



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 036 460
A1

EUROPEAN PATENT APPLICATION

Application number: **80300885.3**

Int. Cl.³: **C 10 G 73/32**

Date of filing: **21.03.80**

Date of publication of application: **30.09.81**
Bulletin 81/39

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Designated Contracting States: **DE FR GB IT NL**

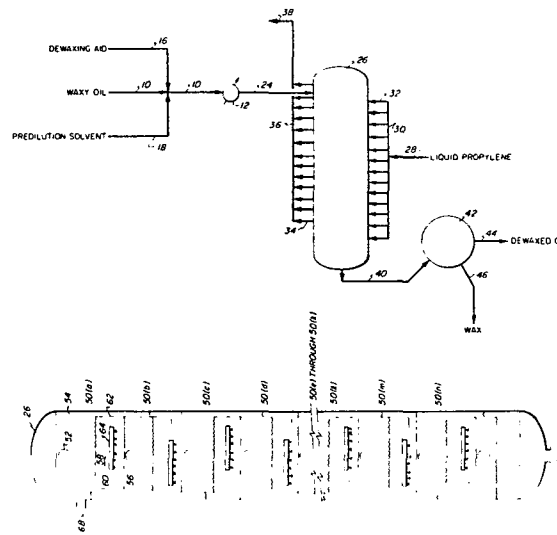
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A continuous process for dewaxing waxy oil using dewaxing solvent and auto-refrigerant, and apparatus therefor.

A continuous solvent dewaxing process wherein a waxy oil (10) is prediluted (18) with a non-autorefrigerative solvent, e.g. ketone, and then passed (24), at a temperature above its cloud point to the top of a chilling zone (26), which is an autorefrigerant chilling zone operating on a continuous basis. The chilling zone (26) comprises a vertical, multi-staged tower, operating at substantially constant pressure. In this chilling zone, wax is precipitated from the oil to form a waxy slurry and the soformed slurry is further chilled down to the wax filtration temperature by stage-wise contact with liquid propylene (28) or other autorefrigerant which is injected into the liquid layer (58, Fig. 2) in each of a plurality of said stages and evaporated therein so as to cool the waxy slurry at an average rate of between about 0.06 to 11.12 °C per minute with an average temperature drop across each stage of 1.11 to 11.12 °C. Some of the propylene remains in the oil which serves to further dilute and reduce the viscosity of the slurry, and the vaporized propylene (34) in each stage exits therefrom (52, Fig. 2) without contacting liquid at least in more elevated stages. The dewaxed oil containing slurry may then be fed (40) directly to wax filters (42) without having to pass through scraped-surface chillers and filter feed drum.

In one type of embodiment, the non-autorefrigerative solvent is employed cold so as to partially solvent dewax

the waxy oil to a temperature within of from about 16.65 to 61.2 °C of the final wax filtration temperature before being contacted with autorefrigerant in the autorefrigerative chilling zone (26) to be chilled down to the desired wax filtration temperature.



EP 0 036 460 A1

0036460

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Ref: US 974070/974072

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A Continuous Process for Dewaxing Waxy Oil Using Dewaxing
Solvent and Auto-Refrigerant, and Apparatus Therefor

The present invention relates to a continuous process for dewaxing waxy oil using dewaxing solvent and autorefrigerant, and apparatus therefor.

More particularly, one type of embodiment of this invention relates to a continuous, solvent dewaxing process and apparatus wherein a waxy oil is prediluted with a non-autorefrigerative dewaxing solvent, with the prediluted oil, at a temperature above its cloud point, then being fed to a chilling zone comprising a vertical, staged tower operating continuously at essentially constant pressure. In the chilling zone wax is precipitated from the oil to form a waxy slurry and the so-formed slurry is further cooled down to wax filtration temperature by contact with a liquid autorefrigerant injected into a plurality of said stages, said liquid autorefrigerant evaporating in each of said stages so as to maintain an average slurry cooling rate of from 0.1 to 20°F (0.056 to 11.12°C) per minute and an average temperature drop per stage of from about 2 to 20°F (1.11 to 11.12°C). The dewaxed oil-containing slurry is then fed to wax filters. This process is particularly useful for dewaxing wax-containing lubricating oil fractions and the like.

In another type of embodiment, this invention relates to a continuous, combination non-autorefrigerant/autorefrigerant solvent dewaxing process employing two chilling zones wherein a majority of the wax is precipitated in a first chilling zone in the presence of a non-autorefrigerant dewaxing solvent to form a waxy slurry which is then fed directly to a second chilling zone comprising a vertical, staged tower operating continuously at essentially constant pressure. In ————— 7

1 the second chilling zone the slurry is cooled down to wax
2 filtration temperature and additional wax is precipitated
3 from the oil by contact with a liquid autorefrigerant injected
4 into a plurality of said stages, as previously described.

5 2. Description of the Prior Art

6 It is well known in the art to dewax wax-containing
7 hydrocarbon oils, particularly the lube oil fractions of
8 petroleum oil, in order to remove at least a portion of the
9 wax therefrom to obtain a dewaxed oil of reduced cloud and
10 pour points. The most common method of removing the wax or
11 waxy constituents from waxy hydrocarbon oils is via the use
12 of various solvent dewaxing processes. In solvent dewaxing
13 processes the temperature of the wax-containing oil is low-
14 ered sufficiently to precipitate the wax therefrom as solid
15 crystals of wax. At the same time, solvents are added to
16 the waxy oil in order to improve the fluidity and reduce the
17 viscosity thereof so that various filtration or centrifuga-
18 tion processes can be used to separate the solid particles
19 of the wax from the dewaxed oil. Strong wax antisolvents
20 (weak oil solvents) such as MEK are often added to decrease
21 wax solubility in the oil/solvent mixture while strong oil
22 solvents (weak wax antisolvents) such as MIBK or toluene are
23 used to modify the solubility characteristics of the solvent
24 so as to allow wax precipitation, while at the same time
25 avoiding oil immiscibility at wax separation temperatures.
26 Solvent dewaxing processes produce what is known as a pour-
27 filter temperature spread. This is the temperature differ-
28 ential between the wax filtering temperature and the pour
29 point of the dewaxed oil. This pour-filter temperature
30 spread is greater when more non-polar hydrocarbon solvents
31 are used than with more polar solvents such as ketones. Thus,
32 an autorefrigerant dewaxing process employing propane can
33 produce a pour-filter spread of 40°F, which means that
34 the wax filtration must be done at -40°F in order to pro-
35 duce a dewaxed oil having a pour point of 0°F. When ketones
36 or mixtures of ketone and aromatic solvents are used, the

1 pour-filter spread may range from 0°F to 20°F depending
2 on the oil and solvent used.

3 Both ketone and autorefrigerant dewaxing processes
4 have certain advantages and disadvantages. Thus, although
5 ketone dewaxing processes result in a lower pour-filter
6 spread at the wax filtration temperature and although larger
7 wax crystals can be grown in a ketone environment than in an
8 autorefrigerant environment without dewaxing aid, ketones
9 are relatively non-volatile compared to autorefrigerants,
10 and, therefore, chilling of the solvent/oil mixture must be
11 accomplished by either indirect means or by mixing cold
12 ketone solvent with the oil. In the latter case, practical
13 considerations limit the amount and temperature of cold
14 ketone solvent that can be added and the temperature to which
15 the solvent/oil mixture can be cooled. Therefore, some
16 means of indirectly chilling the waxy slurry following the
17 addition of solvent is required in all ketone dewaxing pro-
18 cesses in order to bring the slurry down to the required
19 wax filtration temperature. The most common method of in-
20 direct chilling is via the use of scraped surface chillers
21 which are expensive and difficult to maintain. Also, the
22 scraped surface chillers tend to damage the wax crystals by
23 the shearing action of the scraper blades.

24 Conversely, wax crystals grown in an autorefriger-
25 ant environment, such as propane or propylene, are generally
26 small which necessitates the use of costly dewaxing aids in
27 order to achieve good filtration rates, although evaporation
28 of the autorefrigerant enables one to reach the wax filtra-
29 tion temperature without the necessity of employing scraped-
30 surface chillers or indirect heat exchangers following the
31 solvent dewaxing operation. Additionally, it has been found
32 necessary to employ batch chilling in autorefrigerant dewax-
33 ing processes in order to allow a gradual reduction in a
34 pressure. This prevents sudden flashing of the autorefrig-
35 erant at the point of pressure release, thereby avoiding sud-
36 den large temperature drops of the oil slurry (shock chilling),

1 which would result in even smaller wax crystals and concomi-
2 tant slower filter rates of the wax from the dewaxed oil.

3 In some ketone solvent dewaxing processes, the
4 waxy oil and solvent, at a temperature above the cloud point
5 of the oil, are mixed before being cooled. This solution is
6 then cooled at a uniform, slow rate under conditions which
7 avoid agitation of the solution as the wax precipitates out.
8 In another method, ketone dewaxing solvent is added to the
9 oil at several points along a chilling apparatus, but the
10 waxy oil is first chilled without solvent until some wax
11 crystallization has occurred and the mixture has thickened
12 considerably, after which a first increment of solvent, at
13 the temperature of the oil, is introduced in order to main-
14 tain fluidity. Cooling continues, more wax is precipitated
15 out and a second increment of solvent, at the temperature of
16 the mixture, is added to maintain fluidity. This process is
17 repeated until a temperature typically ranging from about
18 30°F to 60°F is reached, at which point an additional amount
19 of solvent at the same temperature as the mixture is added
20 in order to reduce the viscosity of the mixture which is
21 further chilled in scraped-surface chillers to the desired
22 filtration temperature. In these processes, if the solvent
23 is introduced at a temperature lower than that of the oil or
24 oil/solvent mixture, shock chilling occurs resulting in the
25 formation of small and/or acicula shaped wax crystals with
26 attendant poor filter rate.

27 It is now well known that the adverse shock chil-
28 ling effect can be overcome by introducing the waxy oil into
29 an elongated, staged cooling zone or tower at a temperature
30 above its cloud point and incrementally introducing cold
31 dewaxing solvent into said zone, along a plurality of points
32 or stages therein, while maintaining a high degree of agita-
33 tion in said stages, so as to effect substantially instantane-
34 ous mixing of the solvent and wax/oil mixture as they pro-
35 gress through said zone. The basic concept of this commer-
36 cially successful process is disclosed in U.S. Patent No.

1 3,773,650, the disclosures of which are incorporated herein
2 by reference and shall hereinafter be referred to as DILCHILL*
3 dewaxing process.

4 Commercially successful processes employing auto-
5 refrigerative cooling, wherein the waxy oil is mixed with a
6 liquid autorefrigerant which is permitted to evaporate there-
7 by cooling the oil by the latent heat of evaporation, are
8 batch or semi-batch operations. This mixture of liquid auto-
9 refrigerant and oil are introduced into an expansion chamber
10 wherein the pressure is slowly reduced to achieve controlled
11 evaporation of the autorefrigerant and controlled cooling of
12 the oil, thus avoiding the shock chilling which would result
13 if the autorefrigerant were allowed to flash off. However,
14 batch processes are cumbersome, difficult to operate and
15 energy inefficient.

16 A number of attempts have been made to develop a
17 continuous autorefrigerant process for dewaxing oils, includ-
18 ing combinations of ketone/autorefrigerant processes. Thus,
19 U.S. Patent No. 3,549,513 discloses an autorefrigerative
20 batch dewaxing process that is described as continuous but
21 which really operates via the sequential use of a multiple
22 number of batch chillers or expansion chambers. Waxy oil
23 is diluted with an aromatic/ketone solvent mixture and with
24 liquid autorefrigerant and cooling is achieved by controlled
25 evaporation of the autorefrigerant by reducing the pressure
26 in each batch chamber in a manner such that the autorefrigerant
27 evaporates at a controlled rate. U.S. Patent 3,658,688
28 discloses an autorefrigerant dewaxing process wherein a por-
29 tion of the wax is precipitated from the oil in a DILCHILL
30 dewaxing tower wherein the cooling occurs by the injection
31 of cold autorefrigerant into the tower to produce a waxy
32 slurry, followed by autorefrigerative cooling of the slurry
33 in batch chillers. U.S. Patent 2,202,542 suggest a contin-
34 uous autorefrigerant dewaxing process wherein a waxy oil above
35

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1 its cloud point is premixed with warm, liquid propane. This
2 mixture is introduced into a multi-staged cooling tower and
3 liquid CO₂ is injected into each stage out of direct contact
4 with the oil. This patent emphasizes the point that the
5 liquid CO₂ must be introduced into each stage out of direct
6 contact with the oil in the tower in order to avoid shock
7 chilling. However, this is impractical because the vapor
8 loads on the tower would be far in excess of what could be
9 accommodated in a reasonably sized commercial tower. Also,
10 refrigeration requirements are three times those normally
11 needed and conditions for nucleation and growth of wax cry-
12 stals are poor. U.S. Patent 3,720,599 discloses a continuous
13 process for dewaxing a waxy petroleum oil stock wherein the
14 oil is premixed with acetone. This mixture is then introduced
15 into a horizontal, elongated chilling vessel containing a
16 plurality of stages operating at different pressures, with
17 the pressure in each stage controlled by a back pressure
18 regulator on each stage. Liquid autorefrigerant is intro-
19 duced into the stages along the length of the chilling vessel
20 while maintaining a high degree of agitation therein to
21 avoid shock chilling. The autorefrigerant is partially evap-
22 orated in each stage, with the amount of evaporation being
23 controlled by the pressure in each stage. Unfortunately,
24 there are problems which currently preclude commercialization
25 of this process, not the least of which is a practical, effec-
26 tive way of getting the slurry to flow from stage to stage
27 without plugging up the entire apparatus with wax or without
28 multiple transfer pumps which would be expensive and would
29 also tend to destroy the wax crystal structure. Another
30 disadvantage entails the impracticality of providing sep-
31 arately driven agitators for each stage and the mechanical
32 difficulties associated with a common horizontal drive shaft.
33 Additionally, 3,720,599 provides for the nucleation and
34 initial growth of wax to occur in the presence of substantial
35 amounts (i.e., > 25%) of autorefrigerant solvent, which, in
36 the absence of dewaxing aid, has been found to produce wax

1 crystals inferior to those produced when nucleation occurs
2 by chilling in the presence of ketones or ketone/aromatic
3 solvents followed by autorefrigeration. For example, when
4 mixtures of ketone and high percentages (> 40%) of propylene
5 were used in the DILCHILL dewaxing process, a distillate oil/
6 wax slurry was produced which filtered very poorly.

7 It would be an improvement to the art if one could
8 combine both ketone and autorefrigerant solvent dewaxing pro-
9 cesses into a continuous process and in such a manner so as
10 to carefully form the wax nuclei and begin crystal growth in
11 a substantially non-autorefrigerant solvent environment such
12 as ketone, to achieve large, stable, spherical crystals with-
13 out the use of dewaxing aid and then further precipitate
14 additional wax without destroying the spheres via direct con-
15 tact with an evaporating autorefrigerant, thereby avoiding
16 the need for scraped surface chillers following the ketone
17 dewaxing step.

18 SUMMARY OF THE INVENTION

19 What has now been discovered is a continuous autore-
20 frigerant process and apparatus for solvent dewaxing waxy
21 oils which comprise the steps of:

22 (a) prediluting the waxy oil with a non-auto-
23 refrigerant dewaxing solvent to form a mixture of waxy oil
24 and solvent;

25 (b) passing said mixture from step (a), at a temp-
26 erature above its cloud point, into the top of a continuous,
27 autorefrigerative chilling zone which comprises a vertical,
28 elongated, multi-staged tower operating at a constant pres-
29 sure wherein each stage contains a liquid space and a vapor
30 space above the liquid space, each of said vapor spaces also
31 containing means for removal of autorefrigerant vapor there-
32 from;

33 (c) cooling said mixture as it passes down from
34 stage to stage in said chilling zone to precipitate wax from
35 said oil thereby forming a slurry comprising solid particles
36 of wax and a dewaxed oil/solvent solution and further chill-

1 ing the so-formed slurry by contacting same, in said chilling
2 zone, with a liquid autorefrigerant which is introduced under
3 flow rate control conditions into a plurality of the stages
4 in said zone and allowed to evaporate therein so as to
5 achieve an average cooling rate of the slurry in said zone
6 ranging from between about 0.1 to 20°F per minute with an
7 average temperature drop across each stage into which said
8 liquid autorefrigerant is introduced and evaporated ranging
9 from between about 2 to 20°F and wherein the evaporated
10 autorefrigerant is removed from each of said stages into which
11 said liquid autorefrigerant was injected in a manner such
12 that the autorefrigerant vapor formed in any given stage does
13 not pass through the slurry on all of the stages in the tower
14 above said stage; and

15 (d) separating the wax from the slurry to obtain
16 wax and a dewaxed oil solution.

17 In a preferred embodiment of this invention, the
18 prediluted oil will contain a dewaxing aid and will be intro-
19 duced into the top of the chilling zone at a temperature at
20 or near its cloud point and the slurry will be chilled down
21 to the wax filtration temperature in said chilling zone.

22 Alternatively, the invention may be practiced
23 employing cold non-autorefrigerative dewaxing solvent in
24 which case the process comprises the steps of:

25 (a) passing the waxy oil, at a temperature above
26 its cloud point, into a first chilling zone wherein a por-
27 tion of the wax is precipitated from the oil by cooling
28 same in the presence of a non-autorefrigerant dewaxing sol-
29 vent to form a slurry of oil, solvent and solid particles
30 of wax;

31 (b) passing the slurry from the first chilling
32 zone to a second chilling zone which comprises a vertical,
33 multi-staged tower operating at a constant pressure wherein
34 each stage contains a liquid space and a vapor space above
35 the liquid space, each of said vapor spaces also containing
36 means for removal of autorefrigerant vapor therefrom;

1 (c) cooling said slurry produced in said first
2 chilling zone down to wax filtration temperature and precipitating
3 additional wax therefrom in said second chilling
4 zone by contacting same in said second zone with a liquid
5 autorefrigerant which is introduced under flow rate control
6 conditions into a plurality of the stages in said second zone
7 and allowed to evaporate therein so as to achieve an average
8 cooling rate of the slurry in said zone ranging from between
9 about 0.1 to 20°F per minute with an average temperature
10 drop across each stage into which said liquid autorefrigerant
11 is introduced and evaporated ranging from between about 2
12 to 20°F and wherein the evaporated autorefrigerant is removed
13 from each of said stages into which said liquid autorefrigerant
14 was injected in a manner such that the autorefrigerant vapor
15 formed in any given stage does not pass through the slurry on
16 all of the stages in the tower above said stage; and

17 (d) separating the wax from the slurry to obtain
18 wax and a dewaxed oil solution.

19 The "cloud point" of the oil is defined as a temperature
20 at which a cloud or haze of wax crystals first
21 appears when an oil is cooled under prescribed conditions
22 (ASTM D-2500-66 procedure). "Predilution", as the term is
23 used herein, refers to the mixing of solvent and oil prior
24 to cooling the oil to a temperature below its depressed cloud
25 point and comprises, in one embodiment of this invention,
26 prediluting a waxy oil with at least about 0.1 volume of an
27 autorefrigerative predilution solvent per volume of oil
28 stock or at least 0.5 volume of a non-autorefrigerative predilution
29 solvent per volume of oil stock resulting in the
30 depression of the cloud point of the oil stock. If predilution
31 is used, it is preferred to predilute with non-autorefrigerant
32 solvents, especially ketones. Non-autorefrigerant solvent,
33 as the term is used herein, refers to dewaxing solvents,
34 preferably ketones, that are liquid at normal temperature
35 and pressure, but may include the presence of as
36 much as about 30 LV (liquid volume) % of the autorefrigerant

1 used in the second chilling zone, based on the waxy oil feed.

2 The non-autorefrigerative dewaxing solvent
3 employed as predilution and/or first chilling solvent in
4 this invention includes one or more (a) aliphatic ketones
5 having from 3-6 carbon atoms, such as acetone, methyl-ethyl
6 ketone (MEK), methyl-isobutyl ketone (MIBK), methyl-propyl
7 ketone and mixtures thereof, (b) halogenated low molecular
8 weight hydrocarbons such as C_2 - C_4 alkyl chlorides (e.g.,
9 dichloromethane, dichlorethane, methylene chloride) and mix-
10 tures thereof, (c) normal or isoparaffins having 5 to 10
11 carbon atoms, (d) aromatics such as benzene, toluene, xylene,
12 petroleum naphtha and mixtures thereof, and (e) mixtures of
13 any of the foregoing solvents. Non-autorefrigerant solvent
14 as herein defined may include up to 25 LV % of autorefriger-
15 ant solvent, preferably not more than 10 LV % and still more
16 preferably not more than 5 LV %. For example, the ketones are
17 often used in combination with one or more aromatic compounds
18 such as benzene, toluene, xylene and petroleum naphtha. Pre-
19 ferred solvents comprise ketones. Particularly preferred are
20 mixtures of MEK and MIBK or MEK and toluene. Autorefrigerants
21 used in this invention include liquid, normally gaseous C_2 - C_4
22 hydrocarbons such as propane, propylene, ethane, ethylene and
23 mixtures thereof as well as ammonia and normally gaseous flour-
24 carbons such as monochlorodifluoromethane (Freon 22). Autore-
25 frigerative solvent as herein defined may contain up to about
26 50 LV % of non-autorefrigerative solvent, preferably no more
27 than 10 LV % and preferably no more than 2 LV %.

28 The autorefrigerative chilling zone is a vertical,
29 elongated, multi-staged tower operating at a constant pres -
30 sure and in a manner such that the waxy oil and slurry pass
31 down from stage to stage of the tower by gravity and cold,
32 liquid autorefrigerant is injected into each stage of the
33 tower wherein it contacts the warmer oil or slurry and cools
34 same via autorefrigerative evaporation. At least a portion
35 of the cold, liquid autorefrigerant immediately evaporates on
36 contact with the warmer oil or slurry which results in agi-
37 tation in the area of contact sufficient to achieve sub-

1 stantially instantaneous mixing (i.e., about one second or
2 less of the oil or slurry with the cold liquid autorefriger-
3 ant, thus avoiding the shock chilling effect. As herein-
4 before stated, supra, each stage contains means for re-
5 moving the autorefrigerant vapors therefrom and the slurry
6 flows down from stage to stage in the tower by the action
7 of gravity. The cooled slurry exiting this chilling zone
8 is then passed to means, such as rotary pressure filters,
9 for separating the wax from the dewaxed oil/solvent mixture.

10 In general, this autorefrigerative chilling zone
11 or tower will operate at a constant pressure within the
12 range of from about 0 to 50 psig and more preferably from
13 about 2 to 20 psig. The average chilling rate in the tower
14 is the difference between the temperature of the prediluted
15 oil entering the tower and the temperature of the slurry
16 exiting the tower divided by the residence time of the oil
17 or slurry in the tower and will range from about 0.1 to 20°F/
18 minute and more preferably from about 0.5 to 10°F/minute.
19 This is achieved by controlling the autorefrigerant flow
20 rate into, and oil hold-up in, each stage, rather than by
21 gradually decreasing the pressure in the system as is done
22 in batch chillers. That is, a controlled quantity of autore-
23 frigerant is vaporized in direct contact with controlled
24 quantity of oil or slurry in each stage of the tower. This
25 is accomplished by injecting the liquid autorefrigerant
26 through spray nozzles either submerged in the slurry or above
27 the surface thereof in each stage of the tower under flow
28 rate control conditions. This in turn controls the temp-
29 erature drop for each stage which will range from about 2 to
30 20°F. The stagewise chilling rate then depends on the liquid
31 holdup or residence time for each stage. The autorefrigerant
32 evaporates and cools the oil primarily by its latent heat of
33 vaporization which results in an extremely high heat transfer
34 rate. The autorefrigerant vapor is withdrawn from each stage
35 in a manner so as to avoid vapor overload in the tower. In
36 a preferred embodiment, this is done by separately removing

1 the vapor from the vapor space of each stage directly
2 through and outside of the cooling zone or tower, rather
3 than allowing the vapor to cumulatively pass up through each
4 upper, successive stage, as is disclosed in the prior art.
5 However, under certain circumstances, it may be advantageous
6 to allow the vapor produced in one or more given stages
7 to pass up through the tower or cooling zone through some,
8 but not all, of the stages above said one or more given
9 stages before removing the cumulative vapor from the
10 cooling zone or tower. By way of illustration, it may be
11 advantageous to remove vapor from the zone or tower at every
12 second, third and fourth successive stage. An amount of
13 autorefrigerant is added per stage to give a stagewise temp-
14 erature decrease ranging from 2 to 20°F, and more preferably
15 from 3 to 10°F. Of course, the ultimate temperature to
16 which the slurry is cooled in this tower will depend on the
17 temperature of the prediluted oil as it enters same, the
18 liquid hold-up in each stage, the amount, type and temper-
19 ature of autorefrigerant injected into each stage as well
20 as the pressure in the tower and the number of stages in
21 the tower. Therefore, it is understood, of course, depending
22 on the feed and size of the tower, that it may not always
23 be necessary to inject liquid autorefrigerant into each
24 and every stage of the tower. The cooling zone will, in
25 general, cool and slurry down to a temperature ranging
26 from between about 10 to 40°F and, more preferably, 15 to 30°F
27 below the desired pour point of the dewaxed oil.

28 When employing cold non-autorefrigerative solvents
29 the first chilling zone may be any type of chilling zone
30 used in conventional ketone dewaxing processes described
31 under DESCRIPTION OF THE PRIOR ART, supra, including scraped-
32 surface chilling zones. However, in a preferred embodiment
33 of this invention, the first chilling zone will be an incre-
34 mental DILCHILL zone of the type disclosed in U.S. Patent
35 3,773,650 discussed, supra, the disclosures of which are
36 incorporated herein by reference. That is, a waxy oil at

1 a temperature above its cloud point is introduced into an
2 elongated, staged chilling zone or tower and cold, non-
3 autorefrigerant dewaxing solvent, such as ketone, is incre-
4 mentally introduced into said DILCHILL zone along a plurality
5 of stages therein, while maintaining a high degree of agi-
6 tation so as to effect substantially instantaneous mixing of
7 the solvent and wax/oil mixture as they progress through said
8 zone. When employing cold non-autorefrigerative solvent, it
9 is also preferred to precipitate most of the wax from the oil
10 in this first chilling zone.

11 The slurry from the cold non-autorefrigerative
12 chilling zone is passed directly to the top of a second
13 chilling zone employing autorefrigerative solvent which is
14 the vertical, multi-staged, constant pressure tower wherein
15 the slurry is further cooled down to the wax filtration tem-
16 perature and additional wax is precipitated therefrom, as
17 was previously described.

18 Any waxy petroleum oil stock or distillate fraction
19 thereof may be dewaxed employing the process of this invention.
20 Illustrative, but non-limiting examples of such stocks are
21 (a) distillate fractions that have a boiling range within
22 the broad range of 500°F to about 1300°F, with preferred
23 stocks including a lubricating oil and specialty oil fractions
24 boiling within the range of between about 560°F and 1200°F,
25 (b) heavy feedstocks containing at least about 10 wt.% of
26 residual material boiling above 1050°F, examples of which
27 include bright stocks and deasphalted resids having an
28 initial boiling point of above about 800°F and (c) broad
29 cut feedstocks that are produced by topping or distilling
30 the lightest material or for crude oil leaving a broad cut
31 oil, the major portion of which boils above about 500°F or 650°F.
32 Additionally, any of these feeds may be hydrocracked prior to
33 distilling, dewaxing or topping. The distillate fraction
34 may come from any source such as the paraffinic crudes ob-
35 tained from Aramco, Kuwait, the Panhandle, North Louisiana,
36 etc., naphthenic crudes such as Tia Juana, Coastal crudes,

1 etc., as well as the relatively heavy feedstocks such as
2 bright stocks having a boiling range of 1050+°F and syn-
3 thetic feedstocks derived from Athabasca Tar Sands, coal
4 liquids, etc.

5 When mixtures of MEK and MIBK are used as the
6 non-autorefrigerant dilution solvent and/or coolant, MEK to
7 MIBK ratios may vary from 90% MEK/10% MIBK to 10% MEK/90%
8 MIBK and more preferably from 70% MEK/30% MIBK to 70% MIBK/30%
9 MEK. Ketone to oil volume ratios may vary from 0.5/1 to
10 10/1 and more preferably from 1.0/1 to 4/1. Predilution
11 volume ratios of either autorefrigerant or non-autorefrigerant
12 solvent may vary from 0/1 to 3/1 and more preferably from
13 0/1 to 2/1 depending on prediluent and feedstock. Chilling
14 rates in the first chilling zone may vary from 0.1°F/min.
15 to 20°F/min. and more preferably from 0.5°F/min. to 10°F/min.
16 Outlet temperatures from the first chilling zone may vary
17 from -20°F to +90°F and more preferably from 20°F to 80°F.
18 Lower outlet temperatures are better for distillate stocks
19 while higher outlet temperatures are better for residual
20 stocks. When employing cold non-autorefrigerative solvents,
21 it is preferred that most of the wax crystallize out of the
22 oil in the first chilling zone.

23 When propylene is used as the autorefrigerant in
24 the autorefrigerant chilling zone, from about 0.2 to 2.5
25 volumes of propylene per volume of waxy oil and more pref-
26 erably from about 1.0 to 2.0 volumes per volume are used, to
27 reduce the temperature of the slurry down to the wax fil-
28 tration temperature, and to reduce the viscosity of the
29 slurry sufficiently for wax filtration. Chilling rates in
30 the autorefrigerative chilling zone will generally range from
31 about 0.1 to 20°F/min. and more preferably from about 0.5 to
32 10°F/min. The temperature of the cold slurry exiting the
33 chilling zone may vary from about -50°F to +30°F to produce
34 a dewaxed oil having a pour point ranging between about
35 -30°F to +80°F. In a preferred embodiment, the slurry will
36 exit the chilling zone at a temperature of from -30°F to

1 +10°F in order to produce a dewaxed oil having a pour point
2 ranging from between about -10°F to +30°F.

3 BRIEF DESCRIPTION OF THE DRAWINGS

4 Figure 1 is a flow diagram of an embodiment of a pro-
5 cess incorporating the instant invention utilizing non-
6 autorefrigerative dilution.

7 Figure 2 is a schematic diagram of a preferred
8 embodiment of a multi-staged, vertical tower comprising
9 the chilling zone of this invention.

10 Figure 3 is a schematic diagram of a preferred
11 embodiment of a process incorporating the instant invention
12 utilizing cold non-autorefrigerative chilling.

13 DESCRIPTION OF A PREFERRED EMBODIMENT

14 Referring to Figure 1, a warm paraffinic lube oil
15 distillate at a temperature of about 160°F and having a
16 viscosity of 150 SUS at 100°F is mixed with dewaxing aid
17 from line 16 and then prediluted with a solvent comprising
18 a 70/30 volume mixture of MEK/MIBK in an amount of about 1.2
19 volumes of ketone predilution solvent per volume of waxy
20 oil. The prediluted waxy oil/dewaxing aid mixture is then
21 passed from line 10 through heat exchanger 12 wherein it is
22 cooled to a temperature of about 90°F or just above its
23 cloud point and from there into multi-staged autorefrigerant
24 chilling tower 26. Liquid propylene at a temperature of -30°F.
25 is fed into the various stages of tower 26 via line 28, mani-
26 fold 30 and multiple injection points 32. Multiple injec-
27 tion points 32 are fed to each of the various stages in tower
28 26 wherein the liquid propylene contacts the slurry in each
29 stage via a sparger located under the surface of the slurry
30 in each stage. About 1.5 volumes of liquid propylene are
31 used in tower 26 per volume of slurry entering therein via
32 line 24. Tower 26 operates at a pressure of about 2 psig.
33 About 1.2 volumes of the liquid autorefrigerant per volume
34 of fresh feed evaporates upon contact with the slurry, with
35 the autorefrigerant vapors being removed from each stage via
36 multiple tower exit ports 34, manifold 30 and line 38 at

1 an average temperature of about 24°F. Thus, none of the
2 vapor produced in any stage passes through the slurry on
3 any other stage in the tower. The remaining C.9 volume of
4 propylene per volume of feed go into solution with the MEK/
5 MIBK and dewaxed oil in the wax slurry. Tower 26 contains
6 approximately 14 stages in which the average slurry chilling
7 rate is about 3°F per minute with an average temperature drop
8 across each stage of about 8.6°F. The waxy slurry is further
9 cooled in tower 26 to a temperature of about -30°F. The
10 slurry comprising solid wax particles, oil, ketone and
11 liquid propylene is then fed to rotary pressure filter 42
12 via line 40 wherein the wax is filtered from the dewaxed oil
13 solution. The dewaxed oil solution leaves filter 24 via
14 line 44 and from there is sent to solvent recovery while
15 the wax is removed via line 46 and sent to solvent recovery
16 and further wax processing if desired. The dewaxed oil
17 solution yields a dewaxed oil having a pour point of about
18 -10°F.

19 Figure 2 illustrates a preferred embodiment of
20 autorefrigerant chilling tower 26. The diameter of the
21 tower is sized so as to provide a superficial vapor velocity
22 low enough to avoid entrainment of the oil in the vapor. The
23 tower comprises about 14 discrete stages, 50a through 50n.
24 Each stage contains an autorefrigerant vapor collector, vapor
25 space, slurry tray, slurry downcomer, weir and liquid autore-
26 frigerant sparger. This is illustrated for stage 50a wherein
27 52 is the vapor collector, 54 represents the vapor space, 56
28 is the slurry tray, 58 is the slurry, 60 is the downcomer, 62
29 is the weir and 64 is the sparger. The sparger 64 and
30 autorefrigerant vapor collector 52 are detailed in Figures
31 2-b and 2-c, respectively. Sparger 64 comprises piping
32 containing a plurality of small holes 66. Vapor collector 30
33 is shown as a pipe containing a plurality of rectangular
34 holes 68. In operation, slurry from tower 16 is fed to tower
35 26 via line 24, entering tower 26 through feed inlet 68
36 passing through downcomer 60 wherein it is directed downward

1 and under the surface of the slurry 58 held up on stage 50a.
2 Liquid propylene is introduced into stage 50 from injection
3 point 32 through sparger 64 and holes 66. The holes are
4 sized so as to provide a level of agitation such that there
5 is substantially instantaneous mixing (i.e., 1 second or
6 less). The holes are directed downward, opposing slurry
7 flow through the stage. Some of the propylene vaporizes as
8 it enters the warmer slurry and the vapors bubble up
9 through the slurry, with the remainder of the propylene
10 going into solution. Propylene vapors are removed through
11 vapor collector 52 and the cooled slurry flows over weir
12 62 wherein it enters downcomer 60 and is directed under the
13 surface of the slurry on the next stage 50b. This process
14 is repeated from stage to stage as the slurry passes down
15 the tower until it exits from slurry outlet 70 at wax
16 filtration temperature and fed to wax filter 42.

17 Referring to Figure 3, a warm paraffinic lube oil
18 distillate at a temperature of about 160°F and having a
19 viscosity of 150 SUS at 100°F is passed from line 10
20 through heat exchanger 12 wherein it is cooled to a temp-
21 erature of about 84°F or just above its cloud point and
22 from there into multi-staged DILCHILL tower 16 via line 14.
23 In tower 16 it is cooled by contact with a cold (-30°F)
24 ketone solvent comprising a mixture of 70% MEK/30% MIBK
25 (volume basis) which is injected into the various stages of
26 tower 16 via line 18, manifold 20 and multiple injection
27 points 22. About 1.2 volumes of the cold ketone dewaxing
28 solvent enters the tower per volume of feed. Each stage
29 (not shown) in tower 16 contains a rotating impeller so
30 that the cold ketone dewaxing solvent entering therein is
31 substantially instantaneously mixed in the waxy oil. In
32 tower 16 most of the wax is precipitated from the waxy oil
33 producing a slurry which leaves the bottom of tower 16 via
34 line 24 at a temperature of about 30°F. The cold, ketone-
35 containing slurry in line 24 is passed directly into multi-
36 staged chilling tower 26. Liquid propylene at a temperature

1 of -30°F is fed into the various stages of tower 26 via
2 line 28, manifold 30 and multiple injection points 32.
3 Multiple injection points 32 are fed to each of the various
4 stages in tower 26 wherein the liquid propylene contacts
5 the slurry in each stage via a sparger located under the
6 surface of the slurry in each stage. About 1.5 volumes of
7 liquid propylene are used in tower 26 per volume of slurry
8 entering therein via line 24. Tower 26 operates at a pressure
9 of about 2 psig. About 0.6 volume of the liquid autore-
10 frigerant per volume of fresh feed evaporates upon contact
11 with the slurry, with the autorefrigerant vapors being
12 removed from each stage via multiple tower exit ports 34,
13 manifold 30 and line 38 at an average temperature of about
14 -12°F. Thus, none of the vapor produced in any stage passes
15 through the slurry on any other stage in the tower. The
16 remaining 0.9 volume of propylene per volume of feed go
17 into solution with the MEK/MIBK and dewaxed oil in the wax
18 slurry. Tower 26 contains approximately seven stages in
19 which the average slurry chilling rate is about 3°F. per
20 minute with an average temperature drop across each stage
21 of about 8.6°F. The waxy slurry is further cooled in tower
22 26 to a temperature of about -30°F. The slurry comprising
23 solid wax particles, oil, ketone and liquid propylene is
24 then fed to rotary pressure filter 42 via line 40 wherein
25 the wax is filtered from the dewaxed oil solution. The de-
26 waxed oil solution leaves filter 24 via line 44 and from
27 there is sent to solvent recovery while the wax is removed
28 via line 46 and sent to solvent recovery and further wax
29 processing if desired. The dewaxed oil solution yields a
30 dewaxed oil having a pour point of about -10°F.

31 The invention will be more readily understood by
32 reference to the following example:

33 EXAMPLE I

34 This example provides laboratory data demonstrating
35 the process of this invention utilizing non-autorefrigerative
36 solvents as dilution solvents. The feedstock used was a

1 paraffinic, waxy distillate having a viscosity of 600 SUS
 2 at 100°F (600N). A pilot plant autorefrigerant chilling
 3 unit was employed which comprised a vessel operating at a
 4 constant pressure of about 5 psig. Liquid propylene, at
 5 a temperature of about -30°F was continuously injected into
 6 the unit below the surface of the slurry contained therein.
 7 Part of the liquid propylene vaporized with the vapors being
 8 continuously withdrawn from the constant pressure vapor
 9 space above the slurry. A slurry chilling rate of about
 10 5°F/min. was maintained by controlling the rate of injection
 11 of the liquid propylene into the slurry. Before the feed-
 12 stock was placed into the autorefrigerant chilling unit, it
 13 was mixed with a Paraflow/Acryloid dewaxing aid and pre-
 14 diluted with MEK at a temperature above its cloud point in
 15 an amount of one volume of MEK per volume of feed. The
 16 prediluted feed was then prechilled to a temperature of 120°F,
 17 which was approximately the cloud point of the prediluted
 18 feed, before being added to the unit. As hereinbefore stated,
 19 the prediluted feed was chilled in the autorefrigeration
 20 unit at a rate of 5°F/min. The waxy slurry formed in the
 21 unit was chilled down to a temperature of -30°F and then
 22 filtered at -30°F. The amount of propane that dissolved
 23 in the oil in the unit was 1.5 volume per volume of feed
 24 oil.

25 The results of this experiment are contained in
 26 Table A below. These results illustrate the operability of
 27 the present invention.

28	<u>TABLE A</u>	
29	<u>CONTINUOUS CONSTANT PRESSURE</u>	
30	<u>AUTOREFRIGERATION DEWAXING</u>	
31	Feedstock	600N
32	Dewaxing Aid Type	P/A
33	Aid Dose, wt.% on Feed	0.2
34	Predilution Solvent	100% MEK
35	Predilution Ratio on Feed	1.0
36	Prechilling Start °F	150
37	Finish °F	120
38	Rate °F/Min.	10.8
39	Autorefrig. Pressure	5 psig

1	Autorefrig. Start °F	120
2	Finish °F	-30
3	Rate °F/Min.	5
4	C3 Makeup to Chiller	Variable
5	Dilution to Filter	2.5
6	Solv. Comp. to Filter	40/60 MEK/Propane
7	Filtration Temp. °F	-30
8	Feed Filter Rate GPHPSF	5.0
9	Wax L/S Ratio	6.3
10	Wax Oil Content, wt. %	62
11	Mean Crystal Dia., Microns	19
12	Crystals <10 Microns, %	3
13	DWO Pour, °F	0

14 EXAMPLE

15 This example provides laboratory data comparing the
16 combination process of this invention employing cold non-
17 autorefrigerative solvents and autoregrigerative solvent chil-
18 ling with conventional DILCHILL ketone dewaxing followed by
19 scraped surface chilling. Three paraffinic lube oil feedstocks
20 were used, a bright stock, and two distillates having viscos-
21 ities of 150 (150N) and 600 SUS (60CN) at 100°F. A pilot plant
22 DILCHILL unit was used for the DILCHILL dewaxing with ketone
23 solvent to produce a ketone-containing slurry comprising solid-
24 particles of wax and a mixture of partially dewaxed oil and
25 ketone dewaxing solvent. The temperature of the cold ketone
26 solvent fed into the DILCHILL unit was about -30°F. The bright
27 stock was prediluted with 1 volume of warm ketone solvent
28 per volume of feed before being fed into the DILCHILL unit.
29 The waxy slurry produced in the DILCHILL unit was then fed to
30 either scraped surface chillers or to a simulated continuous,
31 autorefrigerant chilling unit for further chilling down to
32 wax filtration temperature. The cold slurry was then filtered
33 to separate the wax from the dewaxed oil/solvent mixture and
34 both the dewaxed oil and wax were recovered.

35 The autorefrigerant chilling unit comprised a ves-
36 sel operating at a constant pressure of about 2 psig wherein
37 liquid propylene was continuously injected into the unit,
38 below the surface of the slurry contained therein. Part of
39 the liquid propylene vaporized with the vapors being continu-
40 ously withdrawn from the constant pressure vapor space above

1 the slurry. A slurry chilling rate of about 2°F/min. was
2 maintained by controlling the rate of injection of the
3 liquid propylene into the slurry.

4 The results of these experiments, correlated to
5 common dewaxed oil pour points, are contained in Table B,
6 below. These results illustrate not only the operability of
7 the present invention, but also that superior results can
8 be achieved by its use. Thus, using the present invention
9 gave faster feed filter rates, drier wax cakes and wax
10 cakes containing less oil than the DILCHILL dewaxing process
11 followed by scraped surface chilling. Further, these results
12 were obtained without the use of dewaxing aid.

TABLE B

COMBINATION DEWAXING PROCESS COMPARED TO DILCHILL
FOLLOWED BY SCRAPED SURFACE CHILLING

Process	Combination				DILCHILL Dewaxing Followed by Scraped Surface Chilling			
	MEK/MIBK/Propylene ^a		B.S. ^b		MEK/MIBK		B.S. ^b	
Solvent	150N	600N			150N	600N		
Feedstock								
Predilution - Solvent	-	-			-	-		
- Vol. Ratio	-	-			-	-		
MEK/MIBK Ratio	70/30	70/30	50/50		50/50	40/60	15/85	
Cold Dilution Vol. Ratio								
- MEK/MIBK	1.2	1.8	2.4		2.2	3.3	3.9	
- Propylene	0.9	1.5	1.5		-	-	-	
First Zone Outlet Temp., °F.	30	35	77		29	25	53	
Second Zone Outlet Temp., °F.	-30	-30	-30		-11	-5	-6	
Feed Filter Rate, GPHPSF ^d	8.8	6.7	4.4		8.4	5.0	3.6	
DWO Pour, °F.	-10	-4	-4		-10	-4	-4	
Wt. % Oil in Wax (No Wash)	54	50	49		65	51	50	
Average Cake Liquid/Solids	4.3	5.1	5.8		7.0	5.5	6.1	

(a) Liquid propylene at a temperature of -30°F.

(b) Bright stock.

(c) Outlet temperature of slurry from scraped surface chillers for DILCHILL plus scraped surface dewaxing.

(d) Gallons per hour per square foot of filter surface.

Conversion of Units

Temperatures expressed in $^{\circ}\text{F}$ are converted to $^{\circ}\text{C}$ by subtracting 32 and then dividing by 1.8.

Relative temperatures in $^{\circ}\text{F}$ are converted to relative temperatures in $^{\circ}\text{C}$ by dividing by 1.8.

Pressures in pounds per square inch (gauge) (psig) are converted to kg/cm^2 equivalent by multiplying by 0.07031.

Liquid volumes in gallons are converted to litres by multiplying by 3.785.

Areas in square feet are converted to square metres by multiplying by 0.09290.

CLAIMS:

1. A solvent dewaxing process in which a waxy oil (10) is mixed with a dewaxing solvent (18) to reduce the solubility of wax in the oil and then chilled to cause wax to precipitate out and form a slurry of solid wax particles, characterised in that a mixture (24) comprising waxy oil and dewaxing solvent is passed continuously into the top of a continuous, autorefrigerative chilling zone which comprises a substantially vertical, elongated multi-staged tower (26) operating at a substantially constant pressure wherein each stage (50, Fig.2) contains a liquid space (58) and a vapour space (54) above the liquid space, each of said vapour spaces (54) being provided with means (52) for the exit or removal of autorefrigerant vapour therefrom and wherein said mixture is cooled down to wax filtration temperature and wax is precipitated to form a slurry containing solid wax particles as the mixture passes from stage to stage by contacting the mixture in the autorefrigerative chilling zone with a liquid autorefrigerant which is introduced (via 64, Fig.2) under flow rate control conditions into a plurality of the stages (50a ... 50n) in said autorefrigerative zone (26) under conditions permitting or causing evaporation therein so as to achieve an average cooling rate of the mixture in said zone in the range of from 0.1 to 20°F (0.06 to 11.12°C) per minute with an average temperature drop across each stage (50) in the range of from 2 to 20°F (1.11 to 11.12°C), and wherein evaporated autorefrigerant vapour is discharged or removed (via 52) from each stage into which liquid autorefrigerant is introduced in such a manner that autorefrigerant vapour in any given stage does not pass through all the stages in the tower above the said given stage, and wherein the resulting slurry (40, Fig.1) is separated (42) into a dewaxed oil solution (44) and wax (46).

2. A process as in claim 1 characterized in that the said mixture (24) passed to the continuous autorefrigerative chilling zone (26) comprises a non-autorefrigerant dewaxing solvent (18) and is formed either by: (a) prediluting the waxy oil (10) with a non-autorefrigerant dewaxing solvent (18, Fig.1) to form said (24) mixture at a temperature above its cloud point, or: (b) cooling the waxy oil (10) in a cooling zone (16, Fig.3) wherein a portion of the wax is precipitated from the oil by cooling in the presence of a non-autorefrigerant dewaxing solvent (18, 20, 22, Fig.3) to form a slurry (24, Fig.3) comprising a mixture of oil, solvent and solid particles of wax.
3. A process as in claim 2 characterised in that in step (b), most of the wax is precipitated from the waxy oil in the cooling zone (16, Fig.3).
4. A process as in claim 2 characterised in that the prediluted waxy oil mixture (24, Fig.1) produced in step (a) is at a temperature which is at or near to its cloud point on entering the autorefrigerative chilling zone (26).
5. A process as in claim 2 or claim 3 characterised in that the mixture (24, Fig.3) produced by step (b) is at a temperature which is at or above its cloud point when it enters the autorefrigerative chilling zone (26).
6. A process as in any one of claims 2, 3 or 5 characterised in that in step (b), no more than 30 LV% of autorefrigerant (28, Fig.3), based on the waxy oil feed (10), is present in the said cooling zone (26).
7. A process as in claim 2 or claim 4 characterised in that in step (a), no autorefrigerant is present in or with the predilution solvent (18, Fig.1).

8. A process as in any one of claims 2 to 7 characterised in that the non-autorefrigerant dewaxing solvent (18) comprises one or more solvents selected from (i) one or more of the C_3 to C_6 aliphatic ketones; (ii) one or more of the halogenated low molecular weight hydrocarbons; (iii) one or more of the C_5 to C_{10} normal- or iso-paraffins; (iv) aromatics selected from benzene, toluene, xylene, petroleum naphtha and mixtures thereof; and (v) mixtures of any of the foregoing solvents (i) to (iv).

9. A process as in any one of claims 1 to 8 characterised in that the liquid autorefrigerant (28) is selected from the normally gaseous C_2 to C_4 hydrocarbons, ammonia and normally gaseous fluorocarbons.

10. An apparatus for use in a continuous autorefrigerative dewaxing process which may preferably be performed at a relatively low pressure, characterised in that it comprises a substantially vertical tower (26, Fig.2) containing therein a plurality of vertically separated stages ($50a \dots 50n$), means (68) for introducing waxy oil into the top of the apparatus and means (70) for removing a wax-containing slurry from the bottom of the apparatus, each of said stages (50) comprising a liquid space (58), a vapour space (54) above said liquid space, oil or slurry tray means (56) for retaining said liquid oil or slurry, weir means (62) for maintaining a predetermined amount of liquid or slurry (58) on said tray means (56), downcomer means (60) for providing a flow path for said liquid or slurry from a location above said stage (50) to said liquid space (58) of said stage (50), means (64) for introducing cold liquid autorefrigerant into said stage (50) in a manner such that said liquid autorefrigerant directly contacts said oil or slurry (58) in said stage (50) thereby vaporising at least a portion of said autorefrigerant, and means (52) for discharging or removing said vaporised autorefrigerant from said stage (50) in a manner such that said vapors do not contact liquid or slurry in all of the other stages of said apparatus at least above said stage.

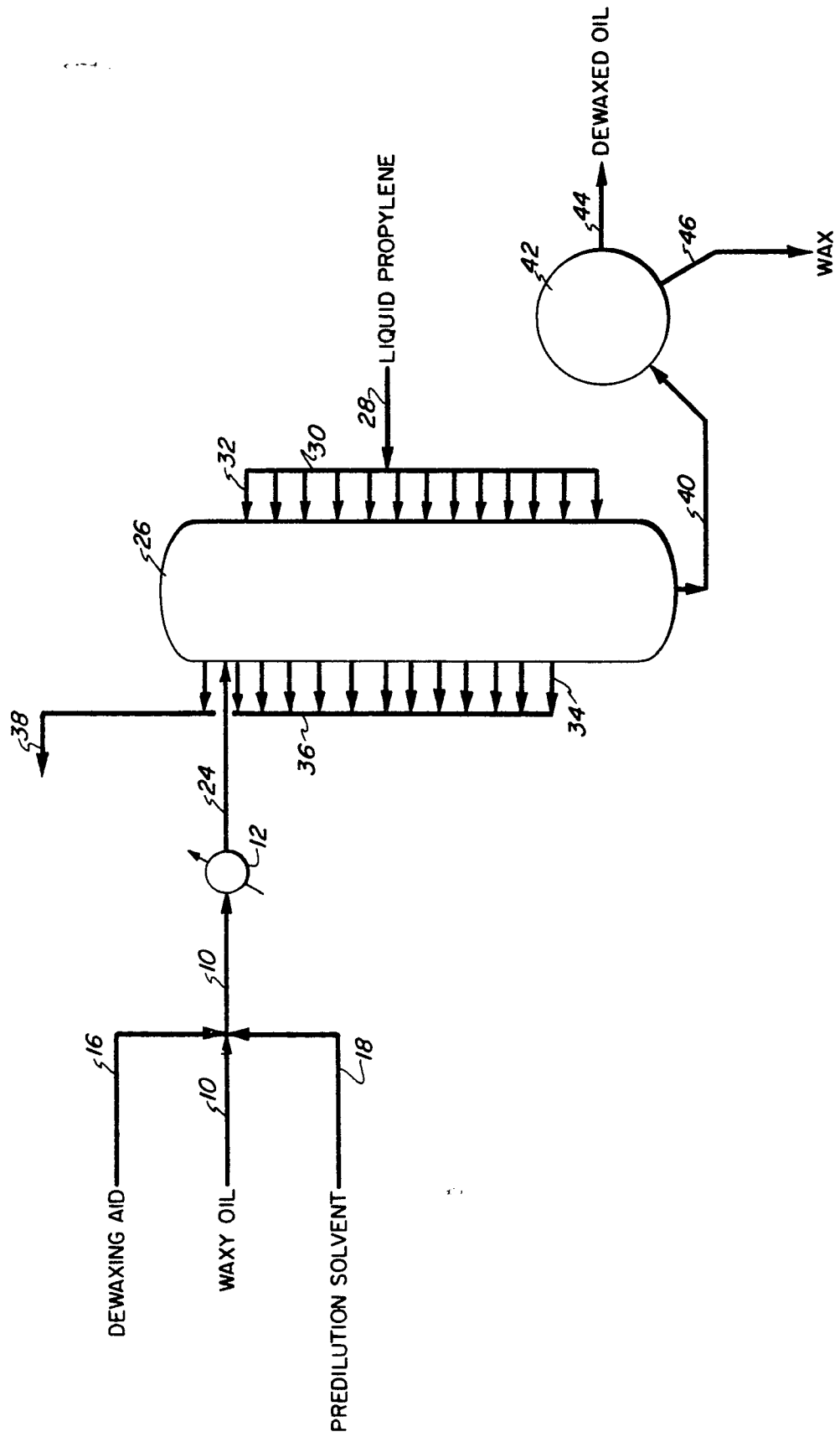


Figure 1

0036460

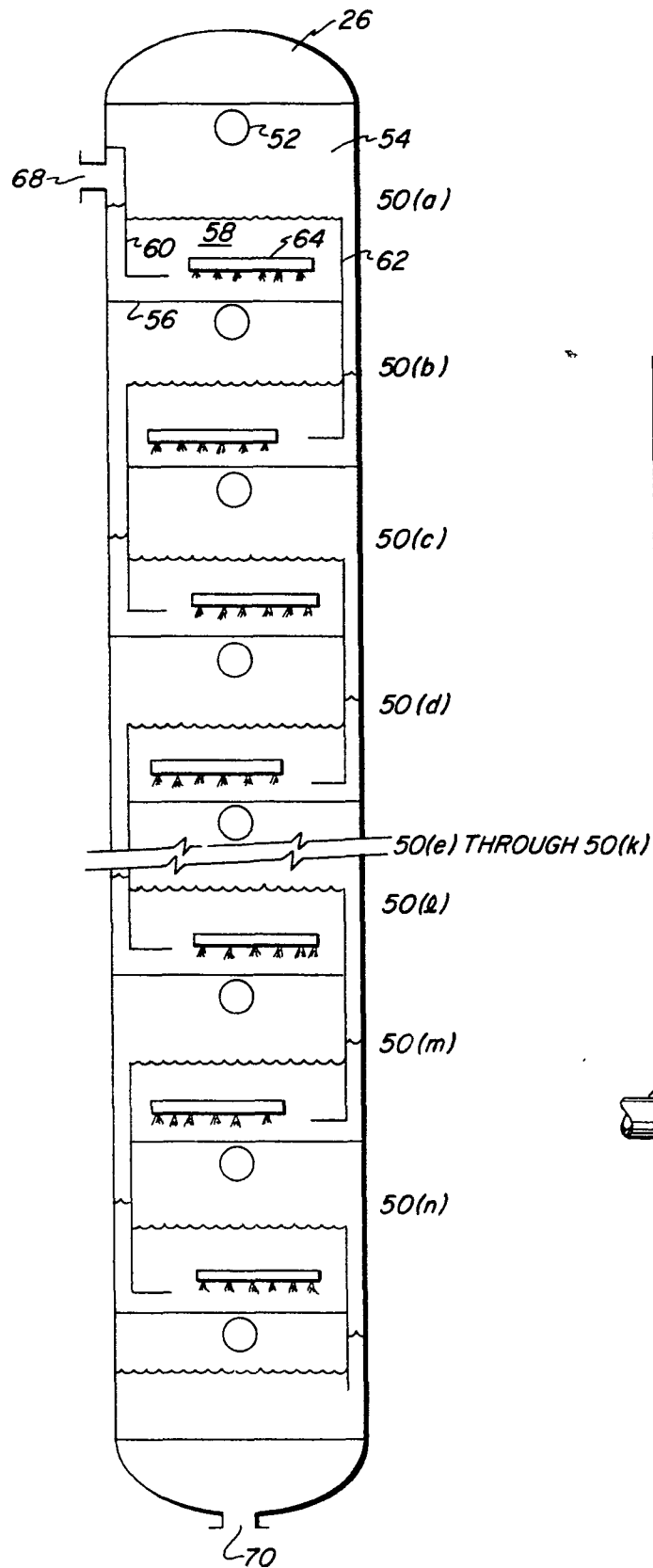


Figure 2(a)

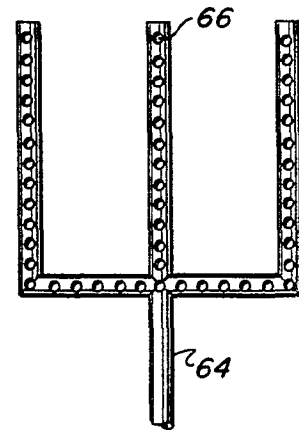


Figure 2(b)

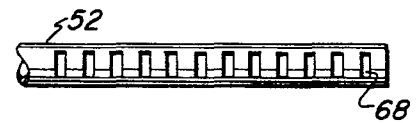


Figure 2(c)

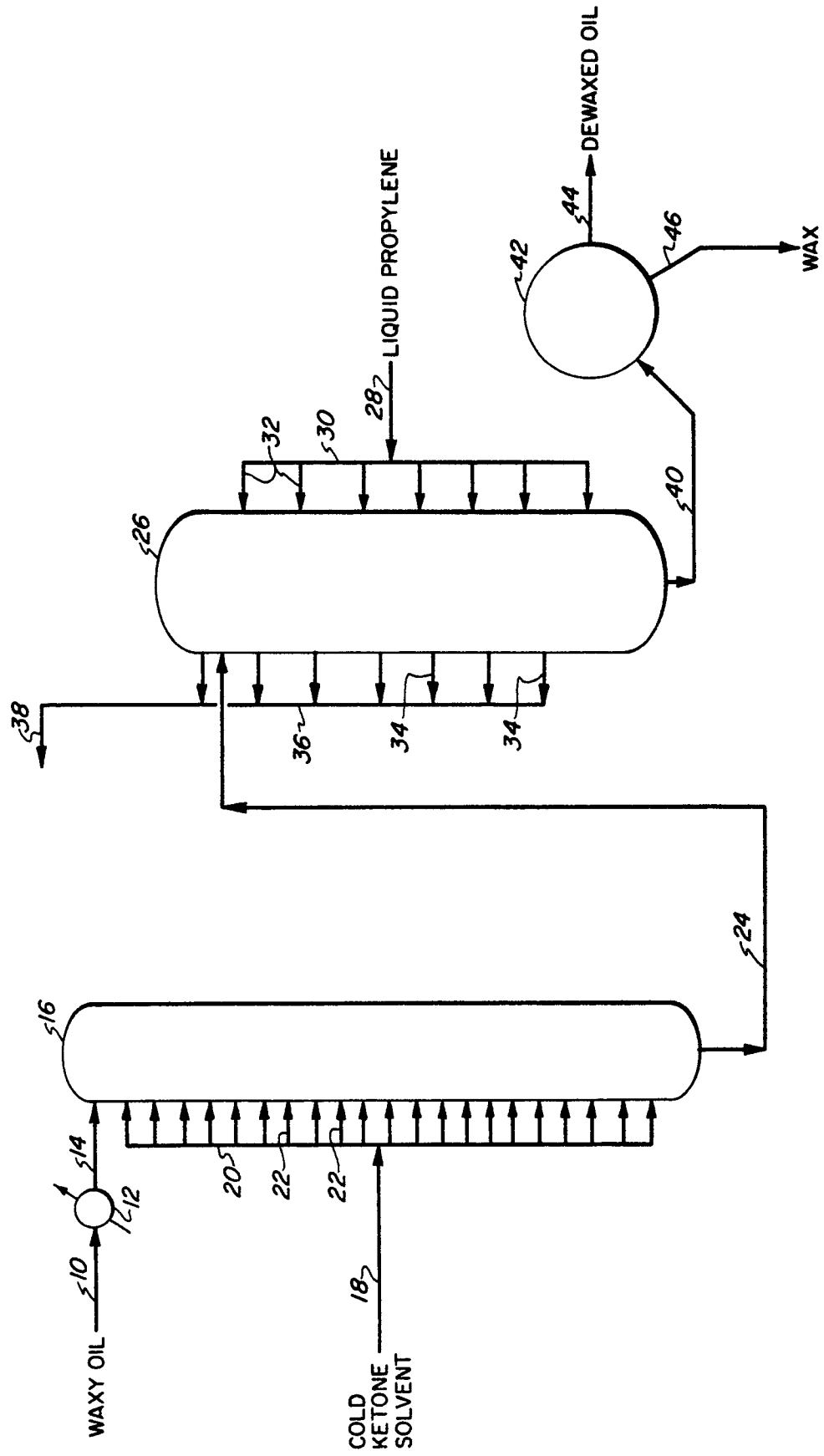


Figure 3



European Patent
Office

EUROPEAN SEARCH REPORT

0036460

Application number

EP 80 30 0885

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D	<u>US - A - 3 549 513</u> (R.A. WOODLE) * Abstract; column 2, lines 22-65 column 3, lines 16-28; claims 1-8; figure *	1,2,8, 9,10	C 10 G 73/32
	--		
D	<u>US - A - 3 720 599</u> (L.R. GOULD) * Abstract; column 3, line 13 - column 4, line 4; column 4, lines 13-55; column 5, lines 3-13, 49-60; column 5, line 61 - column 6, line 40; claims 1-17; figures 1,2 *	1,8,9, 10	
	--		
	<u>US - A - 2 085 521</u> (A.P. ANDERSON) * Page 1, right-hand column, lines 26-44; page 2, left- hand column, lines 34-67; page 3, left-hand column, lines 1- 13; claims 1-11; figure *	1,2,8, 9,10	C 10 G 73/06 73/08 73/32
	--		
DA	<u>US - A - 2 202 542</u> (V. VOORHEES)		
DA	<u>US - A - 3 773 650</u> (D.B. HISLOP)		
DA	<u>US - A - 3 658 688</u> (F.A. BIRI- BAUER)		
A	<u>US - A - 2 775 542</u> (J.A. CARVER)		

☒ The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
Place of search The Hague		Date of completion of the search 24-11-1980	Examiner LO CONTE