June 25, 1935. B. K. BROWN 2,005,988

DEWAXING WITH NONMISCIBLE REFRIGERANT

Filed March 19, 1932 3 Sheets-Sheet 1

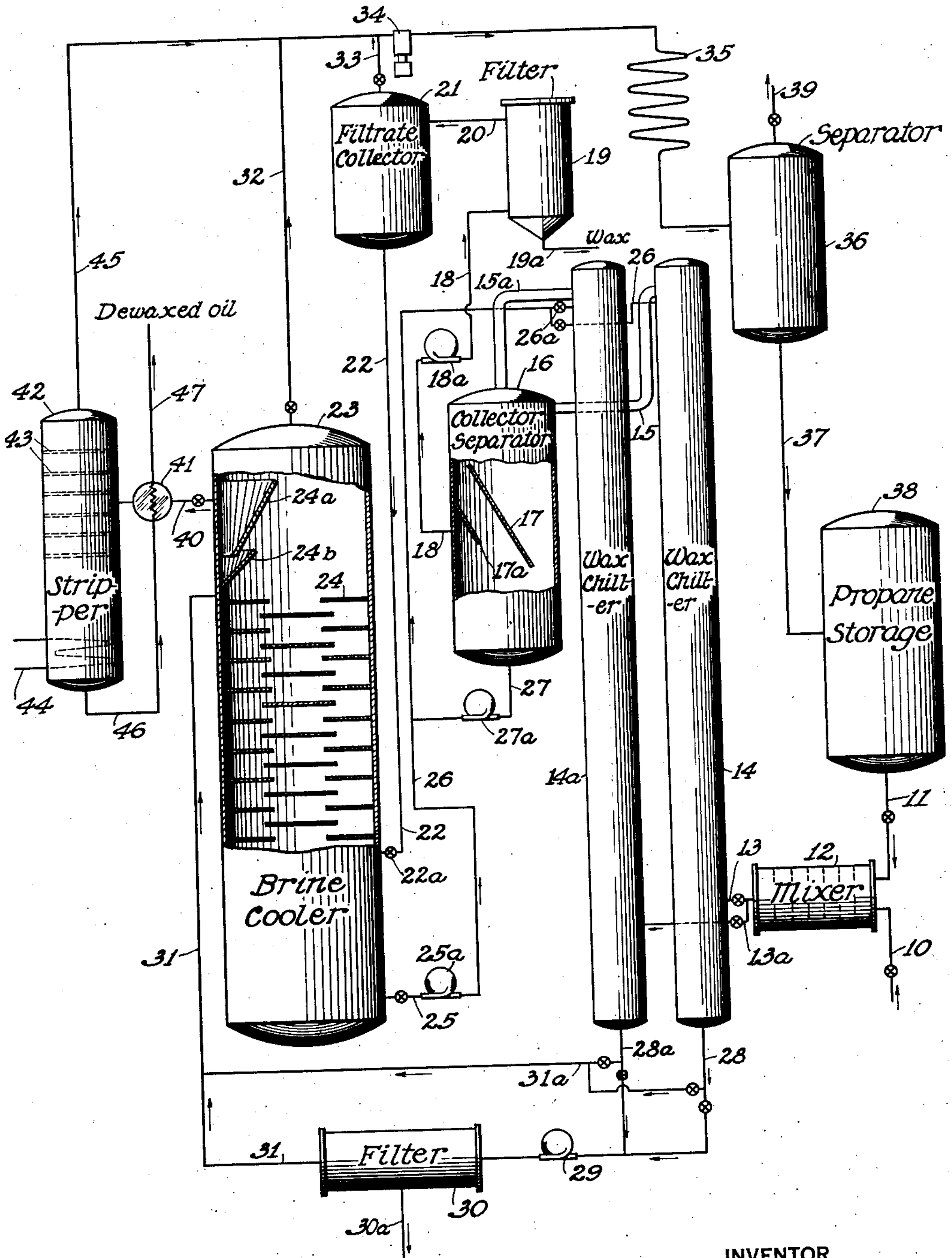

Fig. 1

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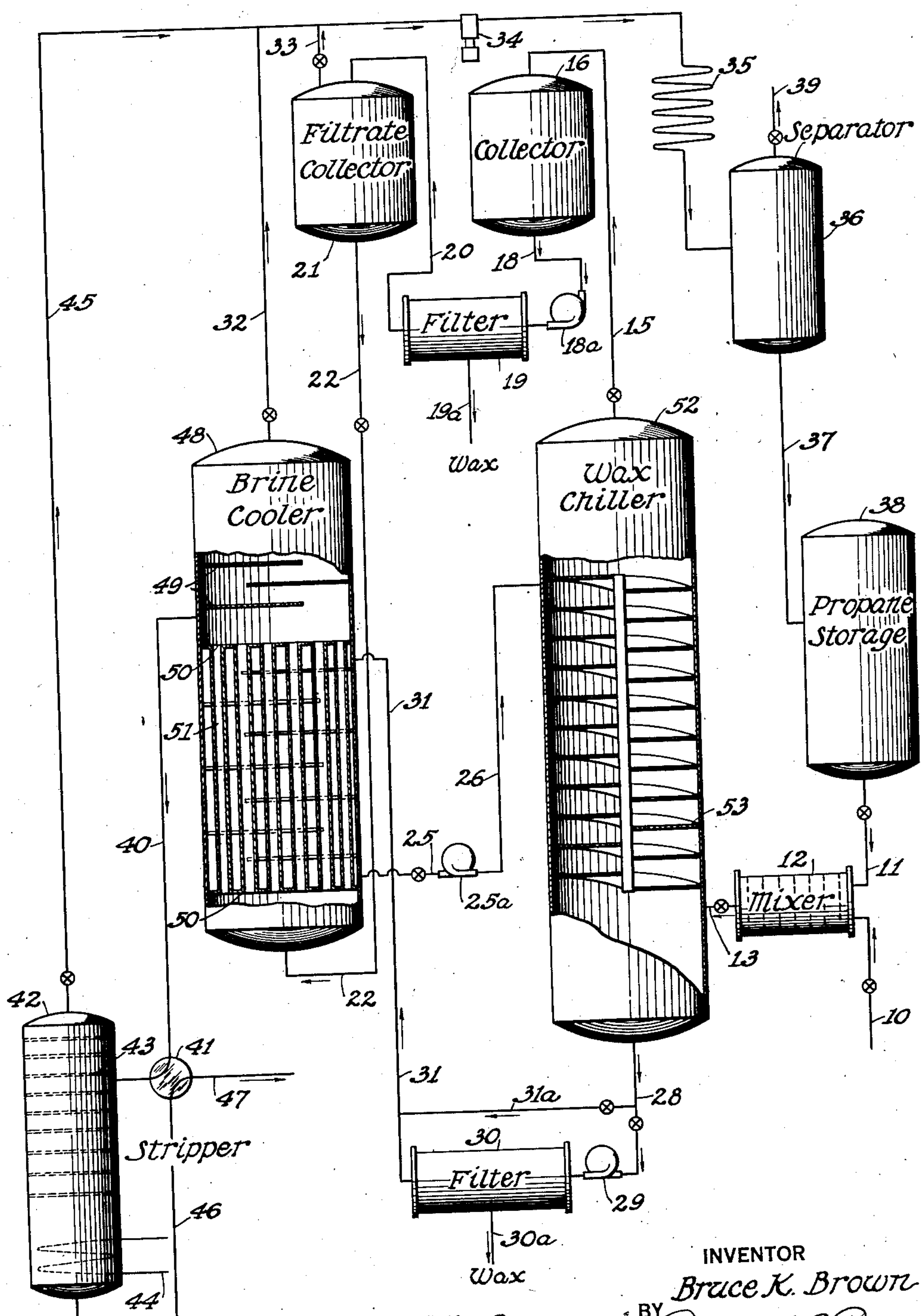

Fig. 2

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3 Sheets-Sheet 3

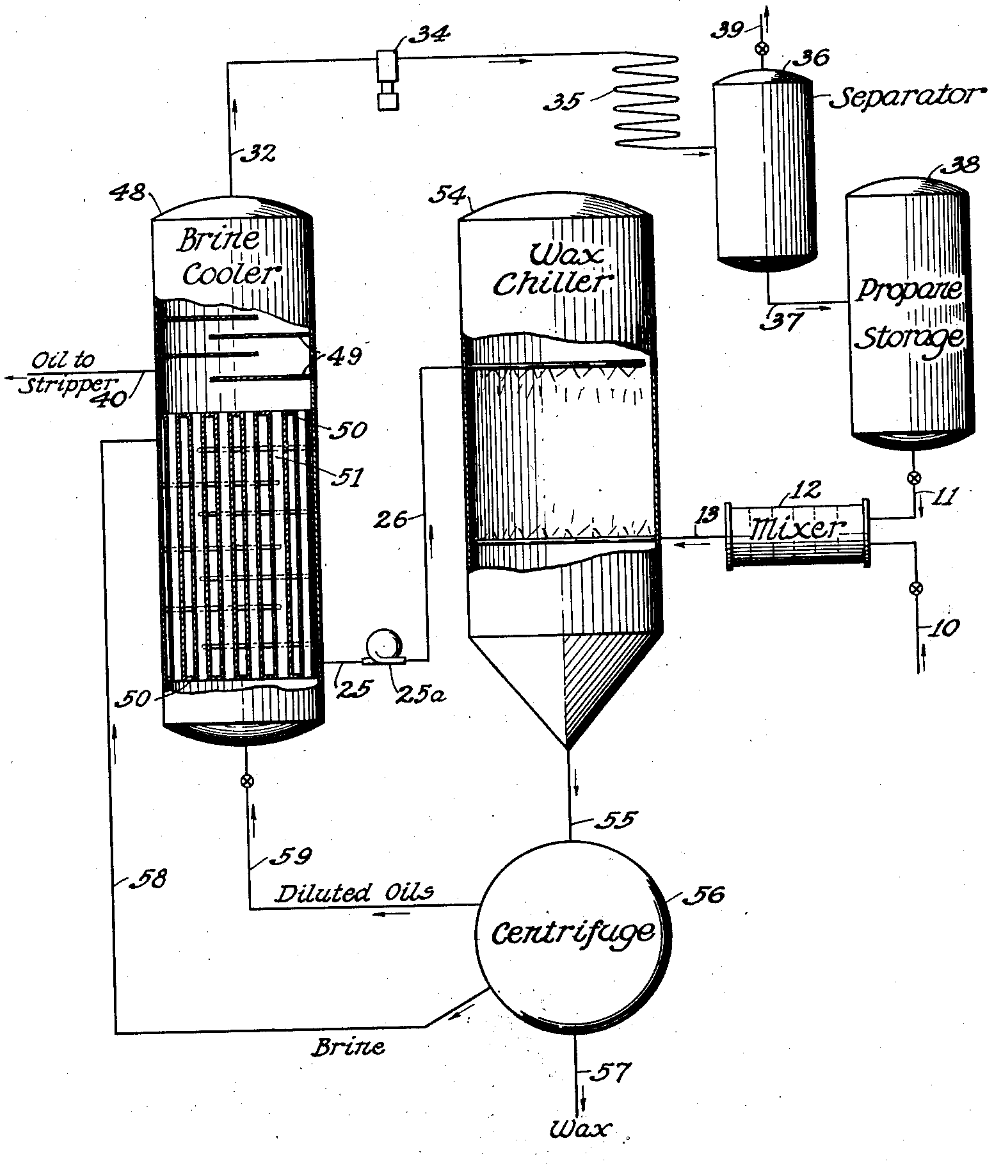

Fig. 3

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DEWAXING WITH NONMISCIBLE REFRIGERANT

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Application March 19, 1932, Serial No. 600,023

8 Claims. (Cl. 196—18)

This invention relates to the separation of wax from oils, and it pertains more particularly to the use of a non-miscible refrigerant, such as brine, for chilling an oil-wax mixture and crystallizing the wax therefrom.

It has been the common practice in refining heavy, wax-bearing mineral oils to dilute said oils with naphtha, to chill the solution for solidifying or precipitating the wax, and to separate the solidified wax from the chilled oil by settling, filtering or centrifuging. Liquefied light hydrocarbon diluents, such as butane and propane, have been found to be remarkably effective as diluents because they reduce the viscosity of the oil much more than other diluents, they bring about an increased difference between the specific gravity of the wax and that of the oil-diluent mixture, and they effect the solidification of wax in crystals which can be readily filtered or otherwise separated from the diluted oil.

The object of my invention is to increase the efficiency of this so-called "propane-dewaxing" system. More particularly my object is to obtain better crystallization, to throw substantially all of the wax out of the solution, and to throw it out in the form of crystals which can be easily and rapidly separated from the diluted oil. A further object is to avoid the loss of diluent in the chilling step so that a constant diluent ratio may be maintained, thereby assuring uniformity of results. A further object is to obtain the advantages of direct refrigeration without sacrificing the advantages incident to the use of liquefied light hydrocarbon diluents.

A further object is to provide a system in which the refrigeration value of chilled oil and liquefied propane may be effectively utilized. At the same time I desire to avoid the indirect transfer of heat to the wax slurry in the chiller because of resulting lowered efficiency and because of the tendency of the wax to accumulate on chilled surfaces. Other objects will be apparent as the following detailed description of my invention proceeds.

In practicing my invention I contact diluted oil directly with a cold, non-miscible refrigerant, such as brine, to effect separation or solidification of wax crystals. I then cool the brine in a separate chamber by flashing diluent from oil in heat exchange relation to the brine.

In the accompanying drawings, which form a part of this specification, I have diagrammatically illustrated three preferred embodiments of my invention:

Figure 1 is a diagrammatic elevation of one form of my improved system.

Figure 2 is a similar view with a different type of brine cooler, and

Figure 3 is a diagrammatic elevation of a system using a centrifuge.

My invention is applicable to the removal of wax from oil generally, and, although I will describe the dewaxing of a heavy petroleum lubricating oil, it should be understood that the invention is not limited thereto. I will describe the dewaxing of an S. A. E. 50 mid-continent petroleum lubricating oil (viscosity about 80 sec. Saybolt at 210° F.) which has been treated with about one pound of sulfuric acid per gallon of oil, but the invention is, of course, applicable to oils from any source, whether acid treated or not. Lighter oils may be more easily dewaxed and will require lesser amounts of diluents.

As my preferred example of a diluent I will describe the use of a commercial propane mixture which consists of about 70% propane and 30% butane. I do not limit myself to any particular diluent, however, and it should be understood that other liquefied normally gaseous hydrocarbons, substitution products thereof or mixtures of hydrocarbons and substitution products, may be used instead of propane and butane. I prefer to use a liquefied, normally gaseous mixture of extremely low viscosity; the diluent in the preferred example will be called "propane".

Wax-bearing oil is conducted from a suitable storage tank (not shown) by pipe **10**, mixed with propane from pipe **11** in mixer **12** and then selectively introduced by pipe **13** or **13a** into wax chiller **14** or **14a**. The wax chillers may consist of tall, cylindrical pipes or narrow tanks designed to withstand pressures of about 150 to 200 lbs. per square inch. The diluted oil-wax mixture is preferably introduced into the chillers at a point about three or four feet from the bottom thereof to leave a space wherein oil may separate from brine, as will be hereinafter described.

In practice, the chiller will be filled with a non-miscible refrigerant, which in the preferred example is calcium chloride brine having a freezing point of about −40° to −50° F. This brine is introduced into the chiller near the top thereof, as will be hereinafter described, and the chilled, diluted oil-wax mixture is floated off of the top of the brine through large conduits **15** and **15a** to collector and separator **16**. A large amount of brine will be carried into the separator with the diluted oil-wax mixture, and I provide inclined baffles 17 and 17*a* to direct the brine away from the outlet for the wax slurry.

The diluted oil-wax slurry is pumped through conduit 18 by means of pump 18*a* to filter 19. The pump is preferably of the sliding vane type so that it will produce a uniform pressure and at the same time will not mash the wax crystals; if the pump produces a pulsating pressure on the filter it may be necessary to insert a pressure stabilizer or air cushion between the pump and filter. The filter is preferably of the closed, leaf type, as exemplified by U. S. Patent 869,372, the filter cake being removed at intervals by reverse flow and withdrawn through wax conduit 19*a*. It should be understood, however, that I may use a continuous filter or, in fact, any filter designed to separate wax from oil.

The filtrate which consists of oil diluted with propane runs from the filter through pipe 20 to filtrate collector 21, thence through conduit 22 and reducing valve 22*a* into brine cooler 23. In brine cooler 23 the pressure is considerably reduced so that a large amount of propane is vaporized and there is a constant evolution of propane vapors. The propane-oil mixture is contacted with brine in cooler 23, as will be hereinafter described, and in order to obtain intimate contact between the diluted oil and the brine I provide baffles 24, which may be of the disc and doughnut type, as shown in the drawings.

In order to maintain a quiescent settling zone at the top of the brine cooler, I provide an inclined baffle 24*a*; the gases are deflected by one side of this baffle so that the liquids on the other side of the baffle may be settled in a quiescent state. An auxiliary inclined baffle 24*b* deflects gases away from the opening at the bottom of inclined baffle 24*a*. In operation, oil with a little brine runs over the top of baffle 24*a* into the quiescent settling zone. Oil is withdrawn from the upper part thereof, and brine settles and is returned to the main portion of the brine cooler by flowing under the lower end of baffle 24*a*, between baffle 24*a* and 24*b*, and thence over the upper end of baffle 24*b*.

Brine from the base of the brine cooler is conducted by pipe 25, pump 25*a* and pipe 26 to the top of wax chillers 14 and 14*a*. Brine from the bottom of separator 16 is withdrawn through pipe 27 and forced by pump 27*a* into conduit 26. Brine from the bottom of the wax chiller is conducted through pipes 28 and 28*a*, pump 29, wax-brine filter 30 and pipe 31 to the upper part of brine cooler 23, wax being removed from the filter through pipe 30*a*. If desired, the filter may be omitted and the brine passed directly through pipes 28 or 28*a* and pipe 31*a* to the brine cooler.

Vapors are removed from the top of the brine cooler through pipe 32 and from filtrate collector by pipe 33, they are compressed by compressor 34, liquefied in condenser 35, separated from air or non-condensibles in separator 36, and returned by pipe 37 to propane storage tank 38, which is designed to withstand pressures of about 150 to 200 pounds per square inch at 100° F. Non-condensible gases are removed from the separator through pipe 39. It should be understood, of course, that suitable pressure and vacuum relief valves, pipe fittings, control valves, insulation, etc. will be used where necessary.

A pipe 40 leads from the upper part of brine cooler 23 through heat exchanger 41 to stripper 42, which is provided with suitable baffle plates 43 and steam coils 44. Propane from the stripper is conducted by pipe 45 to compressor 34, etc. back to the storage tank. The dewaxed oil, when freed from propane, is withdrawn from the bottom of the stripper through pipe 46 and, after passing through heat exchanger 41, it is conveyed by pipe 47 to a suitable storage tank (not shown).

The operation of the system above described is as follows: About four parts of propane are mixed with one part of wax-bearing oil in mixer 12 and introduced into one of the chillers. Since the chiller is full of brine, this diluted oil-wax mixture will be intermingled with the cold brine and will pass upwardly countercurrent thereto. By using this countercurrent principle the diluted oil-wax mixture at the top of the chillers is practically at the temperature of the incoming brine, about −40° F. There is a large difference between the specific gravity of the chilled slurry and that of the brine and I therefore flow the slurry off of the top of the brine through large conduits 15 and 15*a* to collector or brine separator 16. In the wax chillers the liquid to liquid contact insures maximum thermal efficiency, and the chilling of the wax under these conditions brings about a very desirable crystal formation so that the wax may be easily and quickly separated from the oil by filtration.

Baffles 17 and 17*a* prevent brine from being withdrawn with the oil-wax slurry through conduit 18. The brine is withdrawn from the base of the collector-separator 16 through pipe 27 by pump 27*a*, and it is mixed with the brine from the base of the brine cooler 23 and introduced through pipe 26 at the top of the wax chillers. Brine from the base of the wax chillers is returned through wax-brine filter 30 or through pipe 31*a* to wax cooler 23 at a point above baffles 24. The filtrate in collector 21 may be cooled to or maintained at a temperature slightly below −40° F. by the vaporization of part of the propane, the vapors being withdrawn through pipe 23 by suction pump 34. This cold filtrate mixture is passed through reducing valve 22*a* into the base of the brine cooler below baffles 24. Here, again, countercurrent cooling is effected, but this time it is accompanied by considerable agitation due to the vaporization of the propane. The pressure in the brine cooler may be maintained slightly below atmospheric by withdrawing vapors through pipe 32 and suction pump 34. The heat of vaporization of the propane is absorbed from the brine and the brine is thereby cooled to about −40° and returned from the base of the cooler to the top of the wax chiller. A quiescent settling is obtained in the top of the brine cooler as hereinabove explained, so that practically no brine is entrained in the propane which leaves the cooler through pipe 40. Only about one-half of the propane is required for cooling the brine and the remaining propane serves to cut the viscosity of the oil so that it may be easily withdrawn from the brine cooler through pipe 40.

The last traces of propane are stripped from the oil in steam stripper 42, propane vapors being compressed and liquefied as hereinabove described.

I have found that with the diluted oil-wax mixtures and the diluted filtrate, as hereinabove described, a very satisfactory separation can be obtained between the non-miscible and the oil components. It is possible, however, that with some oils a small amount of wax might be carried by the brine from chiller 14 to brine cooler 23, and it is for this reason that I provide a wax-brine filter 30. This filter will not have to handle large volumes of wax and it will cause no trouble; in fact, it may usually be cut out of the system by by-passing the brine through pipe 31a.

I have found that by chilling the wax with brine the entire cooling operation may be accomplished in ten or twenty minutes. The wax crystals may be filtered in about twenty minutes on a leaf filter (building up a cake thickness of five eighths inch) and a filter rate of about 1.5 gallons per square foot per hour may be obtained on the entire cycle. The finished oil has a pour point below 0° F.

In some cases it may be desirable to use a filter aid or precoat of fibrous or cellular substances like infusorial earth to increase filter rates and/or lower the cold test of the finished oil. Precoats may be applied to the filter leaves by spraying or by filtering a small amount of a slurry thereof. Filter aids may be mixed with the incoming oil or added to the diluted oil-wax slurry.

In Figure 2 I have shown an alternative structure which will be described by pointing out its difference from Figure 1. This modification is designed to handle wax slurries wherein there is no tendency for the wax to settle out and therefore the brine trap-out is omitted from the collector 16; it should be understood, however, that the collector will be so positioned that the slurry may flow thereto by gravity from the upper part of the chiller and, if desired, the structure shown in Figure 1 may be employed.

In Figure 2 I employ a different type of brine cooler 48. In the top of this cooler I provide baffle plates 49 to serve as entrainment arresters and in the lower part of this cooler I provide a heat exchange system consisting of headers 50 and vertical tubes 51. The pressure in the cooler is maintained at or below atmospheric by the withdrawal of propane vapors through pipe 32 and suction pump 34. The reduced temperature is obtained as in the previous example, but in this case the brine does not mix directly with the finished oil, and the oil may be continuously withdrawn through pipe 40 from the portion of the cooler which surrounds the vertical tubes.

I prefer to introduce the brine into the space surrounding tubes 51 near the upper header 50, and to cause the brine to follow a zigzag course downwardly to the bottom of this space. The diluted oil may be cooled by partial flashing in the filtrate collector, and it is preferably introduced at the bottom of the cooler, so that it may bubble up through the tubes. A large proportion of the propane will be vaporized, the heat of vaporization being abstracted from the brine, but here again enough propane remains in the oil to allow it to flow freely from the brine chiller to the steam stripper through pipe 40.

Another feature of Figure 2 is the use of a baffled wax chiller tower 52. I may employ a continuous helical baffle with sufficient pitch to obtain the desired velocity (the oil should move through the chiller in about 15 or 20 minutes). In a vertical plane, each section of the baffle is horizontal so that a liquid stream of uniform depth may be directed thereby from one end of the tower to the other. With such a baffle the oil mixture flows from the bottom of the chiller to the top thereof on the under side of the baffle, and the brine flows downwardly countercurrent thereto. This gives a long, liquid to liquid countercurrent contact with minimum agitation and it is desirable if the particular oil has a tendency to emulsify in the brine. In this apparatus the lighter mixture floats on the brine through the entire circuitous path from the bottom to the top of the tower countercurrent to the downwardly moving stream of cold brine. I may, of course, employ baffles of the disk and doughnut type, or baffles that alternate from side to side.

It should be understood that centrifuges may be used instead of filters for separating wax from oil and, in fact, the oil, brine and wax may be separated from each other by a centrifuge. An example of such a system is shown in Figure 3. The mixed oil and propane is introduced into chill chamber 54 and cooled by brine, as in the preceding embodiment. In this case the use of baffles may be avoided and the oil and brine may be simply sprayed into the chill chamber, which may consist simply of an enlarged conduit. The mixture of brine, diluted oil and wax is then withdrawn through pipe 55 to centrifuge 56, where the diluted oil, brine and wax are separated into three different streams. The wax is withdrawn through pipe 57, the brine is introduced by pipe 58 to the portion of brine cooler 48 surrounding the vertical tubes and the diluted oil is introduced by pipe 59 to the lower part of the brine cooler. Propane vapors are withdrawn through pipe 33 by compressor 34, etc. to effect refrigeration, the oil, containing enough propane to flow freely, is withdrawn from the top of the cooler through pipe 40 to a suitable stripper, and the cooled brine is returned by pipe 25, pump 25a, and pipe 26 to wax chiller 54.

While I have described preferred embodiments of my invention it should be understood that I do not limit myself to the details hereinabove described except as defined by the appended claims, which should be construed as broadly as the prior art will permit. I may, for instance, use a wax chiller similar to the brine cooler in Figure 2; this would retain the advantage of conserving the refrigeration value of expanding propane, but it would lose the advantage of direct contact of diluted waxy oil with the non-miscible refrigerant. While I have described calcium chloride brine as a non-miscible heat transferring liquid, it should be understood that other inert, non-miscible fluids, such as other salt solutions, alcohol, glycol, etc. may be used.

I claim:

1. The method of separating wax from a wax-bearing oil, which comprises diluting said oil with a liquefied, normally gaseous diluent, introducing the mixture into a body of cold inert refrigerant liquid, mechanically separating the solidified wax, the inert refrigerant liquid, and the diluted oil respectively from each other, vaporising the diluent from the diluted oil in heat exchange relation to the refrigerant liquid, and returning the refrigerant liquid for contact with further amounts of diluted waxy oil.

2. The method of separating wax from a wax-bearing oil which comprises mixing said oil with propane, chilling said mixture by heat exchange with a non-miscible refrigerant liquid, separating said refrigerant liquid from said diluted oil-wax diluent mixture, separating the wax from said mixture, separating propane from the diluted oil in heat exchange relation to said refrigerant liquid whereby said refrigerant liquid is cooled, and returning said cooled refrigerant liquid for chilling the diluted oil-wax mixture.

3. The method of removing wax from a wax-bearing oil which comprises mixing a liquefied, normally gaseous diluent with said oil, chilling said mixture by direct contact with a non-mis-

cible refrigerant, separating said diluted oil-wax mixture from said refrigerant, separating wax from said mixture, vaporizing the diluent from said oil in heat exchange relation to said refrigerant whereby the heat is absorbed from said refrigerant, and returning said refrigerant to the step of chilling the diluted oil-wax mixture.

4. The method of claim 1 wherein the liquefied normally gaseous diluent is propane.

5. The method of separating wax from a wax-bearing oil, which comprises mixing said oil with propane to form a propane solution, countercurrently passing said propane solution in heat exchange relation with a cold non-miscible refrigerant liquid to cause solidification of the wax, separating the refrigerant liquid from the cold diluted oil-wax mixture, separating wax from said mixture, contacting said wax-free mixture with the non-miscible refrigerant liquid which has been warmed in the heat exchange step whereby said non-miscible refrigerant is again cooled, and returning said cooled refrigerant liquid for chilling further amounts of diluted oil-wax mixture.

6. The method of removing wax from a wax-bearing oil, which comprises diluting said wax-bearing oil with liquefied propane to form a solution of said oil in said propane, countercurrently contacting said solution with a cold non-miscible refrigerant liquid for solidifying the wax, separating the refrigerant liquid from the solidified wax-diluted oil mixture leaving the countercurrent contacting zone adjacent the introduction of cold refrigerant, separating wax from the diluted oil, separating wax from the refrigerant leaving the opposite end of the countercurrent contacting zone, contacting the wax-free refrigerant with the wax-free diluted oil whereby the oil is heated and the refrigerant is cooled, and returning the cooled refrigerant to the countercurrent chilling zone.

7. The method of removing wax from a wax-bearing oil which comprises mixing said oil with a liquefied, normally gaseous diluent, chilling said mixture by direct contact with cold brine, separating the diluted oil, wax and brine respectively, vaporizing the diluted oil in heat exchange relation to the brine whereby said brine is cooled, and returning said cooled brine to chill said dilute wax-bearing oil.

8. The method of separating wax from a wax-bearing oil which comprises mixing said oil with a liquefied diluent, chilling said mixture with cold brine, centrifuging the mixture to separate the wax, brine and diluted oil respectively, reducing the pressure on the diluted oil to cause vaporization of the diluent therefrom, and abstracting the heat of vaporization from said brine whereby the brine is cooled for further use in chilling diluted oil.

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