and propane flash tower 42 or the filtrate from separator 37 may be discharged through valve 43 into line 44 and cooling coil 45 where it is further expanded and still further refrigerating effect obtained from evaporation of the propane contained in it. It is preferred, however, to employ another refrigerant in coil 45 in order to more easily obtain the low temperature desired at this point. This may be suitably supplied by feeding pure propane to this coil directly from propane storage reservoir 46. This may be led through line 47 and valve 48, line 44 from which it is expanded into coil 45, the vapors being removed by line 49 into drum 50. Any liquid collecting in this drum is withdrawn by valve 51 and line 52 to pump 41, previously described. The vapors from drum 50 are led by line 53 to compressor 54 which is one of a series of stage compressors, the others being 55, 56 and 57. Each compressor increases the pressure of the vapor which is led from one stage to the next by line 58 and the vapor is discharged from compressor 57 into line 59 leading to propane recovery condenser 60, thence into propane storage reservoir 46. Other refrigerating means may be used for cooling the inert gas, for example, an ammonia compression or absorption system may suitably be used, especially to obtain chilling in the low temperature stage.

The filtrate, after being introduced into flash tower 42, is heated by steam coil 61 to drive off the remaining propane under sufficient pressure to bring about its condensation in coil 60 to which it is led by line 62. The oil is then further flashed by leading it through line 63 and valve 64 to low pressure flash drum 65 which is connected by line 66 and valve 67 to compressor 54, previously described. Filtrate oil substantially free from propane is discharged in drum 65 by line 68 and forms the principal product of the process. It may be subsequently treated with acid or selective solvents, for example, nitro-benzene, dichlor-diethyl ether, cresylic acid, etc. and it is usually desirable to treat it with fuller's earth to obtain the required color. It may also be redistilled to produce any different viscosity grades desired. Propane which is condensed in tower 7

descends down through the cooling coils therein, is withdrawn from the bottom by valved line 69 and return to propane storage.

Another modification of the cold filtrate-inert gas heat exchange apparatus is shown in Fig. 2. In this arrangement the cold filtrate which is led from the filter by line 70 first enters heat exchange coil 71, which is located near the gas outlet end of the chilling tower. The filtrate is then conducted by line 72 to coil 73 and thence by line 74 to coil 75, the temperature being progressively higher toward the gas inlet end. Some vaporization occurs in the warmer coils and the filtrate and propane vapors are led by line 76 to separating drum 77 where the vapors are discharged by line 78. The filtrate is then led by line 79 through valve 80, through coil 81, thence by line 82 to separator 83 and thence by line 84 to valve 85, into coil 86 and distilled under pressure where further quantities of propane are evaporated. The filtrate is led by line 87 to separator drum 88 where further vapors are removed by line 89 and the filtrate is conducted by line 90 through valve 91 into coil 92 where still further quantities of propane are vaporized and the filtrate is discharged by line 93 at substantially atmospheric pressure into drum 94. In drum 94 the vapors are removed by line 95 and the remaining filtrate flows by line 96 to pump 97 which forces it into flash tower 98. The recovery of propane from the filtrate is similar to that described in connection with Fig. 1, the vapors being discharged under sufficient pressure to later condense them in coil 99, being led thereto by line 100. The oil is further freed from propane in flash drum 101 from which vapors are conducted by line 102 to compressor 103. A substantially propane-free oil is discharged by line 104.

The compression system is similar to that described in Fig. 1, consisting of stage compressors 103, 105, and 106, interconnected by line 107 into which vapors are discharged from drum 88 by line 89, from drum 83 by line 108 and from drum 77 by line 78. Liquid propane condensing in the cooling tower 109 is withdrawn by line 110 and passes through propane storage reservoir 111 where it may be withdrawn for use in other parts of the process and for diluting the original lubricating oil supplied to the dewaxing system.

The apparatus just described illustrates a design for recovering in a most effective manner the refrigeration available in the propane oil filtrate. The sensible refrigeration is obtained by countercurrent flow under high pressure without vaporization and thereafter the filtrate is passed concurrently with the circulating gases and the pressure is reduced to a minimum by this arrangement.

Fig. 3 illustrates the gas refrigerating tower and the propane oil chiller in a single column. In this design the propane oil solution is admitted by line 120, passes down through the lower section of tower 121 over baffle plates 122 and is discharged at the bottom by line 123 leading to the wax filter. Inert gases are recirculated from the base of the tower to the top by line 124 and blower 125. Propane which condenses in the gas cooling section of the tower flows back into the tower and combines with the oil-propane slurry therein, thus maintaining the diluent ratio in the slurry at a constant value. This enables the process to be operated on a slurry with a lower initial propane ratio, for example, as low as one volume of propane to one volume of oil, or even less.

Referring to Fig. 4, a solution of propane in oil is admitted by line 130 to chilling stage 131 maintained at a pressure above the vapor pressure of the incoming solution. The slurry passes over baffle plates 132 and flows out through line 133 and pump 134 to a second chilling stage 135. Inert gas is circulated through chilling drum 131 by line 136 and blower 137. Additional gas may be introduced into the system by line 138 as desired. The gas passes upward through the chiller and is brought into contact with heat exchange coil 139 which condenses a portion of the propane from the gas, the condensed propane falling back into the slurry and thereby maintaining a constant composition therein.

This operation is repeated in much the same manner in each of a series of stages, for example, five stages 131, 135, 140, 141 and 142. The cooling fluid supplied to the heat exchange coils in each stage may suitably be cold filtrate which is introduced by line 143 and may be further cooled between each stage, if desired, by vaporizing a portion of the propane therefrom. For this purpose the filtrate, after passing through coil 144, is discharged into drum 145 and the vapors are removed therefrom by line 146 and compressed by compressor 147 into line 148 which leads to the propane recovery condenser. The remaining filtrate is led by line 149 to the chilling coil 150 in the next preceding chilling stage.

In the final chilling stage 142 it is preferred to use a different refrigerant, for example, pure propane which may be admitted by line 151 and expanded through valve 152 into coil 153, thence to drum 154 and compressor 155. The cold slurry containing wax is discharged from the last stage 142 through line 156 which leads to the wax filter.

Although this process has been described as applied to several specific modifications it should be understood that it is limited only by the scope of the following claims.

I claim:

1. The process of dewaxing a wax bearing petroleum lubricating oil comprising dissolving the oil in liquefied hydrocarbon gas, continuously introducing the resulting solution, at a pressure in excess of its vapor pressure and a temperature sufficient to retain substantially all the wax in solution, into a chamber where it is brought into countercurrent contact with a current of an inert gas maintained at a pressure substantially equal to or above the vapor pressure of the entering oil solution and precooled to a temperature approximating that desired for the oil treated, controlling the volume of the gas contacted with the solution so that the temperature of the solution is reduced partly by evaporation of diluent to a point where substantially all the wax contained therein is crystallized, filtering the wax from the cold slurry of wax, oil and liquefied gas, and employing the refrigerating effect of the resulting filtrate to cool the said gas before contacting with the oil solution.

2. The process of claim 1 wherein the filtrate is heat exchanged countercurrently with the said gas in an indirect cooling zone and the gas is recycled from the oil cooling chamber to said cooling zone.

3. The process of claim 1 wherein the filtrate is heat exchanged countercurrently with the said gases without vaporization of liquefied hydrocarbon gases from said filtrate and thereafter concurrently with vaporization of liquefied hydrocarbon gases from said filtrate.

4. In a process of removing wax from viscous

wax-containing oils, wherein the wax is crystallized from the oil by diluting the oil with a liquefied normally gaseous hydrocarbon and cooling in a manner to produce crystalline wax in a form which is subsequently removable by filtration, the method of chilling the solution of waxy oil in liquefied normally gaseous hydrocarbon, comprising preparing the said solution of waxy oil and normally gaseous hydrocarbon at a temperature sufficient to insure substantially complete solution of said wax, continuously contacting the solution with a current of an inert refrigerating gas preliminarily cooled to a temperature approximately that desired for the oil whereby a portion of the diluent is evaporated at a pressure greater than the vapor pressure of the diluent at the temperature prevailing and the solution of oil and diluent is cooled by the combined refrigerating effect of the cold gas and the evaporation of part of the diluent said contacting step being carried out by causing said solution to flow countercurrent to said refrigerated gas in an elongated cooling zone.

5. The process of claim 4 wherein the cooling operation is performed entirely at the same pressure.

6. The process of claim 4 wherein the cooling operation is performed entirely at a single pressure substantially equal to the vapor pressure exerted by the diluent in the oil solution charged to the cooling operation.

7. The process of continuously chilling and dewaxing a solution of wax-containing lubricating oil and propane which comprises introducing said solution at a temperature above which the wax is all dissolved, into countercurrent flowing contact with a current of inert gas, thereby causing propane to evaporate into said gas and cooling said oil, thereafter cooling said gas to a temperature approximating that desired for the oil, condensing liquid propane from said gas and returning it to the solution whereby the ratio of propane to oil in solution is maintained substantially constant, and subsequently continuously filtering separated wax from the cooled solution of oil and propane.

8. The process of continuously chilling and dewaxing a solution of wax-containing lubricating oil and liquefied normally gaseous hydrocarbon which comprises preparing said solution at a temperature at which the wax is substantially all dissolved continuously introducing said solution without substantial drop in pressure, into a chilling zone in countercurrent flowing contact with a current of cold inert gas thereby causing part of said liquefied normally gaseous hydrocarbon to evaporate into said inert gas, thereafter withdrawing said inert gas from said chilling zone, separating said hydrocarbon gas from said inert gas, cooling said inert gas to a temperature approximating that desired for the cold oil solution and returning it to said chilling zone, and continuously filtering separated wax from the cooled solution of oil and liquefied normally gaseous hydrocarbon.

9. The process of claim 8 wherein the said hydrocarbon gas is reliquefied on separating from said inert gas and returned to the chilling zone.

10. In a process of removing wax from viscous wax-containing oils, wherein the wax is crystallized from the oil by diluting the oil with a liquefied normally gaseous hydrocarbon and cooling in a manner to produce crystalline wax in a form which is subsequently removable by filtration, the method of chilling the solution of waxy oil in liquefied normally gaseous hydrocarbon comprising completely dissolving the wax in said oil, continuously and countercurrently contacting the solution with a current of an inert cold refrigerating gas preliminarily cooled to a temperature approximating that desired for the oil, evaporating a portion of the said diluent at a pressure greater than the vapor pressure of the diluent at the temperature prevailing and the solution of oil and diluent is cooled by the combined refrigerating effect of the cold gas and the evaporation of part of the diluent, withdrawing the refrigerating gas from the chilling operation, refrigerating the gas to a lower temperature than that of the chilling operation and recycling said refrigerating gas back to the chilling operation.

11. The process of claim 8 wherein the solution of wax-containing lubricating oil and liquefied normally gaseous hydrocarbon is prepared at about room temperature and chilled in a single continuous chilling zone to a temperature of about —40° F. by means of a current of inert gas supplied at a temperature of about —40° F.

12. In the process of continuously dewaxing lubricating oils wherein a solution of a waxy lubricating oil and a liquefied normally gaseous hydrocarbon is continuously chilled, the improvement comprising conducting the chilling operation without contacting the solution with supercooled surfaces and without subjecting the solution to sudden reduction of pressure causing flash chilling resulting in formation of wax crystals substantially impossible to remove by filtration, by initially preparing the solution of waxy oil and liquefied normally gaseous hydrocarbon at a temperature sufficient to insure that substantially all wax is dissolved, introducing the solution at the said temperature and substantially without drop in pressure into one end of an elongated contact zone, introducing a cold inert gas cooled to a temperature approximating that desired for the waxy oil solution at the other end of said elongated zone, causing the gas to flow countercurrently and in intimate contact with the said solution in said contact zone, abstracting heat therefrom partly by its direct cooling effect and partly by evaporation of liquefied hydrocarbon gas, withdrawing said gas and hydrocarbon vapors from said contact zone, subjecting them to cooling and returning them to said contact zone, withdrawing cooled waxy oil solution from said contact zone and filtering crystallized wax therefrom.

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