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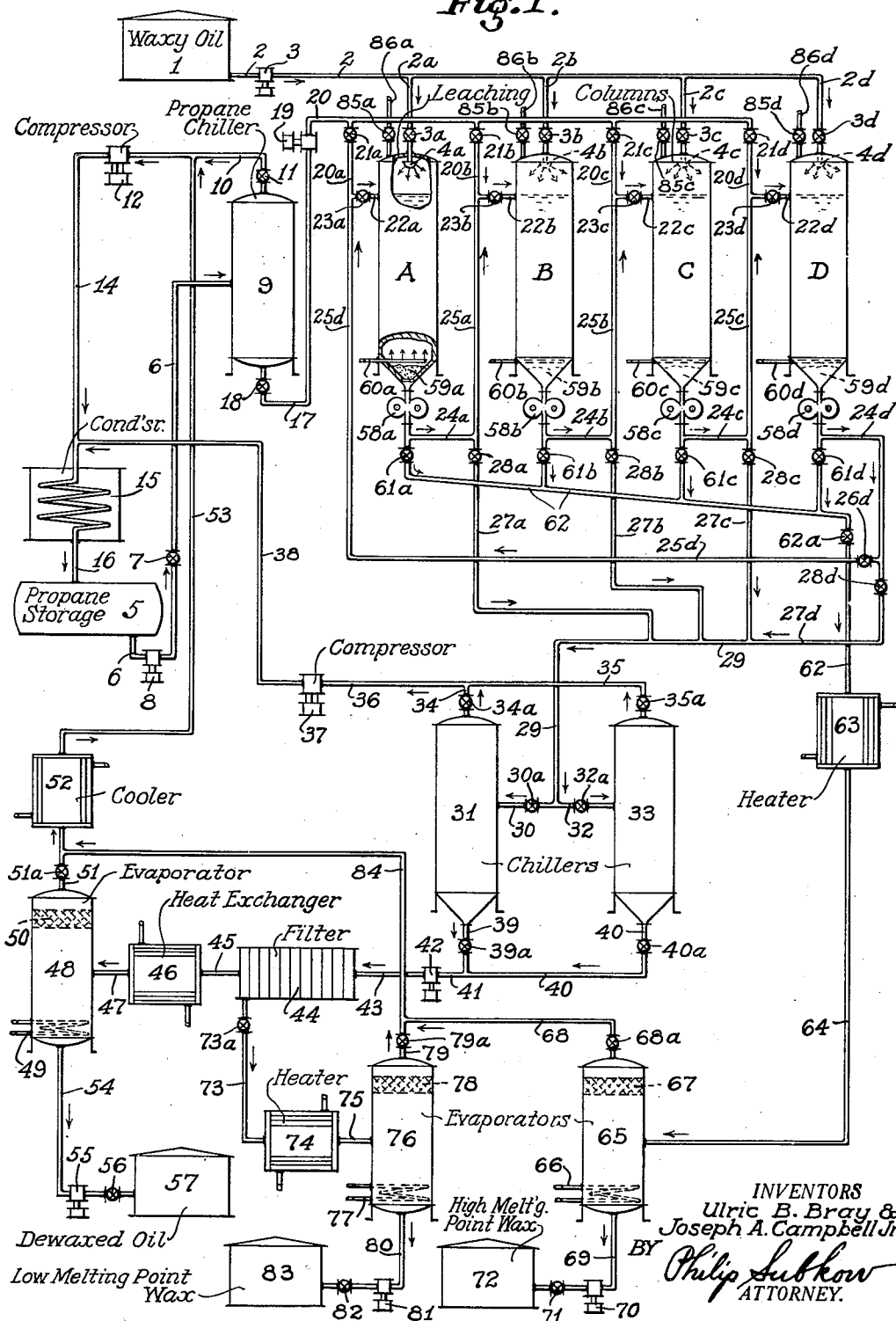
U. B. BRAY ET AL
PROCESS FOR DEWAXING OILS

2,194,968

Filed March 31, 1936

2 Sheets-Sheet 1

Fig. 1.



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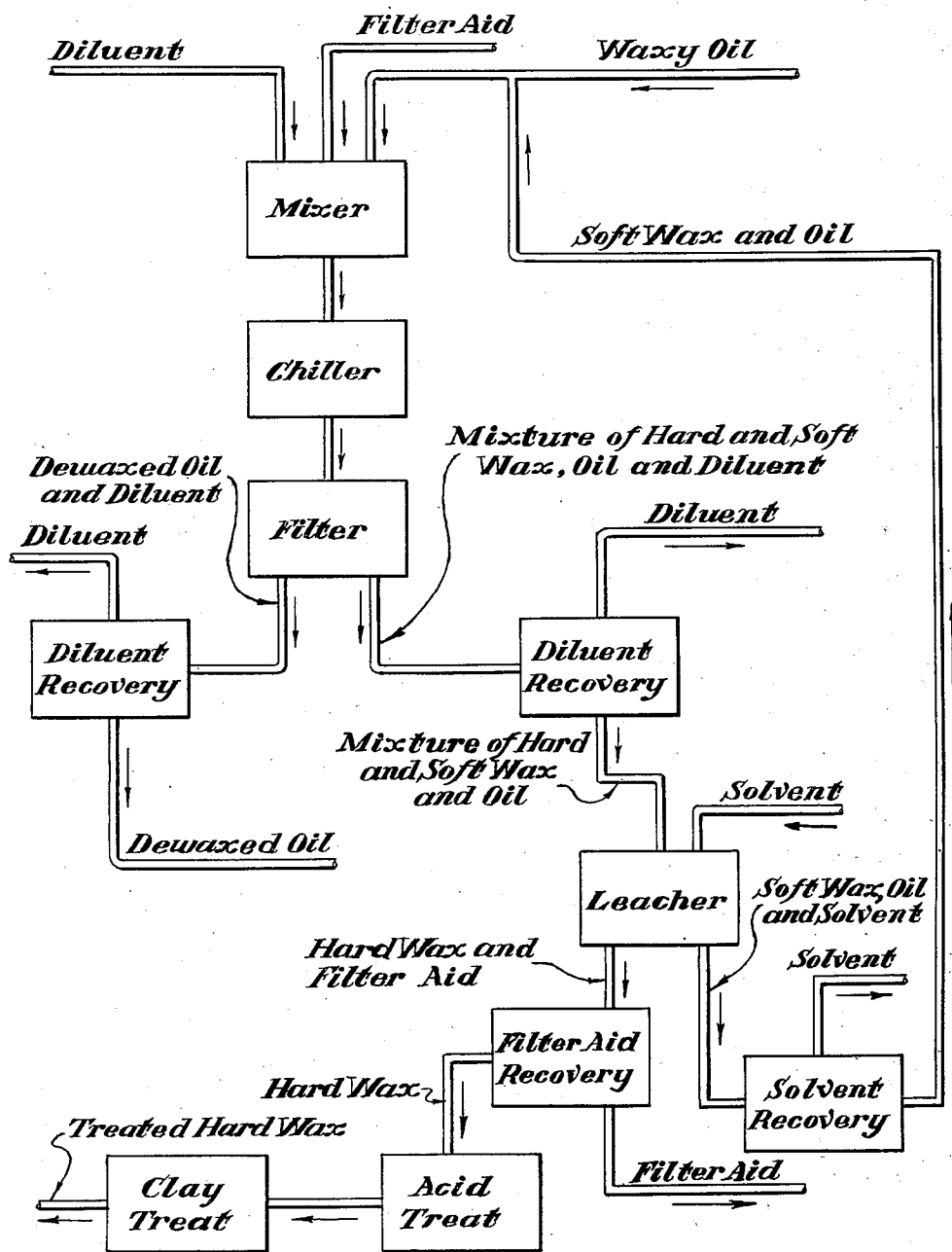


Fig. 2.

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UNITED STATES PATENT OFFICE

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PROCESS FOR DEWAXING OILS

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12 Claims. (Cl. 196—17)

The present invention relates to a process for the separation of wax from oil. The invention also relates to the fractionation of wax separated from oils to produce both high and low melting point waxes. The invention particularly relates to a process for separating high melting point wax from oil or from a mixture of low and high melting point waxes by a process corresponding to a leaching out of the oils and soft waxes by means of a suitable solvent from solidified discrete particles of oil, soft and hard waxes, the discrete particles being produced by contact of the mixture with the cold leaching solvent at a temperature at which the soft wax and oil is soluble in the solvent but the hard wax is insoluble therein.

It has heretofore been proposed to separate wax from oils in the presence of a diluent, preferably a liquefied normally gaseous hydrocarbon, such as liquid propane. In this process, the waxy oil is dissolved in the liquid propane under super-atmospheric pressure and the mixture is chilled by reducing the pressure and vaporizing a portion of the solvent. By reducing the pressure to substantially atmospheric, temperatures as low as -40° F. may be obtained. The chilled mixture is then filtered, centrifuged or cold settled to remove the wax from the chilled mixture. The foregoing process of separating wax from oil is commonly referred to as the solution and precipitation method for dewaxing oils.

It has also been proposed by Bray, applicant for patent Serial No. 745,417, filed September 25, 1934, to separate wax from oil by a process corresponding to leaching of the oil from solidified wax structures. In this process, the waxy oil is sprayed into a body of cold solvent or diluent which is maintained at a wax crystallization temperature, say -40° F., whereupon the waxy oil is crystallized or solidified to form a plurality of congealed or solidified particles of oil and wax. Upon continued contact of the solidified waxy oil particles, such as that which takes place when these particles settle to the bottom of the container of chilled solvent, solution of the oil in the resulting solvent takes place leaving wax matrices undissolved. This process is commonly referred to as the cold leaching method for dewaxing oils.

In either of the above processes, when operating at a temperature of -40° F. which is apparently necessary in order to produce lubricating oils of low pour test, the wax cake contains a wide variety of paraffins as regards their melting point. In other words, the wax cake con-

tains not only the high melting point normal straight chain paraffins but also the lower melting point paraffins having varying degrees of iso-paraffin characteristics. It has been found that the low melting point iso-paraffins must be removed from the lubricating oil in order to obtain an oil of satisfactorily low pour point. We have now found that these low melting point iso-paraffins must also be removed from the wax cakes before the latter can be used for many commercial purposes. In other words, it is not only necessary to deoil the wax cakes completely in the usual sense of the word corresponding to the removal of all the lubricating oil fractions which are definitely liquid, at say 30° F., but it is also necessary to refractonate the wax to eliminate iso-paraffin compounds which heretofore have not been recognized as being present in the slack waxes to any considerable extent.

In order to accomplish the foregoing, we have found it desirable to rework the wax cake produced at temperatures sufficiently low to produce desirable low pour point oils by operating at higher temperatures. In reworking such waxes, use is made of such solvents at such pressure and temperature conditions that not only the oil contained in the wax mixture is soluble, but the lower melting point waxes or iso-paraffins would also be soluble to any desired degree. We have found the liquefied normally gaseous hydrocarbons to be particularly useful in this connection. Such solvents include ethane, ethylene, propane, propylene, butane, butylene, iso-butane and mixtures thereof. The cold leaching method aforementioned is particularly adapted for the fractionation of waxes. With the use of the aforementioned solvents, the variation of the temperature of leaching may be accomplished by means of variation of pressure on the volatile solvent. For example, propane held under a pressure of about 30 lbs. per square inch has a temperature of about 20° F. which is a suitable temperature for the fractionation of some waxes. If desired, a volatile solvent or a mixture of volatile solvents may be employed as the leaching solvent which has a boiling point at atmospheric pressure of approximately the desired temperature of leaching. For example, commercial butane consisting of a mixture of normal and iso-butane, may be employed at atmospheric pressure as the leaching solvent. This solvent boils at about 20° F. at atmospheric pressure.

We have also discovered that the mixture of waxes containing considerable amounts of lubricating oil, such as a waxy lubricating oil distil-

late or a slack wax which has been separated from oil, may be fractionated by means of solvents into a high melting point wax, a low melting point wax and a lubricating oil of low pour point in a simple, economical and efficient manner. Thus, instead of separating a mixture of low and high melting point wax from the original oil containing the same at a low temperature of say -40°F . and then fractionating the separated waxes into high and low melting point waxes, we have found it possible to subject the original stock to cold leaching in a suitable solvent in accordance with the method hereinafter described at a temperature at which the oil and soft waxes or iso-paraffins which are soluble in the leaching solvent but in which the high melting point waxes are insoluble. In this process, a separation is made of the high melting point waxes on one hand and the soft wax and lubricating oil dissolved in the solvent on the other hand. The solvent solution of the low melting waxes and oil separated from the high melting point waxes at a temperature in which such waxes are insoluble is then further chilled to precipitate the soft waxes which may be separated from the solution of oil and solvent by any convenient method such as by filtration, settling or centrifuging. When this process is employed, a greater advantage is obtained not only in the improvement obtained in the operation of the process with regard to filter rates and filter operation but that a large percentage of the cost of chilling is eliminated. Thus, when a liquefied normally gaseous hydrocarbon is employed as the diluent-refrigerant for separating the mixture of waxes from the oil to produce a lower pour point oil and for treating the separated mixture of waxes in order to remove the high melting point wax, the cost of reliequifying the gaseous hydrocarbon by compression and condensation represents a material proportion of the cost of operating the entire system. Not only does this cost represent a considerable proportion of the operation of the system but it requires the use of large expensive compressors for recovering the gas and a duplication of refrigeration and auxiliary equipment and also necessitates provision of large storage capacity for the diluent-refrigerant.

Thus, in the operation of the process forming the subject of our invention, it will not be necessary to subject the separated mixture of high and low melting point wax to fractionation in a solvent. It is merely necessary to subject the original stock to a leaching operation at a controlled temperature to separate the high melting point waxes and then further chill the solution containing the soft waxes by evaporating a portion of the solvent under reduced pressure to obtain a lower temperature sufficient to precipitate the softer waxes. This combination of the cold leaching process followed by precipitation of the remaining wax avoids duplication of auxiliary equipment and also the refrigeration required for the dewaxing operation is advantageously employed for the operation of the wax-leaching unit making it unnecessary to provide duplicate refrigeration equipment. However, it will be understood that the fractionation by leaching of the mixture of high and low melting point waxes which have been separated from oils at temperatures sufficient to separate both types of waxes as a mixture is also within the scope of our invention.

It is therefore an object of our invention to

fractionate a mixture of high and low melting point waxes into a low melting point wax and a high melting point wax. It is a further object of our invention to accomplish the fractionation by a leaching process in a suitable solvent, particularly a liquefied normally gaseous hydrocarbon which is maintained at a suitable temperature so that the fractionation of the waxes may be accomplished.

It is a further object of our invention to introduce a wax-oil mixture into a cold leaching solvent maintained at a temperature so that the soft wax and oil are dissolved in the solvent while the hard or high melting point wax remains insoluble in the cold solvent, in separating the solution of soft wax, oil and solvent from the hard wax, in chilling the last mentioned solution to a low temperature sufficient to precipitate the soft wax, in separating the precipitated soft wax from the solution of oil and solvent and in separating the solvent from the oil.

Other objects and advantages of our invention will be apparent from the following description of the invention taken from the drawings which are not to be considered as limiting the invention.

In the foregoing description of the preferred embodiment, the use of commercial propane as a combined diluent and refrigerant has been described. However, it should be understood that other liquefied normally gaseous hydrocarbon such as ethane, ethylene, propane, propylene, butane, isobutane, butylene, etc. may be used separately or in admixture with each other. Instead of using liquefied normally gaseous hydrocarbons other normally gaseous diluent-refrigerants may be employed such as methylether, methyl chloride, dichlor-difluor-methane. Also admixtures of the foregoing normally gaseous diluent refrigerants and normally liquid hydrocarbons, such as gasoline, casinghead gasoline, naphtha, normally liquid anti-solvents for wax such as acetone, acid esters, mixtures of benzene with naphtha, mixtures of acetone and benzol, and the like, may be employed. If desired, the normally liquid hydrocarbons such as pentane and hexane may be employed as the leaching solvent. These may be chilled by external means as is well known by those skilled in the art. In the preferred embodiment practically complete separation of the wax from the oil is effected by the use of commercial propane as the diluent refrigerant.

In the drawings, Fig. 1 represents a schematic flow diagram of a process in which the waxy oil is first subjected to leaching in order to separate the hard wax and then the solution of oil, soft wax and diluent is further chilled and filtered to separate the soft wax. Fig. 2 represents a flow diagram of a process in which a mixture of soft and hard wax is separated from the waxy oil and then the mixture of waxes is subjected to leaching in order to fractionate the wax into soft and hard wax.

Referring to Fig. 1, a waxy stock such as an S. A. E. 20 distillate produced by the vacuum distillation of a Santa Fe Springs crude is drawn from tank 1 via line 2 and pumped by pump 3 through line 2a controlled by valve 3a through spray head 4a into the first leaching column or extractor A. The leaching column is first filled with a cold leaching solvent, for example liquid propane at an appropriate temperature sufficient to dissolve the oil and low melting point iso-paraffin type waxes which may be at a temperature of approximately 10°F . to 40°F . which represents the temperature in which the oil and

soft waxes are soluble in the cold leaching solvent but only small amounts of the harder or high melting point wax are soluble in the solvent.

Filling of the leaching column is accomplished by withdrawing liquid propane from propane storage tank 5 under superatmospheric pressure at about normal temperatures and passing it via line 6 controlled by valve 7 by means of pump 8 into propane chiller 9 where a portion of the propane is vaporized by opening valve 11 on line 10. The vaporized propane being released through valve 11 passes through line 10 to compressor 12 where the propane vapors are compressed which then pass through line 14 to condenser 15 where the compressed vapors are reliquefied and returned to propane storage tank 5 via line 16. By reducing the pressure in chiller 9 to approximately 20 to 65 lbs. per square inch, the temperature of the remaining propane will be lowered to approximately 10° F. to 40° F. The chilled propane is withdrawn from the bottom of chiller 9 via line 17 controlled by valve 18 and is passed by pump 19 into the first leaching column A via lines 20, 20a controlled by valve 21a and line 22a controlled by valve 23a.

When the required amount of propane has been introduced into the leaching column A, the waxy oil at an appropriate temperature is sprayed into the vessel. The temperature at which the waxy oil is heated prior to spraying it into the cold leaching solvent will depend upon whether it is desirable to solidify the sprayed waxy particles in the form of cornflake-like shapes or as pellets, discs or strings when the waxy oil is contacted with the cold leaching solvent. We have found it desirable to effect the solidification of the sprayed waxy oil droplets as cornflake-like shapes since it requires less time for the leaching solvent to leach the oil from the solidified wax structures although the solidification as pellets, discs or strings is within the scope of our invention. The solidification of the waxy oil in the cold leaching solvent as cornflake-like shapes may be accomplished by first heating the waxy oil so that it assumes the viscosity of 350 seconds Saybolt Universal and then spraying the waxy oil through a spray head provided with a large number of small nozzles. The introduction of the waxy oil into the cold leaching solvent at a viscosity above 350 seconds Saybolt Universal results in the solidification of the waxy stock upon contact with the solvent as pellets, discs or strings. For the S. A. E. 20 waxy distillate obtained from the Santa Fe Springs crude oil, it has been found that the desirable temperature of heating prior to the spraying is about 110° F. or 120° F. For an S. A. E. 50 stock the temperature should be about 150° F. This temperature, of course, will vary with other waxy stocks. Also, the temperature of heating will depend somewhat upon the size of the nozzles employed in the spray head as will be readily understood by those skilled in the art.

We have obtained good results when using liquid propane as the leaching solvent with as low as three volumes of the propane to one of the waxy oil in the initial leaching column A. However, by employing larger amounts of propane, say 10 volumes of the propane to one of the oil, the leaching of the oil from the solidified particles of oil and wax will take place more rapidly and also less foaming will be encountered during the addition of the last part of the waxy oil. However, it is not economically desirable to employ more than 10 volumes of propane due

to the large capacity of the leaching columns required to effect the leaching operation and the cost of the chilling and due also to the cost of chilling and recovering additional solvent.

It will be observed that when employing a liquefied normally gaseous hydrocarbon, such as liquid propane, as the leaching solvent, a portion of the solvent will vaporize immediately upon contact with the relatively warm waxy oil thus creating a turbulent condition in the column. This is not desirable since the leached wax matrices being fragile are readily disrupted by any substantial agitation into finely dispersed wax particles which are difficult to separate from the oil solvent solution. It is therefore preferable to maintain quiescent leaching conditions and to prevent substantial boiling in the leaching column. This may be accomplished by controlling the vaporization of the solvent in the columns or by maintaining pressure therein. The pressure may be controlled by means of valves 85a, 85b, 85c, 85d, on lines 86a, 86b, 86c, 86d, respectively, of leaching columns A, B, C, D, respectively. If desired, an extraneous gas, such as air, carbon dioxide or other non-miscible gases may be introduced into the columns to create a pressure therein and suppress boiling. Also, in the case where a liquefied normally gaseous hydrocarbon is employed as a leaching solvent which has a vapor pressure greater than atmospheric at the leaching temperatures, valves 85a, 85b, 85c, 85d, on lines 86a, 86b, 86c, 86d, respectively, are employed for maintaining the pressure in the columns so that the desired temperature may be maintained in the leaching columns. It is also desirable to prevent infiltration of heat from the outer walls of the leaching columns since this causes propane to boil therein. One method for preventing this, is to jacket the outer walls of the columns and to circulate a cold medium through the jacket.

The waxy stock is allowed to remain in contact with the leaching solvent for a period of time, say 15 minutes to 2 hours, to allow a substantial quantity of the oil occluded in the wax matrices to be leached by the solvent. At the end of the leaching period, the fresh propane is introduced at the top of the vessel from propane chiller 9 and valve 23b is opened and the solution is drawn off from the first leaching column A and is transferred by pump 58a through lines 24a, 25a and 22b into the second leaching column B. The introduction of solution of oil and solvent into the second leaching column B is continued until substantially all of the solution in column A is displaced with fresh propane whereupon waxy oil from tank 1 is sprayed by line 2b controlled by valve 3b through spray head 4b, the introduction of waxy oil being continued until the required amount of oil has been introduced into the column B. In the meantime, the wax structures in column A are subjected to leaching with fresh solvent which lowers the oil content of the wax structures. When sufficient leaching time has been allowed in column B, the oil propane solution is transferred via the bottom of the leaching column B by pump 58b through lines 24b, 25b and 22c controlled by valve 23c into the final leaching column C. Simultaneously therewith, the relatively more diluted propane oil solution from leaching column A is transferred to leaching column B and fresh propane is introduced into leaching column A.

Waxy oil is then introduced into the column C via lines 2 and 2c controlled by valve 3c and spray

head 4c and the introduction of the waxy oil is continued until the desired amount of oil has been solidified in column C.

The displacement of propane oil solution in leaching column A is repeated a number of times, depending upon the total number of stages or extraction vessels in the system, say three as shown in the drawings, until substantially oil-free propane is withdrawn from the bottom of the leaching column. The oil propane solution is then withdrawn from the bottom of the last leaching stage C via pump 58c and lines 24c and 27c controlled by valve 28c and is passed through line 29 to either of the alternate chillers 31 and 33 via either line 30 controlled by valve 32a or line 32 controlled by valve 32a. The solution in chillers 31 and 33 is further chilled to a temperature sufficiently low to precipitate substantially all of the remaining wax contained therein, preferably by gradually reducing the pressure to substantially atmospheric by operation of valves 34a and 35a on lines 34 and 35 respectively. This causes propane to be vaporized which chills the remaining solution to the desired dewaxing temperature, the propane vapors being withdrawn via line 34 or 35 depending upon which of the chillers are in operation. The vapors then pass into line 36, are compressed by compressor 37 and are returned to propane storage tank 5 via line 38, cooler 15 and line 16. Chilling is preferably accomplished at a rate not in excess of substantially 3° F. per minute.

The chilled oil, propane and wax slurry is withdrawn from the bottom of the chillers 31 and 33 via lines 39 and 40 respectively, which are controlled by valves 39a and 40a respectively, the mixture then passing into line 41 is pumped by pump 42 through line 43 to filter 44 where the wax precipitated from solution by chilling is separated from the oil and solvent. The clear solution is then passed through line 45 through heat exchanger 46 where the temperature of the clear solution is raised to a temperature sufficient to vaporize the propane, after which the preheated solution is passed through line 47 into evaporator 48. The propane is vaporized from the oil in evaporator 48, aided by steam circulated through closed coil 49, the vapors passing through mist extractor 53 and are withdrawn via line 51 controlled by valve 51a and are sent to propane storage tank 5 via cooler 52, lines 53 and 10, compressor 12 and condenser 15. The dewaxed oil is withdrawn from the bottom of the evaporator via line 54 and is pumped by pump 55 through valve 56 into dewaxed oil storage tank 57.

The separated wax in filter 44 is withdrawn via line 73 controlled by valve 73a and is passed through heat exchanger 74 and line 75 into evaporator 76 provided with closed heating coil 77 and mist extractor 78 in which the wax is depropanized. The depropanized low melting point wax is withdrawn from evaporator 76 via line 80 and is pumped by pump 81 through valve 82 into storage tank 83. Propane vaporized in evaporator 76 is withdrawn via line 79 controlled by valve 79a and passes via line 84 into line 51.

As stated above, when substantially all of the oil and soft wax or iso-paraffins have been leached from the wax matrices with fresh propane in the first leaching column, the latter is cut out of the system and the fresh propane is introduced into leaching column B which then becomes the first leaching column in the system. Leaching column D is then cut into the system by filling the vessel with propane oil

solution withdrawn from leaching column C via lines 24c, 25c and 22d controlled by valve 23d. This, of course, is accomplished until the solution in column B has been displaced with fresh liquid propane. Waxy oil is then sprayed into column D via lines 2 and 2d controlled by valve 3d and spray head 4d. As in the case of column A, when the leaching operation in column B is substantially completed, the propane oil solution in column D is passed to the chillers via lines 24d, 27d controlled by valve 28d, line 29 and either line 30 or 32. The propane solution from column B is then transferred to column C and thence to column D, fresh propane being introduced into column C via line 20c controlled by valve 21c and line 22c controlled by valve 23c. Column C then becomes the first leaching column, column B the second leaching column and column A after removing the wax therefrom becomes the third leaching column.

We have thus described a process for separating wax from oil involving leaching of the wax structures wherein a plurality of leaching columns are provided so interconnected that the flow from one leaching column may be diverted from one to the other and the leaching columns are so interconnected that they may be rotated in such manner that a semi-continuous operation may be carried out with the use of an extra leaching column. Also, in the above description, discontinuous batch leaching is shown. However, the invention is not to be considered as limiting thereto since it embraces continuous flow of leaching solvent from one column to another, that is, the operation may be carried out in such manner that fresh propane is continuously introduced into the first leaching column and concentrated propane oil solution containing iso-paraffins or soft wax is withdrawn from the last leaching stage and passed to the chillers. Thus, we may operate in such manner that the oil solvent solution and soft wax may be continuously passed to the chillers. The production of the oil propane solution from the last leaching column is controlled by time, for example, if approximately one hour is calculated from the rate of flow of wash propane in the system to be required for displacing the propane oil solution in any of the leaching columns, then the first hours withdrawal of propane solution from the vessel just charged with oil is sent to the chillers. The propane solution withdrawn subsequently is then used as wash propane in the second leaching column. If in charging an empty leaching column for a new cycle, all of the propane solution required for leaching and washing the waxy stock for the first time is accumulated in the leaching column before introducing the waxy stock, it is desirable, although not necessary, to interrupt the flow of wash propane while the waxy stock is being introduced, giving periodical interruptions in the flow of both wash propane and propane oil solution. To avoid interruption in the flow of wash propane, the introduction of waxy stock into the fresh or empty leaching column may be begun after only a part of the propane solution required for filling the leaching column is introduced and the rate of addition of waxy stock be adjusted so that the addition of waxy stock is completed by the time the liquid reaches the proper level.

In order to minimize the amount of entrained wax particles in the solution withdrawn from the bottom of the leaching vessels, filter beds 59a, 59b, 59c, 59d, are provided at the bottom of the

leaching vessels to hold the leaching wax structures in the column while the propane solution is allowed to wash through it. For this purpose, any desirable material may be provided, such as pads of steel wool, broken glass, stones, pebbles, sand, graded aggregate, tile, sawdust, fire brick and/or canvas filter.

After the washing of the wax structures in any extractor is considered complete and the extractor is cut out of the system, the wax structures are then removed from the leaching column and are distilled to recover the wax and solvent. The removal of the wax structures may be accomplished by introducing a warm liquid into the leaching columns via lines 60a, 60b, 60c and 60d to partially or totally melt the wax structures, the melted wax being withdrawn from the bottom of the leaching columns by pumps 58a, 58b, 58c, and 58d, and valves 61a, 61b, 61c, and 61d respectively, and passed into line 62 controlled by valve 62a to heater 63 where the structures are heated to a sufficient temperature to vaporize the propane after which the mass is passed through lines 64 into evaporator 65 where the propane is vaporized from the wax aided by steam circulating through closed coil 66, the vaporized propane passing through mist extractor 67 into line 68 controlled by valve 68a. The high melting point wax withdrawn from the bottom of the evaporator 69 is pumped by pump 70 through valve 71 into high melting point wax storage tank 72. This wax may be further treated such as with sulfuric acid and alkali and/or clay to produce a high melting point water white wax suitable for the production of candles and the like.

In another method for removing the wax from the leaching column the wax structures may be partially disintegrated by mechanical agitation such as by means of scrapers or stirrers built into the leaching columns or by blowing the structures with propane or other gas. The mass may be transferred from the bottom of the leaching column by means of a screw conveyor or transferred as a slurry by pressure, the slurry being produced if desired, by mixing the wax with propane to form a pumpable mass. This mass may be filtered, centrifuged or settled to concentrate the wax particles and recover chilled propane suitable for washing other wax structures. The concentrated wax or wax cake may be washed with further quantities of fresh propane to reduce the oil content still further. The use of a continuous oil drum type filter is preferred for washing and filtering the wax taken out of the leaching columns. The wash propane may be employed for washing other wax structures in keeping with the spirit of the invention.

When employing filter beds in the extraction columns, the wax structures may be removed by first withdrawing as much of the liquid propane as possible through the filter bed without however bringing the liquid level below the top edge of the filter bed. The filter is then back blown with propane gas and additional wash propane is introduced at the bottom of the filter bed. The back blowing washes wax out of the filter bed into the wax slurry on the top. The back blowing can be very violent, if desired, in fact so violent that the entire filter bed is blown up into suspension along with the wax in the propane liquid which will have now been brought to a convenient height in the extraction vessel. Upon stopping the violent agitation by blowing the heavy filter bed material will settle with extreme rapidity leaving practically all of the wax suspended

as a slurry in the propane phase which can then be decanted off at a point just above the top of the filter bed. In this manner the filter is then cleaned and ready for another cycle. In beginning a fresh cycle the first production may be recycled if cloudy.

The foregoing invention has been described as used for the separation of wax from an S. A. E. 20 lubricating oil distillate produced from Santa Fe Springs crude petroleum. It should be understood, however, that the invention is equally applicable for the separation of wax from any wax-bearing oil whether it consists of a lubricating oil distillate or a waxy petroleum residue. The invention is also applicable for the fractionation of waxes containing only a small amount of oil such as slack waxes which have been separated from petroleum fractions.

In some instances, we find it desirable to introduce the wax-oil mixture into the cold leaching solvent as a finely divided solid. The wax-oil mixture may be solidified by lowering its temperature to produce a solid mass which can then be mechanically broken up by any suitable means into ribbons, strings, or irregular shaped particles which could then be mechanically introduced into the cold solvent. It is desirable to break the mass into such particles that the solvent need not penetrate over $\frac{1}{8}$ th inch sections and preferably not over $\frac{1}{16}$ th inch sections as sections thicker than this do not leach within a reasonable length of time.

There are several methods which are applicable for solidification and break-up of the oil-wax mixture. One method involves the solidification of the oil and wax mixture in blocks or rods which is then broken up by slicing off thin wafers by means of warmed knives, similar to a butcher's slicing machine.

In another method, the wax-oil mixture is maintained in a trough in a fluid condition by heating, if necessary. A chilled cylinder is allowed to dip into the liquid which is rotated at such a speed that a film of solidified wax-oil mixture of the desired thickness of $\frac{1}{8}$ th to $\frac{1}{16}$ th inch is deposited on the cylinder. This film may then be removed by a scraper to produce flakes of the solidified material which can then be fed into the cold leaching solvent.

In another method, the oil-wax mixture is chilled to a temperature below the ordinary solidification point but still the temperature is sufficiently high that the mixture can be mechanically worked or kneaded into a plastic condition. This plastic material is then extruded through small orifices of $\frac{1}{8}$ th inch or less in diameter and preferably about $\frac{3}{16}$ ths inch. The extruded material is then allowed to fall into the cold solvent to be solidified as strings or "worms." However, in this method, the pumping of the plastic material any distance presents obvious difficulties. These may be overcome by pumping the wax-oil mixture through most of the required distance at a temperature high enough to insure liquid characteristics, but just before extrusion into the leaching vessel it is chilled in a jacketed pipe with simultaneous mechanical kneading and the degree of chilling controlled to obtain the desired plastic condition. Mechanical devices for chilling the wax-oil mixture below its solidification point and at the same time keeping the chilled material plastic by mechanical working are well known to those skilled in the art, and therefore need not be fully described herein.

The introduction of the wax-oil mixture as a

free-falling stream at a sufficiently high temperature that it is liquid, has been described above. However, in some instances it is desirable to adjust the temperature of the wax-oil mixture prior to its introduction as near the solidification point of the particular oil-wax mixture as possible.

If desired, the liquefied oil-wax mixture and solvent may be introduced simultaneously as impinging sprays in the vapor spaces of the leaching vessel and then allowed to fall together into the liquid in the vessel. The solvent may be introduced either in a pre-cooled condition or when a liquefied normally gaseous hydrocarbon is employed, it may be introduced under pressure and allowed to expand in direct contact with the oil-wax mixture. In the latter case, the expansion of the liquefied normally gaseous hydrocarbon results in a vaporization of a portion of the solvent and thus chills the remainder of the solvent and also the oil-wax mixture. The length of fall is preferably sufficient so that the oil-wax mixture is solid when it finally comes to rest in the vessel. When using a liquefied normally gaseous hydrocarbon as the leaching solvent, solidification takes place so rapidly as to be practically instantaneous. The oil-wax mixture should be sprayed through small orifices so that the resultant solidified particles present sections $\frac{1}{16}$ th to $\frac{1}{8}$ th inch. This method of operation has the advantages of a saving in charging time when used in the countercurrent downflow leaching.

There is a tendency when employing certain solvents for the solidified oil-wax mixture to float on the solvent for such a length of time that there is a serious loss of time efficiency in charging the wax-oil mixture to the leaching vessel. This difficulty may be overcome by gentle mechanical agitation of the solidified particles in the leaching vessels such as by means of stirrers or a portion of the solvent or solvent and oil from the bottom of the leaching vessel may be recirculated so that a stream of the liquid is continually sprayed over the surface of the oil-wax mixture in the leaching vessel. This will enable the solidified wax-oil particles to settle to the bottom of the vessel.

In some cases it is desirable to introduce other materials into the oil-wax mixture for the purpose of strengthening the solidified particles. We have found this to be particularly desirable in oil-wax mixtures of low wax content. We have found that when the wax structure after the removal of the oil or oil and soft waxes represents less than 12% to 15% by volume of the original wax-oil mixture, it is very thin and tenuous and is easily crushed by the weight of the wax above it, or it is broken up by boiling or by eddy currents of the solvent. When broken up, the wax structure settles and becomes compacted into an impervious mass which retards or prevents further leaching. We have found that the addition of other materials to the wax-oil mixture before solidification will prevent this occurrence. For this purpose we may use materials which have heretofore been used to improve filtration characteristics of the chilled mixtures containing precipitated wax. Such materials include asphalt, cracked petroleum residues, oxidized wax and the like. In some instances we find it desirable to increase the wax content of the particular wax fraction desired to be removed by leaching so that the wax content represents at least 12% to 15% by volume of the wax-oil mixture introduced into the leaching vessel. If desired, emulsified water in the oil-wax mixture may be used for strengthening the wax

structures. If desired, the laying down of alternate layers of solidified oil-wax mixture and ice, asphalt or sand or the random mixture of the solid particles of ice, asphalt or sand in the solidified oil-wax mixture in the solvent may be employed.

The separation of the added asphalt and the like from the wax after leaching may be accomplished by breaking up the leached structures after the desired degrees of leaching has been accomplished. This may be done either in the leaching vessel or in a separate container but preferably in the latter. The mixture may be heated to a temperature which is sufficiently high to dissolve all the wax and allowing the mixture to settle. The asphaltic materials or oxidized wax and the like present will then separate out either in a liquid or solid phase and are separated from the wax by decantation or filtration. If desired, the wax slurry as removed from the bottom of the extraction vessels may be heated without first removal of solvent and the heated mixture then passed to a quiescent zone under pressure where the asphaltic bodies will settle out.

To illustrate the advantages obtainable by carrying out the process of extracting wax from oils forming the subject of our invention, the following is submitted which, however, is not to be considered as limiting our invention.

An S. A. E. 20 waxy distillate obtained from a Santa Fe Springs crude oil is first enriched with about 8% by volume of hard wax previously obtained from the same stock and is then heated to a temperature of about 110° F. or about 20° F. above its pour point so that the waxy oil has a viscosity of about 350 seconds Saybolt Universal. The pre-heated waxy oil is then sprayed into three leaching stages in accordance with the foregoing disclosure. Propane at about 20° F. and maintained under pressure of about 30 lbs. per square inch is employed as the leaching solvent. The initial ratio of propane to oil employed in the first stage of leaching was approximately 5 volumes of propane to one of the waxy oil, and the total amount of propane passing through the leaching vessel for complete extraction of the charge was 15 volumes based on original charge of waxy oil. The propane oil solution withdrawn from the bottom of the first stage was employed as leaching solvent in the second stage and that withdrawn from the bottom of the second stage was employed in the third stage. In the subsequent leaching stages the pressure and temperature conditions were maintained substantially the same as that maintained in the first leaching stage. The propane-oil solution from the third stage of leaching, corresponding to the third use of the propane, at a temperature of about 20° F. was further chilled by evaporative refrigeration, that is, by vaporizing propane from the chilled mixture at a rate not substantially greater than 3° F. per minute until a temperature of -40° F. was attained in the chiller. The chilled mixture was then filtered to remove the soft wax which precipitated upon chilling. Upon completion of the run approximately 75% of dewaxed oil was produced having a pour point of -5° F. The high melting point wax was recovered from the leaching columns, after depropanization, had a melting point of 145° F. and represented approximately 16% of the enriched waxy oil. Approximately 17% of the soft wax was recovered by further chilling the propane-oil solution from the leaching column and had a melting point of 100° F.

As another example, an S. A. E. 20 waxy distillate in which 0.5% by weight of oxidized wax had been dissolved was commingled with 250 volume percent of liquid propane at a temperature of approximately 140° F. The solution was chilled by gradually releasing the pressure to atmospheric until a temperature of about -40° F. was obtained in the chiller. During chilling, make-up propane was added to the charge in order to maintain the ratio of 2.5 volumes of propane to one of the waxy stock. The chilled mixture was then filtered to separate the wax and added filtration aid, i. e. the oxidized wax from the solution of propane and low pour point dewaxed oil. The wax cake was then depropanized by distillation to produce a slack wax of about 126° F. melting point.

The slack wax was then purified in accordance with the manner described as follows: It was heated to a temperature of about 145° F. and then extruded through small orifices of about $\frac{1}{16}$ " in diameter and allowed to fall into a body of cold solvent consisting of a mixture of normal and iso-butane maintained at atmospheric pressure and at a temperature of about 20° F. The melted wax was solidified upon contact with the cold butane into worm-like particles. After leaching the wax structures with liquid butane at 20° F. in three stages as aforesaid, employing approximately 15 volumes of the liquid butane, the leached wax structures were discharged from the leaching vessel in the form of a slurry, a portion of the butane being removed along with the wax structures to form the slurry.

The slurry was then heated without distilling off the butane to a temperature of about 200° F. under a pressure of about 220 lbs. per sq. in. and was then passed to a settling chamber where it was allowed to remain quiescent for a period of time. During this quiescent period, settling of the filtration aid took place so that a practically clear butane-wax solution free from suspended solid material was decanted from the settling vessel. The bottoms in the settling vessel consisted largely of the filtration aid. The latter was separated from the solution of butane and wax and after heating to remove contained butane, was recycled for admixture with waxy stock to be dewaxed.

The warm solution of butane and wax was decanted and filtered to remove last traces of entrained solid particles and was then distilled to separate the butane from the wax to produce a high melting point wax. This wax was then treated at a temperature of about 175° F. with about 25 lbs. of 100% H₂SO₄ per barrel of the melted wax. The acid-treated wax was then treated with an adsorbent clay in the proportion of 10% by weight at a temperature of about 350° F. and was then filtered. The thus treated wax had a melting point of 146° F., an NPA color of 1.5 when melted and an oil content of less than $\frac{1}{4}$ %. In some cases we find it desirable to acid and clay treat the wax in a solution of a solvent such as butane, at an elevated temperature. In most cases it is not necessary to treat the acid treated wax or wax solvent solution with alkali when clay treatment is employed although this may be employed.

The solution of butane, oil and soft wax separated from the slurry of hard wax was also distilled to separate the butane from the solution of oil and soft wax, i. e., the foots oil. If desired, the foots oil may be mixed with the original stock undergoing dewaxing, i. e., the S. A. E.

20 waxy distillate in order to recover as much of the oil as possible or it may be subjected to releaching by spraying it at a temperature of about 120° F. in body of liquid propane maintained at a temperature of about -40° F. in which case a low pour point oil may be separated from the chilled structures to produce a low melting point wax.

In the foregoing example, we have described a process wherein a mixture of low and high melting point waxes containing some oil is separated from a waxy distillate by the solution and precipitation method employing liquid propane as a diluent-refrigerant. The high melting point wax was recovered from the separated waxes by a leaching process in liquid butane. Instead of separating the mixture of waxes by the solution and precipitation method, we find it desirable to separate the mixture by leaching in liquid propane at a temperature of -40° F. and then fractionate the mixture of waxes into a high melting point wax and foots oil by introducing into the vessel containing the mixture of waxes, liquid propane under a pressure sufficient to provide a temperature of about 20° F. in order to allow the latter to dissolve the foots oil from the solidified wax structures, and thus produce the high melting point wax. The solution of foots oil in the liquid propane at a temperature of 20° F. may then be chilled by evaporative refrigeration, i. e., by reducing the pressure to atmospheric so as to chill the solution to -40° F. and thus precipitate the soft wax which may be separated from the mixture by melting, filtering or centrifuging.

The foregoing description of our invention is not to be taken as limiting since many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

We claim:

1. A process for separating wax from a wax-oil mixture which comprises chilling a waxy oil to a sufficiently low temperature to precipitate a mixture of soft and hard waxes, separating said mixture of soft and hard waxes from the oil to produce a low pour point oil, introducing said mixture of soft and hard waxes into a cold solvent capable of dissolving the soft wax but incapable of dissolving the hard wax at the temperature employed, solidifying said mixture of waxes by contact with said solvent and allowing said solidified mixture of waxes to remain in contact with said solvent for a sufficient period of time to permit said solvent to dissolve the soft wax, separating the solution of soft wax from the hard wax.

2. A process as in claim 1 in which the solvent employed comprises liquid butane.

3. A process for separating wax from a wax-oil mixture which comprises mixing a waxy oil with a small quantity of a filter aid, chilling the mixture of a waxy oil and filter aid to a temperature sufficiently low to precipitate a mixture of hard and soft waxes containing said filter aid, separating the precipitated hard and soft waxes and filter aid from the oil, heating said separated mixture to melt the same, introducing said mixture into a relatively large body of a cold solvent maintained at a temperature sufficient to dissolve oil and soft wax contained in said mixture but not substantial quantities of the hard wax, solidifying said mixture of waxes by contact with said solvent and allowing said mixture to remain in contact with said solvent

for a sufficient period of time to permit said solvent to dissolve the soft wax and contained oil, separating the solution of soft wax from the hard wax containing filter aid, mixing the hard wax
5 and filter aid with a diluent and heating said mixture to melt the wax, and separating the filter aid from the solution of hard wax and diluent.

4. A process for separating wax from a mixture containing relatively hard wax, relatively
10 soft wax and oil which comprises first separating a mixture of the relatively hard wax and the relatively soft wax from the oil, remelting said mixture of hard and soft waxes, introducing
15 said mixture of relatively soft and hard waxes in the substantial absence of a diluent into a solvent capable of dissolving the soft wax but incapable of dissolving the hard wax at the temperature employed, solidifying said mixture of
20 waxes by contact with said solvent and allowing said solidified mixture of waxes to remain in contact with said solvent for a sufficient period of time to permit said solvent to dissolve the soft wax but not appreciable quantities of hard
25 wax and separating the solution of soft wax from the hard wax.

5. A process according to claim 4 in which the solvent employed is normally gaseous.

6. A process as in claim 4 in which the solvent employed is normally liquid.
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7. A process for separating wax from a wax-oil mixture which comprises commingling said wax-oil mixture with a diluent, chilling the mixture to a sufficiently low temperature to precipitate a mixture of soft and hard waxes, separating
35 said mixture of soft and hard waxes from the oil and diluent, heating said mixture of soft

and hard waxes to melt the same and separating diluent therefrom, congealing said melted wax mixture by contact with a cold solvent maintained at a temperature sufficient to dissolve oil and soft wax but not substantial quantities of
5 hard wax contained in said congealed mixture, extracting the oil and soft wax contained in said congealed wax mixture by means of said solvent to leave a matrix of relatively hard wax substantially free from relatively soft wax and oil
10 and separating the solution of soft wax from the solidified hard wax.

8. A process as in claim 7 in which the solvent employed to dissolve the soft wax content from the mixture of soft and hard waxes is normally gaseous.
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9. A process as in claim 7 in which the solvent employed to dissolve the soft wax content from the mixture of soft and hard waxes is normally liquid.
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10. A process as in claim 7 in which the solvent employed to dissolve the soft wax content from the mixture of soft and hard waxes is normally liquid and has chemical properties similar to acetone.
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11. A process according to claim 7 in which the soft wax separated from the hard wax is subsequently mixed with the wax-oil mixture to be dewaxed.

12. A process according to claim 7 in which
30 the solvent employed to dissolve the soft wax content is different from the diluent employed to separate the mixture of soft and hard waxes from the oil.

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