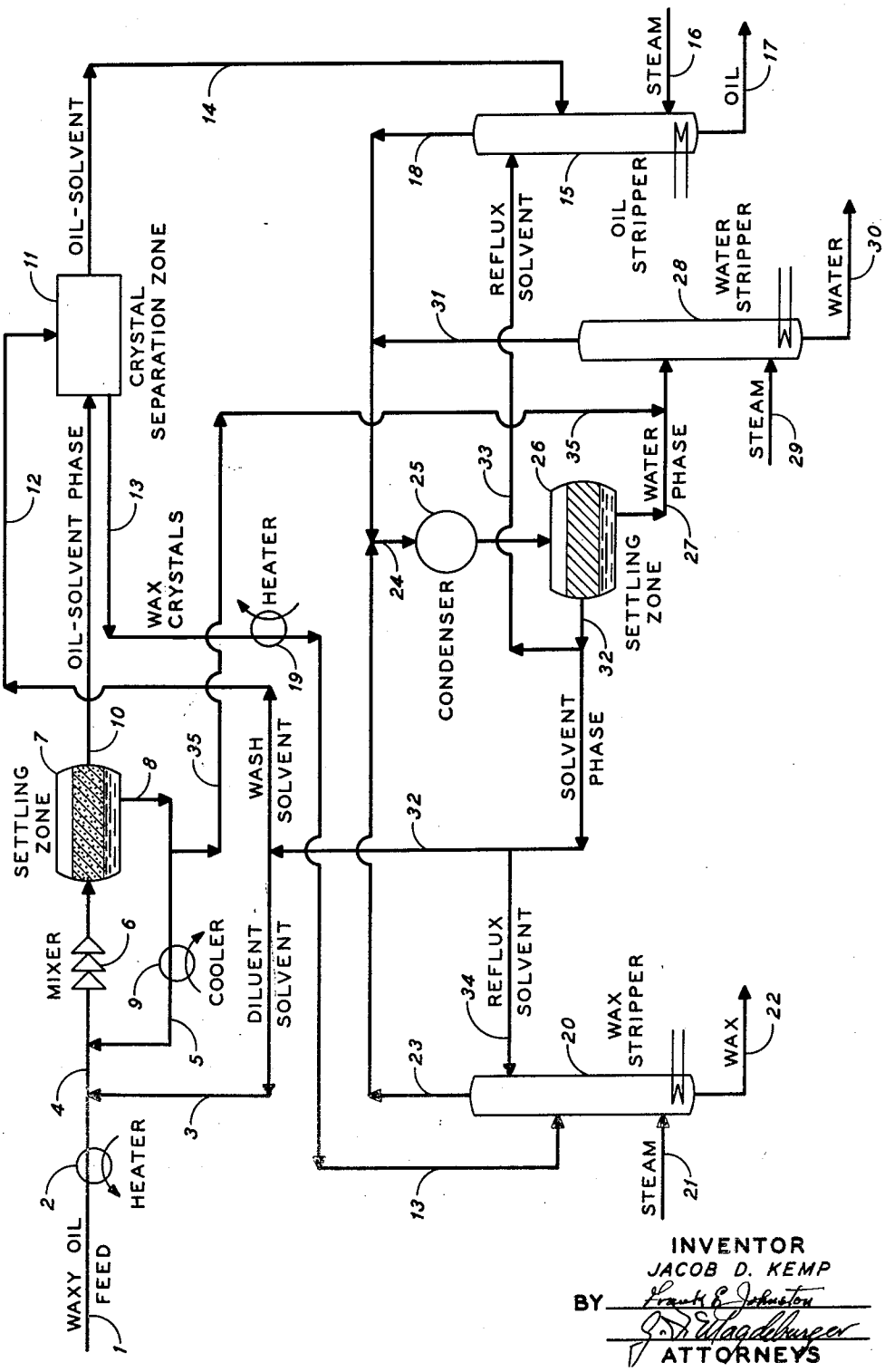
Dec. 4, 1962 J. D. KEMP 3,067,125

DEWAXING PROCESS

Filed Sept. 30, 1959



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United States Patent Office

3,067,125

Patented Dec. 4, 1962

3,067,125

DEWAXING PROCESS

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Filed Sept. 30, 1959, Ser. No. 843,412

4 Claims. (Cl. 208—33)

This invention relates to processes for the solvent dewaxing or de-oiling of wax-bearing petroleum oils. In particular, the invention is concerned with a method of crystallizing wax from an oil-solvent solution by direct chilling with cold water.

The removal of paraffinic constituents in the nature of wax from various hydrocarbon streams is widely practiced, for example, either as a means of producing wax or of producing a low pour point lubricating oil; or both objects may be served in some cases, depending upon the properties of the hydrocarbon oil treated. Various methods have been devised for separating the wax from the oil, the most common of which is generally termed, "solvent dewaxing." In a typical solvent dewaxing process the hydrocarbon oil feed is first diluted with an organic solvent, then chilled by indirect heat exchange, and the crystallized wax is then separated by filtration. The solvent employed is often a low molecular weight ketone containing 3–6 carbon atoms, such as methylethylketone (MEK) or its homologs. These materials exhibit a selective solvent action for the nonwaxy constituents of the oil at low temperatures, whereby rejection of the paraffin wax from the oil-solvent solution is facilitated in the crystallization step. However, in the proportions used the initial warm mixture of ketone and hydrocarbon oil feed presents a completely homogeneous solution. The solvent power of the ketone may be adjusted by adding one or more other solvents, such as benzene, toluene, or other aromatic solvents. The term "solvent" is used herein with reference to the organic diluent, whether of the single ketone class or the combined ketone plus aromatic class.

In a typical solvent dewaxing process of the prior art the wax-bearing hydrocarbon oil and the solvent are mixed together at a temperature above the temperature at which wax will separate out. The solution is then passed through a multitude of serially arranged scraped chillers wherein the temperature is slowly reduced in successive stages, and the wax which separates and crystallizes is continuously removed from the walls of the heat exchangers. Generally, the temperature is ultimately lowered to 0° F. or below, frequently to —20° F., depending upon the degree of wax removal desired. In order to avoid the formation of ice in the low temperature chillers, it is essential that the solvent used be relatively free of dissolved or entrained water. The crystallized wax is commonly recovered from the slurry of wax in oil-solvent liquid by the use of rotary vacuum filters in one or more stages depending upon the quality of wax desired. In the filtration step the wax cake is generally washed with additional solvent, dried with a flow of inert gas provided to reduce the fire hazard, and discharged by a gas blowback. The inert gas, for example, flue gas, may be continually recirculated through a closed system, and it must be refrigerated to prevent melting of the crystals and dehydrated to prevent icing of the filters.

It is a principal object of this invention to provide a simplified solvent dewaxing process which eliminates the use of scraped chillers, and which, by operating at higher temperatures, permits the use of wet solvent and permits the elimination of flue gas dehydration facilities. I have found that the above and other objects may be realized by employing a novel process wherein the oil-solvent solution is chilled by mixing it with cold water. In the

practice of the invention the wax-bearing oil is first diluted with a solvent selective for the non-paraffinic constituents, preferably at a temperature above the temperature at which wax will separate, to form an oil-solvent solution. The solution so obtained is then chilled to a temperature at which wax separates and crystallizes by mixing it with a nonsolvent recycle stream comprising water prechilled to a lower temperature. The mixture so obtained is then separated into an oil-solvent phase containing the wax crystals and a water phase. The water phase is continuously withdrawn and cooled for admixture with additional oil-solvent solution as the aforesaid prechilled recycle stream. The crystallized wax is then physically separated out of the oil-solvent phase by conventional procedures, such as settling, centrifugation, or filtration.

By proceeding in this manner the need for scraped chillers is eliminated since the sensible heat and the latent heat of crystallization are removed by direct heat exchange to the water in the liquid mixture. Furthermore, it is not necessary that the solvent be predried since the temperatures in the system are all above the freezing point of water and a separate water phase is already present. Likewise, if a vacuum filter system is used, it is not necessary to dehydrate the inert gas used for blanketing and/or filter cake blowback since there is no possibility of ice formation. I prefer to perform the crystal separation by centrifugation in a continuously fed solid bowl horizontal centrifuge having an internal rotating screw for discharge of solids, whereby the use of a flue gas system is dispensed with entirely.

The invention may be best understood by reference to the attached drawing, which illustrates a preferred specific embodiment of the invention.

As shown, the waxy oil from which it is desired to remove the wax constituents is shown entering the process via line 1. The waxy oil may comprise any wax-bearing hydrocarbon stream, such as those of lubricating oil viscosity or heavier. Where heavier stocks are used, it is desirable that the material be well distilled to exclude tars and asphalts, since these materials have been found to result in the formation of small crystals and a gummy filter cake. A preferred feed stock comprises a clean broad distillate of a waxy crude. The oil preferably is warmed in heater 2 to insure complete solution of all the constituents therein. Filtration difficulties associated with wax lumps have been observed when the oil was not first made homogeneous. Diluent solvent is then added via line 3 to give in line 4 a solution of oil in solvent which is above the wax nucleation temperature. The ratio of solvent added at this point to oil feed will vary with the nature of the feed stock and the solvent used, but generally it is in the range 1:1 and 1:6, solvent volume: oil volume.

The solvent employed may comprise any of the conventional dewaxing solvents or mixtures thereof. The essential characteristics of the solvent selected are that it exhibit a decreasing solubility for paraffin wax as the temperature is lowered, while selectively retaining the non-paraffinic hydrocarbons in solution, and that it be relatively immiscible with water at normal temperatures, but not necessarily completely immiscible. I prefer to use methylethylketone, which exhibits the above properties, since it is readily available and has been found to be particularly well suited for use with a variety of feed stocks. Additionally, methylethylketone has certain other desirable properties, namely: (1) it is less dense than water, (2) has a boiling point below that of water, (3) forms a favorable constant-boiling mixture with water, and (4) is readily recovered from the wax and oil products by steam-stripping. The solvent may be dried, if desired, but a particular advantage of the process of this invention is

that wet solvent, even water-saturated solvent, may be utilized.

The warm oil-solvent solution in line 4 is then chilled by directly admixing with cold water introduced through line 5. The water temperature and the volumetric ratio of water added to the volume of oil-solvent solution are so correlated as to bring the entire mixture to the desired final crystallizing temperature and to crystallize the wax. For minimum water circulation the water temperature is maintained close to but slightly above its freezing point. Usually the water temperature is above 40° F. A suitable mixing device, such as mixing valve 6, is desirably provided in order to insure intimate contacting of the cold water and the warm oil-solvent solution prior to introduction into settling zone 7. In settling zone 7, the temperature is below the wax crystallization temperature but above the freezing point of water. In general, the temperature will be above 60° F. Under these conditions the water, being immiscible with the oil-solvent solution, settles out as a separate phase below a supernatant oil-solvent phase in which the wax crystals are suspended. The presence of the discrete water phase helps to decrease the solubility of the wax in the oil-solvent liquid, such that the waxy constituents are rendered substantially insoluble in either phase and separate and crystallize without the necessity for using extremely low temperatures. It will be understood that the settler 7 may be equipped with suitable baffling and the like to facilitate separation and segregation of the water and oil-solvent phases.

A portion of the separated water phase is continuously withdrawn through line 8 and passed to cooler 9 where it is chilled by indirect heat exchange with a suitable refrigerating medium to the desired temperature such that on recycling the cooled water through line 5 in admixture with additional oil-solvent solution in line 4 the resulting mixture is brought to the temperature of settling zone 7. The water withdrawn through line 8 is in equilibrium with the oil-solvent phase, and consequently it will have dissolved in it some solvent and possibly a small amount of hydrocarbon, depending on the temperature and the composition of the oil-solvent phase, as will be understood by those acquainted with the art. In some cases it may be desirable to remove one or more of these constituents prior to chilling or reintroduction of the water phase. However, in most instances I prefer to recycle the water phase as is.

The oil-solvent phase, in which the crystallized wax is suspended, is withdrawn from settling zone 7 through line 10 and passed to crystal separation zone 11, which may comprise any conventional solids/liquid separation device, such as a settler, centrifuge, or filter. I prefer to use continuous centrifugation since the crystals formed by the process of this invention are well suited to this method, and the need for flue gas circulating equipment, as would be required in the case of a rotary vacuum filter, is eliminated. The crystals separated in zone 11 are preferably washed with additional diluent solvent introduced through line 12. The wash solvent, which usually comprises the major portion of the solvent used, being 2 to 6 times the volume of diluent solvent originally added to the oil, is supplied at the crystallizing zone temperature in order to avoid redissolving wax. The main functions of the wash solvent are to facilitate the solids/liquid separation by reducing the viscosity of the liquid filtrate and to displace the oil adhering to the wax crystals. Solid wax is discharged through line 13, while the liquid oil-solvent solution, including the wash solvent, leaves via line 14.

The dewaxed oil is recovered from the oil-solvent solution in oil stripper 15, which conveniently comprises any conventional fractionating or steam-stripping column. In the preferred embodiment the oil-solvent solution from line 14 is introduced into the column 15, which, of course, is equipped with contacting trays or the equivalent, reboilers, and the like, and the solvent and water are stripped from the oil using steam introduced through line 16. The purified dewaxed oil is recovered through line 17. Steam and solvent are taken overhead through line 18. Similarly, the de-oiled wax crystals in line 13 are melted in heater 19 and passed to wax stripper 20, where residual solvent and water are stripped from the wax using steam introduced through line 21. Product wax is recovered through line 22, and steam and solvent are withdrawn overhead in line 23.

I have found that the recovery of the solvent for reuse is greatly facilitated by proceeding in accordance with the preferred embodiment of my invention shown in the drawing. The overhead vapor streams comprising solvent and water from the oil stripper and wax stripper, in lines 18 and 23 respectively, are combined with the overhead water and solvent in line 31 from a water stripping operation to be described hereinafter. The combined overhead streams are fed through line 24 to condenser 25. The condensed solvent and water then pass to receiver or settling zone 26 wherein a supernatant solvent phase saturated with water separates from a water phase saturated with solvent. For example, when methylethylketone (MEK) was the solvent, the MEK phase contained 12% water by weight, and the water phase contained 25% MEK, at 85° F. The solvent-saturated water phase is withdrawn through line 27 and fed to stripper 28 where solvent is stripped from the water (rejected through line 30) by stripping with steam introduced through line 29. The overhead mixture of steam and solvent is then combined with the other overhead water-solvent streams as described previously. The water-saturated solvent phase from settling zone 26 is withdrawn through line 32. A portion of this solvent is utilized as reflux for the oil stripper through line 33 and/or the wax stripper through line 34. The bulk of the recovered solvent is utilized as wash solvent, after cooling, via line 12, while the remainder comprises the diluent initially added to the oil feed through line 3.

The direct reuse of the water-saturated solvent is not possible in conventional dewaxing processes. Consequently, it is the usual practice to redistill the wet solvent for recovery of dry solvent and a water azeotrope, which must be further treated to recover solvent. By the process of this invention the wet solvent may be used without further treatment, hence there need be no redistillation step in which a dry reflux would be required. The stripping columns in the solvent recovery section of my process all yield overhead streams of very nearly the same composition, and they may utilize reflux streams of identical composition. Thus, the overhead streams may be combined and condensed in a single unit to provide a condensation suitable for reflux to any of the columns. A significant reduction in the capital expenditure for heat exchangers is thereby realized.

Where solvent saturated with water is used directly as the oil diluent, there will be a tendency for the volume of the water phase in settler 7 to increase gradually since the solubility of water in the oil-solvent phase at the crystallizing temperature will usually be less than its solubility in pure solvent at the temperature in settler 26. To correct this situation a small amount of water may be permitted to overflow with the oil-solvent phase in line 10, or, as shown in the drawing, a small bleed stream may be withdrawn from the recycle water through line 35 and combined with the feed to water stripper 28.

Example

In this example wax was recovered from a 45–70 volume percent broad range distillate, free of tars and asphalts, of a heavy waxy crude of Far Eastern origin. It will be understood that the operating temperatures, relative quantity of solvent used, etc., will be somewhat different when treating other feed stocks. The feed had a boiling range of about 650–950° F., and contained about 40 weight percent wax. The oil was heated to 120° F.,

and then 3 volumes of oil were diluted with 1 volume of methylethylketone containing about 12 weight percent water and supplied at a temperature of 85° F. The resulting oil-solvent solution, in which all the wax was dissolved, was at a temperature of 110° F. This oil-solvent solution was chilled to 70° F. and the wax crystallized by admixing therewith 2 volumes of recycle water, prechilled to 45° F., per volume of oil-solvent solution. The recycle water contained about 10 weight percent dissolved methylethylketone. The mixture of water, oil-solvent, and crystallized wax was allowed to settle, and a portion of the aqueous phase was withdrawn, chilled, and utilized as the aforesaid recycle water. The supernatant oil-solvent phase laden with wax crystals, and still at 70° F., was fed to a Bird centrifuge, where it was contacted with about an equal volume of wet methylethylketone wash solvent, also supplied at 70° F. The crude wax discharged from the centrifuge was melted and then steam-stripped to remove residual methylethylketone and water. The wax product recovered comprised 85 percent of the wax initially present in the feed, and had an oil content of 2 percent by weight. This material is well suited for use as a feed stock to a dehydrogenation and/or cracking process for the production of olefins or other chemical intermediates. Alternately, if a high purity wax is desired for sale as such, this may be readily obtained by recrystallization and filtration, as will be apparent to those skilled in the art. The oil-solvent filtrate from the centrifuge was also steam-stripped to remove solvent and water, yielding a dry oil containing about 10 weight percent residual wax.

I claim as my invention:

1. The method of crystallizing wax from a waxy oil which comprises diluting the oil at a temperature above the wax nucleation temperature with methylethylketone (MEK), to form an oil-MEK solution, chilling the solution so obtained to a temperature at which wax separates and crystallizes by admixing therewith a recycle water stream prechilled to a lower temperature, separating the mixture so obtained into an oil-MEK phase laden with wax crystals and an aqueous phase saturated with MEK, and continuously withdrawing and cooling a portion of the aqueous phase for admixture as the aforesaid prechilled recycle stream with additional oil-MEK solution.

2. The method of crystallizing wax from a waxy crude oil distillate which comprises diluting the waxy oil at a temperature above the wax nucleation temperature with water-saturated methylethylketone (MEK), to form an oil-MEK solution, chilling the solution so obtained to a temperature at which wax separates and crystallizes by admixing with the oil-MEK solution an aqueous recycle stream saturated with MEK and prechilled to a lower temperature, separating the mixture so obtained into an oil-MEK phase containing the wax crystals and an aqueous phase saturated with MEK, and continuously withdrawing and cooling a portion of the aqueous phase for admixture as the aforesaid prechilled recycle stream with additional oil-MEK solution.

3. A process for separating wax and oil from a waxy oil which comprises crystallizing wax from a solution of the waxy oil in methylethylketone (MEK) by admixing therewith a prechilled aqueous stream, passing the mixture so obtained to a settling zone wherein an oil-MEK phase laden with wax crystals separates from an aqueous phase, withdrawing and cooling a portion of the said aqueous phase for admixture with additional oil-MEK solution, withdrawing the oil-MEK phase containing wax crystals and centrifugally separating solid wax from liquid oil-MEK to obtain a wax stream and an oil stream, separately steam-stripping said wax and oil streams thereby removing MEK streams as overhead and obtaining wax and oil products substantially free of MEK and recovering MEK for reuse from the combined overhead streams.

4. A process for de-oiling a broad range distillate of a waxy crude which comprises crystallizing wax from a solution of the waxy distillate in water-saturated methylethylketone (MEK) by admixing therewith a prechilled aqueous stream, passing the mixture so obtained to a settling zone wherein an oil-MEK phase laden with wax crystals separates from an aqueous phase saturated with MEK, withdrawing and cooling a portion of the aqueous phase for admixture with additional oil-MEK solution, withdrawing the oil-MEK phase containing wax crystals and centrifugally separating solid wax from liquid oil-MEK to obtain a wax stream and an oil stream, separately steam-stripping said wax and oil streams thereby removing MEK streams as overhead and obtaining wax and oil products substantially free of MEK and recovering water-saturated MEK for reuse from the combined overhead streams.

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