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2 Sheets-Sheet 1

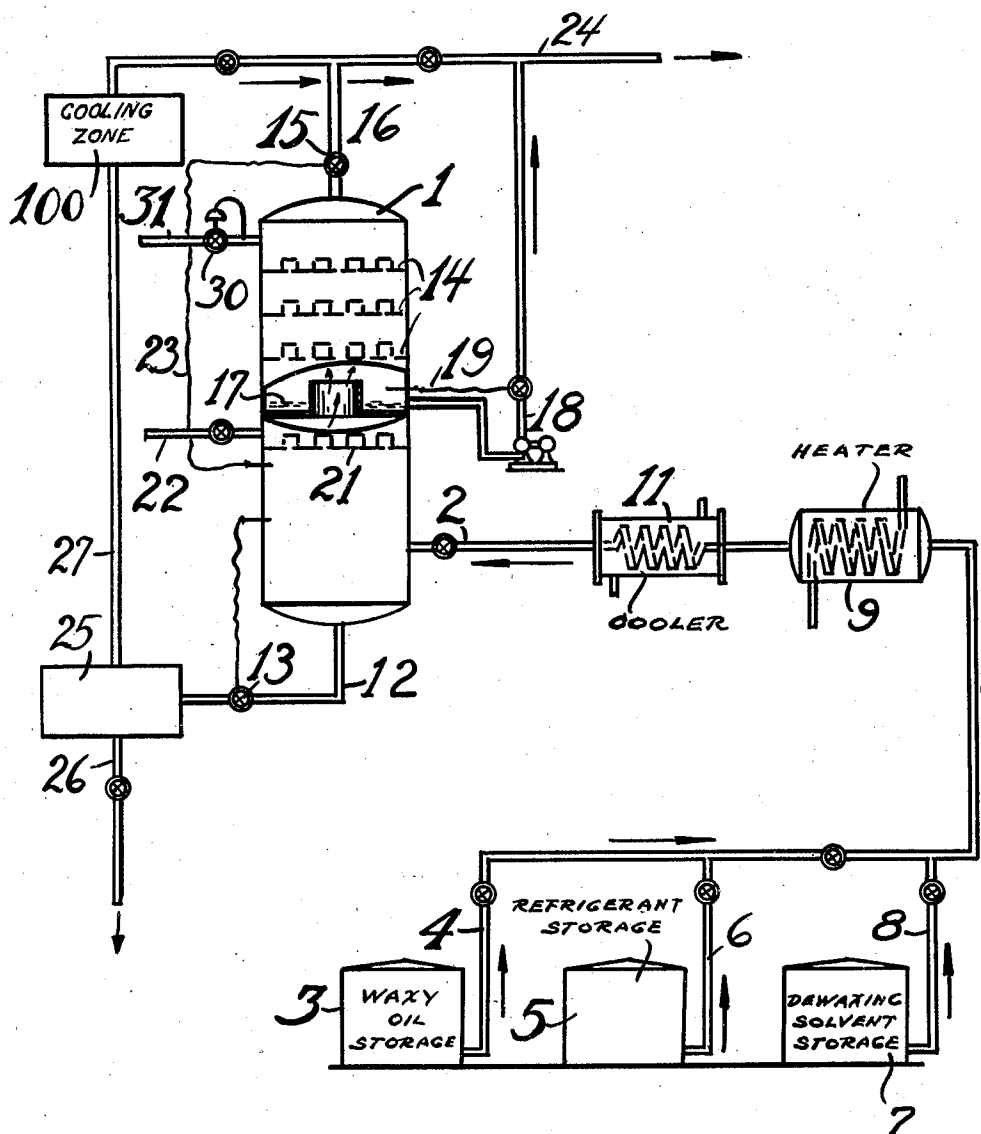


FIG.-1

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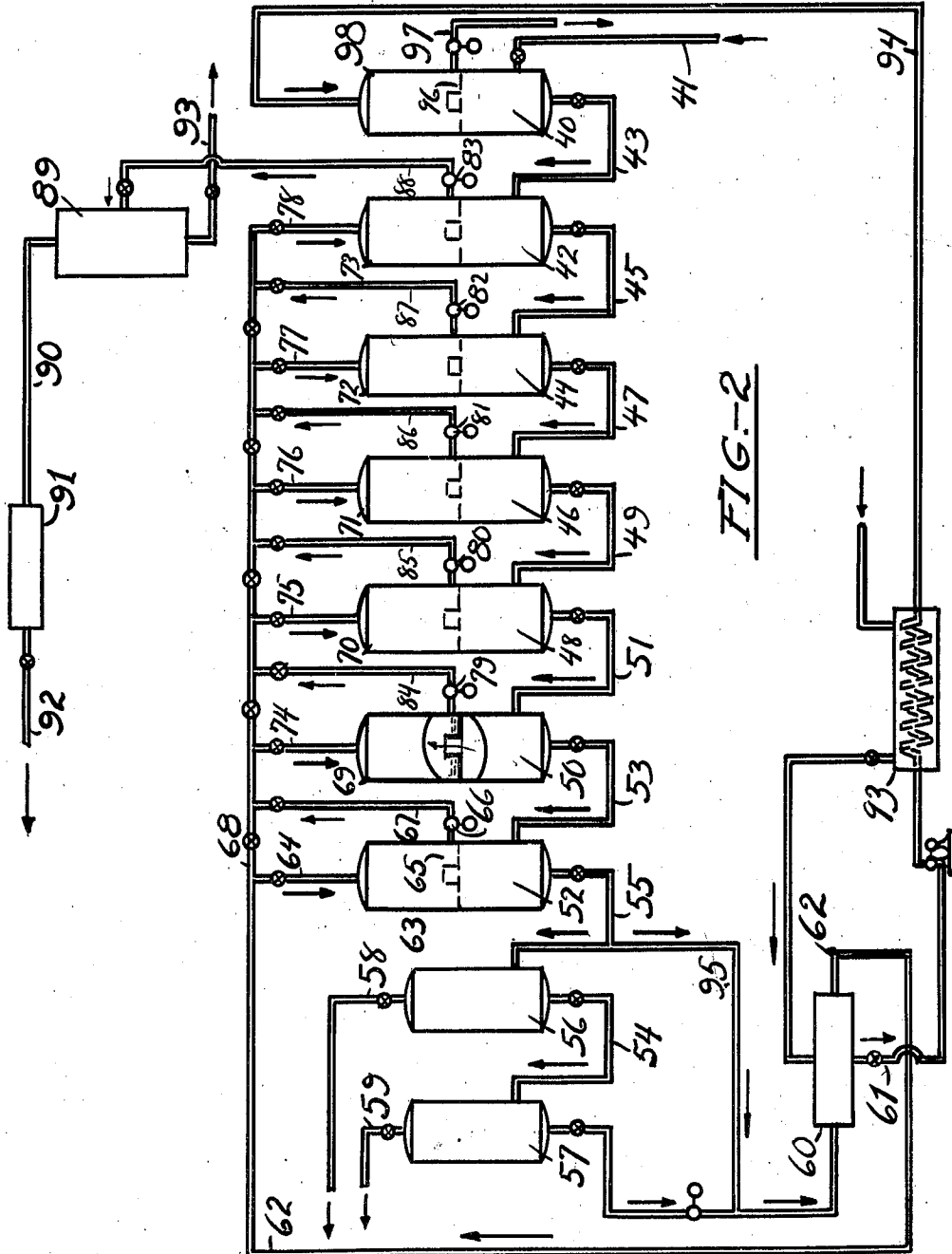
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UNITED STATES PATENT OFFICE

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REFINING OF MINERAL OILS

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10 Claims. (Cl. 62—170)

The present invention relates to the refining of mineral oils and is particularly concerned with the removal of waxy constituents therefrom. The invention is especially directed to an improved process and apparatus for dewaxing waxy petroleum distillates by which it is possible to secure optimum heat transfer and thus materially improve operating efficiencies. In accordance with the present invention, the waxy distillate is mixed with a quantity of a refrigerant and the mixture introduced into a chilling stage wherein the waxy distillate is cooled by evaporation of the refrigerant in a chilling zone of the chilling stage. The vaporized refrigerant passes upwardly from the chilling zone through the chilling stage, and is condensed in an upper or condensing zone of the chilling stage by contact with cold dewaxed distillate, thus raising the temperature of the dewaxed distillate.

It is well known in the art to remove waxy constituents from oils particularly from petroleum oils by various processes. The processes, in general, secure separation of the waxy constituents by chilling the waxy distillate to a temperature at which the waxy constituents crystallize and thereafter filtering the chilled distillate to remove the precipitated waxy constituents. The chilling operation may be carried out by indirect methods, as for example, by passing a refrigerant through either internal or external chilling tubes. This latter chilling operation is not entirely satisfactory due to the difficulty of preventing waxy constituents from precipitating on the tubes or due to the difficulty of securing uniform chilling of the entire mass of waxy distillate. Non-uniform chilling of the waxy distillate produces waxy crystals containing a relatively large amount of oil and also produces crystalline structures which are not readily removed by filtering, centrifuging, or the like. These disadvantages are overcome to a large extent by auto-refrigeration in which a refrigerant of the character of sulfur dioxide, liquefied normally gaseous hydrocarbons, is evaporated in direct contact with the distillate being chilled. These direct cooling methods while producing satisfactory results, with respect to the waxy crystalline structure, are relatively expensive, due to the rather large heat losses. This is due primarily to the difficulty of securing adequate heat transfer between the chilled dewaxed distillate and the waxy distillate being chilled. Heat exchange between the chilled dewaxed oil and the waxy oil being chilled is not readily secured by conventional means, due to plugging

of the heat exchanging equipment by the waxy constituents which materially decrease heat transfer rates and increase pumping difficulties. The usual practice, thus, has been to remove the vaporized refrigerant, such as propane, from the respective chilling stages, to condense the same in suitable condensing equipment and to recycle the liquefied propane to the system. This is not entirely satisfactory since considerable heat losses occur which increase the cost of the dewaxing operation.

I have now discovered a process by which it is possible to more economically and efficiently remove waxy constituents from wax-containing oils. The process of my invention may be readily understood by reference to the attached drawings illustrating modifications of the same.

The drawings illustrate a multi-stage chilling system. It is to be understood that any number of stages arranged in any desirable manner may be employed. Figure 1 illustrates in detail an individual chilling stage, while Figure 2 illustrated a series of chilling stages arranged in accordance with the preferred modification of the present invention. Referring specifically to Figure 1, a waxy solution, which for the purposes of illustration is taken to be a waxy petroleum lubricating oil distillate withdrawn from waxy oil storage 3 by means of line 4, is mixed with a suitable refrigerant withdrawn from refrigerant storage 5 by means of line 6 and then introduced into chilling stage 1 by means of feed line 2. For the purpose of description, it is assumed that the refrigerant is liquefied propane. If desirable, a dewaxing solvent may be withdrawn from dewaxing solvent storage 7 and introduced into the mixture by means of line 8. The waxy solution is preferably heated in heater 9 to secure complete miscibility between the respective constituents and then cooled in cooler 11 before introduction into initial chilling stage 1 by means of line 2 as described. Temperature and pressure conditions are adjusted in chilling stage 1 so that a predetermined quantity of propane will be vaporized from the waxy solution in the chilling zone maintained in the bottom of chilling stage 1. Thus, by controlling the amount of vaporization, the extent to which the waxy distillate is chilled may be readily controlled. The chilled waxy distillate is withdrawn from chilling stage 1 and introduced into filtering or centrifuging plant 25 by means of line 12. The rate of withdrawal and the liquid level maintained in the bottom of chiller 1 may be readily adjusted by a float and control valve arrangement

13. The waxy constituents are separated from the chilled distillate in filter 25, removed by means of line 26, and handled in any desirable manner. The cold dewaxed oil is withdrawn from filter 25 by means of line 27. At least a portion of the chilled dewaxed oil is further cooled in zone 100 and introduced into condensing zone 14 of chilling stage 1 by means of line 16 wherein the chilled dewaxed oil counter-currently contacts upflowing vapors vaporized from the chilling zone in a manner to condense the same. Condensing zone 14 comprises a suitable number of bubble cap plates or equivalent means adapted to secure efficient contact between the upflowing vapors and the downflowing cold dewaxed oil. The amount of chilled dewaxed oil introduced into stage 1 by means of line 16 is controlled by control valve 15 which may be regulated by a thermostat arrangement 23. The cold dewaxed oil solution distributes itself on the distributing plates in the condensing zone and flows downwardly from plate to plate contacting and condensing the upflowing propane vapor. The cold dewaxed oil solution containing the condensed propane is collected in reservoir 17 and withdrawn by means of line 18. The rate of withdrawal of the dewaxed oil solution is controlled by a liquid level control and a control valve arrangement 19. The dewaxed oil solution withdrawn by means of line 18 is mixed with any dewaxed oil not introduced into the condensing zone of stage 1, withdrawn by means of line 24 and handled in a manner to remove the propane from the oil. A preferred arrangement with respect to stage 1 is to maintain a waxy oil entrainment section 21 immediately below reservoir 17 so as to remove from the vaporized propane any entrained waxy oil constituents. If this operation be employed, it is desirable to introduce a cold propane wash on the entrainment section by means of line 22. Another desirable modification of the present invention is to control the temperature in the chilling stage by means of a temperature valve control means 23 which adjusts the quantity of cold dewaxed oil solution admitted into the condensing section. Line 24 permits the by-passing of cold dewaxed oil solution around the chilling stage. Removal of any uncondensed propane or extraneous non-condensable gases may be automatically controlled by a back pressure release control valve 30 which will not permit building up of undue pressure on chilling stage 1. The gases removed by means of line 31 are passed to suitable propane condensing equipment. It is to be understood that stage 1 may be one of several stages in which case the chilled waxy distillate removed by means of line 12 may be passed to a succeeding chilling stage providing stage 1 does not constitute the final chilling stage. The dewaxed oil removed by means of line 24 likewise may be passed to a preceding chilling stage providing stage 1 does not constitute the initial chilling stage. All stages would be operated in a manner similar to the operation described with respect to stage 1.

Figure 2 illustrates the process of the present invention when the dewaxing operation is conducted by means of a series of chilling stages. It is to be understood that the modifications described in Figure 1, with respect to the handling of the waxy feed, the dewaxed oil solution, and the like, may likewise be employed. The waxy solution, comprising the waxy oil and the refrigerant which for the purpose of the descrip-

tion is taken to be propane, is introduced into initial dewaxing chilling stage 40 by means of line 41. It is to be understood that the feed solution may be previously handled in a manner to secure complete miscibility of the respective constituents. Temperature and pressure conditions are adjusted in stage 40 to secure the vaporization of the desired amount of propane in order to cool the waxy oil the desired extent. The partially chilled waxy mixture is then passed to stages 42, 44, 46, 48, 50, and 52 by means of lines 43, 45, 47, 49, 51 and 53 respectively. The liquid levels of the chilled waxy solutions in the bottoms of the respective chillers is preferably controlled with liquid level control adjustments as described with respect to Figure 1. The waxy solution chilled to a desirable temperature is withdrawn from stage 52 by means of line 55 and at least a portion of the same introduced into one or more final chilling units 56 and 57 in which the temperature of the waxy solution is further reduced by evaporation of propane. The propane vapors removed in these final chillers are not condensed by direct exchange with dewaxed oil as in the preceding stages, but are passed to compressing units by means of lines 58 and 59. The compressed and condensed propane then may be recycled or returned to storage.

The waxy solution chilled to a desirable dewaxing temperature is withdrawn from final chiller 57 by means of line 64 and is pumped to filter unit 60 in which the waxy constituents are separated from the oil. Under certain operations, the chilled waxy solution withdrawn from stage 52 by means of line 55 may be passed directly to filter 60 by means of line 95. The waxy constituents are removed from filter 60 by means of line 61, while the cold dewaxed oil solution is returned to the dewaxing system by means of line 62.

The cold slurry of waxy constituents removed from filter 60 by means of line 61 may be heated and the propane recovered in conventional manner. Preferably, however, the cold wax-propane slurry is introduced into an exchanger 93 in which propane may be cooled and used as wash in filter 60. The waxy constituents are thereby partially warmed after removal from the filter and are returned by means of line 94 to the condensing zone 98 of chiller 40. The cold liquid waxy constituents flow downwardly through the condensing zone of stage 40 and condense vaporized propane rising from the waxy charge solution in the chilling zone of chiller 40. These waxy constituents are not mixed with the waxy oil charge but collect in reservoir 96 and are withdrawn by pump 97 for separation of the propane and wax by distillation in a known manner.

The cold dewaxed oil removed from filter 60 by means of line 62 is introduced into condensing zone 63 of chiller 52 by means of line 64. This oil flows downwardly through the condensing zone, condenses upflowing propane vaporized from the waxy distillate in the lower zone of chiller 52 and collects in reservoir 65. The cold dewaxed distillate partially warmed by the heat of condensation of the propane is removed from reservoir 65 by means of pump 66 and line 67. If desirable, in order to maintain the optimum temperature in stage 52, a portion of the dewaxed oil may by-pass chiller 52 by means of line 68. In a similar manner the dewaxed oil is introduced into condensing zones 69, 70, 71, 72, and 73 of chillers 50, 48, 46, 44, and 42, respectively

by means of lines 74, 75, 76, 77, and 78, respectively. The dewaxed oil solution is withdrawn from stages 50, 48, 46, 44, and 42 at progressively higher temperatures by means of pumps 79, 80, 81, 82, and 83 respectively in lines 84, 85, 86, 87, and 88, respectively. The oil is circulated in chilling stages 52, 50, 48, 46, 44, and 42, with respect to the propane, as described with respect to chillers 52 and 50. The relatively warm solution of dewaxed oil is withdrawn from chilling unit 42 by means of line 88 and passed to distillation unit 89 in which the propane is removed by means of line 90, condensed in condensing unit 91 and recycled to the system by means of line 92. The dewaxed oil is withdrawn from 89 by means of line 93 and handled in any manner desirable. If desired, the warm solution withdrawn from chilling unit 42 by means of line 88 may be treated with acid and clay prior to removal of the propane or after removal of a part thereof. It is to be understood that the quantity of the oil introduced into the respective condensing zone may be adjusted by a temperature control arrangement so as to secure the desired temperature in the respective stages. In a similar manner, the level of the dewaxed solution in the respective reservoirs of the chillers may be controlled by a liquid level pump valve control.

The process of the present invention may widely vary. Although the method of contacting may be applied in a single chilling stage unit, the invention is particularly applicable in a dewaxing operation comprising a series of chilling stages. The number of stages is preferably at least four. The structure of the stages will depend, to a large extent, upon the oil being dewaxed, the particular refrigerant being used, the type of waxy constituents to be removed, and the temperature range over which it is desired to cool the waxy distillate in the particular stage. In general, the chilling stage should be so designed that the waxy oil is preferably chilled not more than about 20° F. in each stage throughout the critical range between about 80° F. and 0° F. The reservoir comprising a flat plate and a circular chimney in the center thereof should preferably be at a point above the center section of the chiller and not higher than above the middle third of the chiller. In order to secure desirable results, it is preferred to maintain the entrainment section spaced immediately below the dewaxed oil reservoir. The condensing zone should be designed to secure complete contact between the dewaxed oil and the upflowing refrigerant. In general, it is preferred to control the temperature of the chiller by the amount of dewaxed oil introduced into the condenser section. However, under certain operations, it is very desirable to introduce the entire quantity of the dewaxed oil into the respective chillers. This is preferably secured by automatic control.

Although the process of the present invention may be readily applied when using any refrigerant whose vapors are readily soluble in mineral oils, it is particularly applicable when using liquefied normally gaseous hydrocarbons as refrigerant, particularly when using liquefied propane.

In order to further illustrate the present invention, the following example is given which should not be construed as limiting the same in any manner whatsoever:

EXAMPLE

A waxy lubricating petroleum oil distillate was passed through a seven stage chilling unit in the manner described. The dewaxed oil at a tem-

perature of -50° F., after removal from the filters, was countercurrently passed, with respect to the waxy solution, through the chillers in accordance with the present invention. The temperature of the waxy oil and the dewaxed oil withdrawn from the respective chillers was as follows:

Table 1

	Waxy oil	Dewaxed oil
	° F.	° F.
Charge.....	85	-----
Chiller 1.....	71	-----
Chiller 2.....	63	67
Chiller 3.....	63	62
Chiller 4.....	55	54
Chiller 5.....	40	39
Chiller 6.....	20	-----
Chiller 7.....	0	-----
Final chiller.....	-50	-----
Filters.....	-----	-50

The ratio of propane to oil at the various stages was as follows:

Table 2

	Volume ratio of propane to waxy oil	Volume ratio of propane to dewaxed oil
Warm waxy solution to chiller 1.....	5.3:1	-----
Waxy solution from chiller 5 to chiller 6.....	3.7:1	-----
Waxy solution from chiller 7 to final chillers.....	3.1:1	-----
Waxy solution to filters.....	2.5:1	-----
Cold dewaxed solution to chiller 7.....	-----	3.2:1
Warm dewaxed solution to propane recovery plant.....	-----	5:1

The process of the present invention is not to be limited by any theory or mode of operation, but only in and by the following claims in which it is desired to claim all novelty in so far as the prior arts permits.

I claim:

1. Process for the removal of waxy constituents from petroleum oils comprising mixing a refrigerant with a wax-containing feed oil, passing the mixture into an initial dewaxing stage, chilling the mixture by vaporizing refrigerant therefrom, withdrawing the chilled mixture and passing the same to a succeeding dewaxing stage in which the waxy oil is further chilled in the manner described with respect to said initial stage, removing the chilled waxy oil and separating the waxy constituents therefrom, further chilling the dewaxed oil and countercurrently flowing the further chilled dewaxed oil through the chillers in a manner in which the dewaxed oil contacts the vaporized refrigerant and condenses the same, removing the dewaxed oil containing the refrigerant from the initial stage and subjecting the same to conditions to remove the refrigerant, condensing said refrigerant and recycling the same to the initial stage with fresh feed oil.

2. Process in accordance with claim 1 in which said refrigerant is a liquefied normally gaseous hydrocarbon.

3. Process in accordance with claim 1 in which said refrigerant is propane.

4. Improved chiller comprising a vessel consisting of a chilling zone and a condensing zone maintained in the upper section of said chiller, means for introducing a waxy solution containing a refrigerant into said chilling zone, means for controlling the temperature and pressure conditions in said chilling zone whereby controlled

vaporization of the refrigerant is secured, means for chilling and introducing cold dewaxed oil into the condensing zone of said vessel, means for passing said vaporized refrigerant upwardly into said condensing zone, means for removing said dewaxed oil solution from said vessel without allowing it to flow into said chilling zone.

5. Apparatus in accordance with claim 4 in which said chiller is provided with a means whereby the amount of cold dewaxed oil introduced into said condensing zone is adjusted by the temperature in said chilling zone.

6. Process for the removal of waxy constituents from waxy petroleum oil comprising introducing a refrigerant into a waxy feed petroleum oil, subjecting said petroleum oil in a chiller to temperature and pressure conditions whereby a portion of the refrigerant is vaporized in a chilling zone, contacting the vaporized portions of the refrigerant with chilled previously dewaxed oil in a condensing zone maintained in the top of said chiller, whereby the refrigerant is chilled and condensed in the chiller, withdrawing the dewaxed oil containing condensed refrigerant, subjecting it to conditions to remove the refrigerant, condensing the refrigerant and recycling the same with feed oil.

7. Process in accordance with claim 6 in which the refrigerant is propane.

8. Process for the removal of waxy constituents from a mineral oil containing the same, comprising adding to a wax-containing feed oil a refrigerant, passing the mixture through a plurality of chilling stages under conditions whereby the oil is chilled to a temperature at which the waxy constituents precipitate in the successive stages by the vaporization of refrigerant therefrom, removing the chilled waxy oil from the final chilling stage and separating the precipitated waxy constituents therefrom, further chilling the dewaxed oil then contacting the further chilled dewaxed oil with said vaporized refrigerant under conditions to condense refrigerant, removing the dewaxed oil containing condensed refrigerant and separating the refrigerant therefrom.

9. Process in accordance with claim 8, in which the condensed refrigerant removed from the dewaxed oil containing the same is recycled with fresh feed to the initial stage.

10. Process in accordance with claim 8, in which said refrigerant comprises a liquefied normally gaseous hydrocarbon.

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