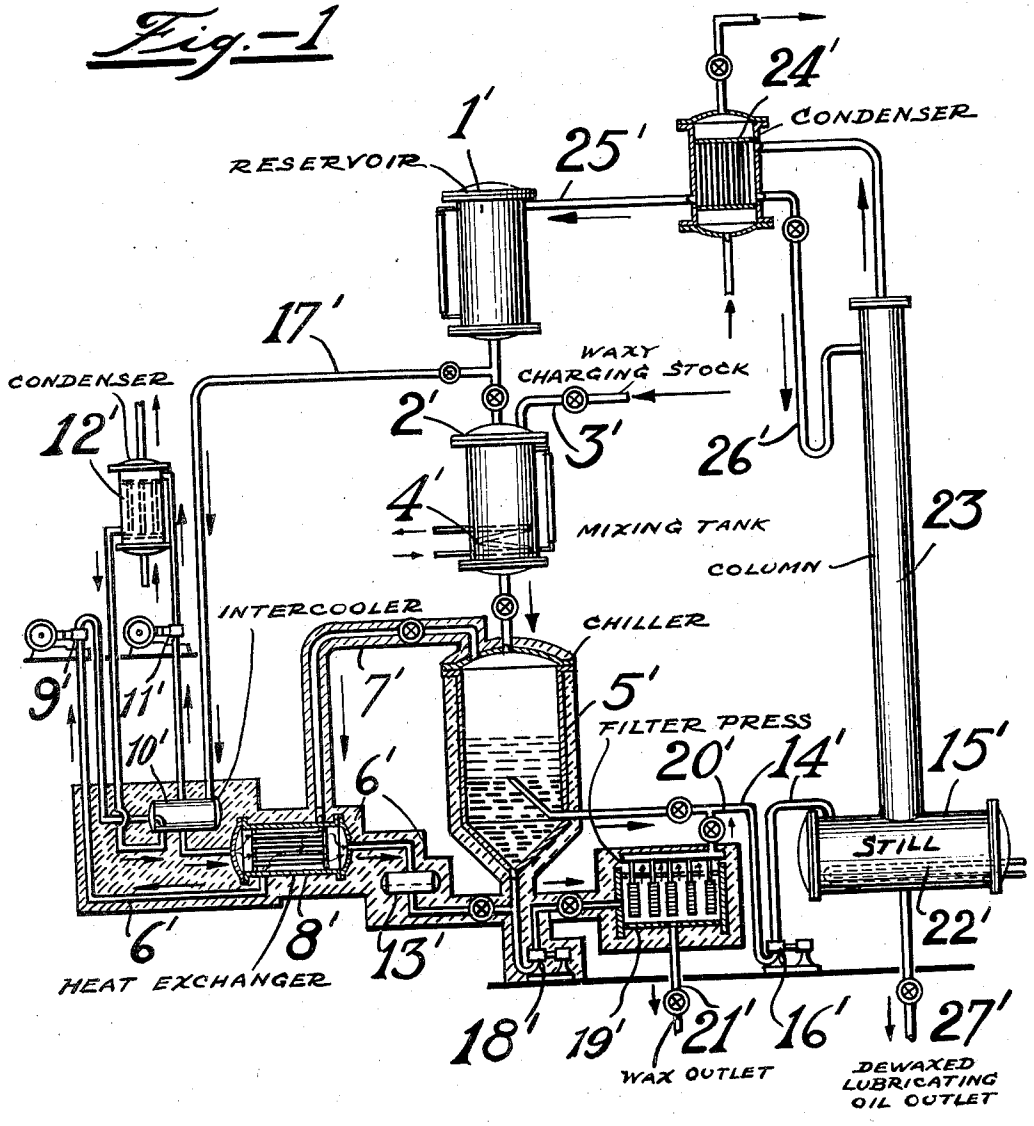
Feb. 13, 1940. W. J. EDMONDS 2,189,885

DEWAXING OILS WITH LIGHT HYDROCARBONS

Original Filed Sept. 18, 1931 2 Sheets-Sheet 1

Fig.-1



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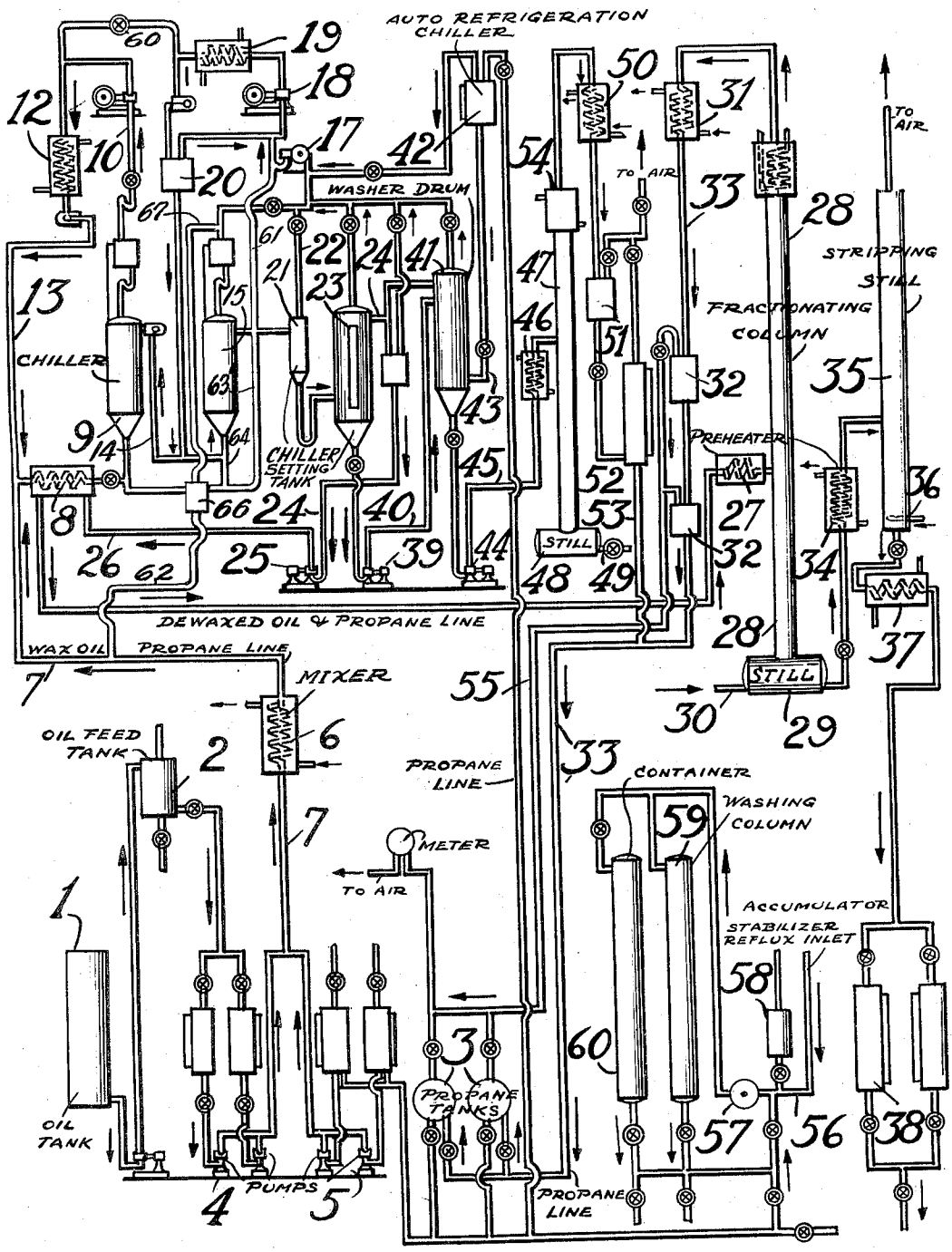


Fig. - 2

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2,189,885

DEWAXING OILS WITH LIGHT HYDROCARBONS

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Original application September 18, 1931, Serial No. 563,557. Divided and this application May 13, 1936, Serial No. 79,412

6 Claims. (Cl. 196—18)

This invention relates to the dewaxing of oils, especially petroleum oils, in which the solvent used comprises liquefied normally gaseous hydrocarbons such as ethane, propane, butane and similar hydrocarbons or mixtures thereof.

This application is a division of my prior application Serial No. 563,557, filed on September 18, 1931, and is directed principally to the method of dewaxing in which the oil to be dewaxed is chilled to successively lower temperatures in a plurality of stages.

The invention will be fully understood from the following description read with reference to the accompanying drawings of which

Fig. 1 is a semi-diagrammatic view in sectional elevation of the apparatus used in a batch operation, and

Fig. 2 is a semi-diagrammatic view in sectional elevation of the apparatus used in a continuous operation.

The drawings will be described simultaneously with the process.

In Fig. 1 numeral 1' designates a reservoir for the liquefied hydrocarbon gas such as propane in admixture with butane, ethane, etc., 2' a mixing tank. The required amount of propane is dropped into the mixing tank 2' from reservoir 1' and is admixed with the molten waxy charging stock admitted through valved line 3' from a reservoir (not shown). The closed steam line 4' serves to bring up the temperature of the propane to the required degree before the molten charge is admitted. The warm solution is then dropped into chiller 5'. The mixed charge is cooled by releasing propane vapors through valved line 7'. The released vapors pass through heat exchanger 8' to the suction valve of the first compressor 9'. The vapors are compressed by 9' and then passed through liquid propane in the intercooler 10', further compressed by compressor 11' and finally condensed with water in the indirect condenser 12'. The liquefied propane is then further cooled by expansion into the intercooler 10' and the residual liquid propane is returned via heat exchanger 8' and float valve 13' to the chiller 5'. Chiller 5', intercooler 10', exchanger 8', and line 7' are provided with insulation 6' against heat loss. The pressure in chiller 5' will be the vapor pressure of the flux. The released propane vapors are compressed in stages until they pass through cooler coils under a pressure such as, for example, 150 pounds per square inch which is sufficient to cause their condensation at the temperature of the cooling water. The arrangements of pressure and compression rates are such that the temperature of the returned liquid propane is only a few degrees higher than that in chiller 5'. Sufficient vapor is released by the expansion of the liquid propane into the chiller to give some agitation which assists in keeping the contents of the chiller at a uniform temperature and concentration. However, if so desired, the chiller may be provided with a mechanical agitator (not shown).

The chilled waxy oil and liquid propane mixture is settled in the chiller which is held at constant temperature and the supernatant liquor drawn off through valved line 14' into a still 15'. A pump 16' may be provided for this purpose. The sludge remaining in the chiller may be washed wth propane. For this purpose propane from the reservoir 1' is flash cooled by expansion through line 17' into the intercooler 10'. Evolved vapors are compressed as before. The cold propane is then admitted to the chiller through float valve 13'. Agitation incident to further expansion is sufficient to mix it with the sludge. When settling is again completed this wash liquor may be sent to still 15' or reserved for use as diluent with, or wash for, the next charge.

Directly after decantation of the original supernantant liquor or after washing with the liquid propane, the sludge may be passed, by means of pump 18'. through the filter press 19'. The filtrate is discharged through lines 20' and 14' into the still 15'. The chiller may be flushed out with the liquid propane and the wax in the press may also be washed with the same. Filtration may be employed entirely to effect the separation by discharging the total chilled flux through the filter press. The recovered wax may be removed through tube 21'.

The dewaxed lubricating oil is separated from the propane and other light hydrocarbons by distillation under pressure in the still 15' provided with closed steam coils 22'. A column 23' is connected with the still and condensation of the vapors is effected in water cooled condenser 24'. the liquefied propane being passed through line 25' to container 1'. 26' is a line for returning reflux to the column 23' and 27' is a discharge line for the dewaxed lubricating oil. Various combinations of distillation and compression may be used for separating from the dewaxed oil the propane and other light hydrocarbons and liquefying the same.

It is apparent from the above description that the liquid propane, pure or admixed with other liquefied hydrocarbons which are gaseous under

normal conditions of temperature and pressure, is employed as the diluent and serves simultaneously as the refrigerating medium inasmuch as the flux of waxy oil and propane is cooled by the evaporation of the latter. Compression of the propane vapors, their condensation and return to a chiller keeps the concentration of the diluent constant in the chiller, although it is not essential that all the liquid be returned in case an excess were provided at the start. This method of chilling may be termed "auto-refrigeration." The rate of "auto-refrigeration" is controlled by the work done in the compressor or compressors. The latent heat of fusion of wax and the specific heat of the flux is removed by the vaporization of propane at a uniform rate and an even temperature is assured hroughout the mass of the flux. The "auto-regrigeration" gives a much better control of the crystal formation than it is possible to obtain when heat is removed by indirect heat transfer from the body of a warmer liquid to a colder surface. Such indirect transfer requires that an appreciable temperature difference be set up across the liquid which results in "shock" chilling and irregular precipitation of the wax crystals. Also with this method of chilling, increasing the capacity increases the temperature difference and consequently the "shock" also increases with the capacity. With "auto-refrigeration," however, rapid chilling can be accomplished without "shock," thus fixing the capacity of the chiller simply by the time required for the crystal growth. This will result in considerable economy in the cost of the apparatus. Other highly volatile solvents may be used to receive the "auto-refrigeration" in place of the normally gaseous hydrocarbons here described, such as acetone, ether, sulfur, dioxide, ammonia, and the like. It is generally preferable to use any of these solvents only in admixture with the normally gaseous hydrocarbons.

The wax crystals are not only uniformly sized due to the "auto-refrigeration" but also grow rapidly and without occlusion of oil, due to the fact that the viscosity of the flux is low, and, further, the solubility of the wax in the flux is also small. The concentration of the liquid diluent is so regulated that the gravity of the flux is between 60 and 120° A. P. I. Under such conditions the flux has a low viscosity and the wax can be readily separatd therefrom. The oil and diluent are completely miscible at the temperature of separation. The so-called wax inhibitors, such as asphalt, my be removed along with the wax, although it may prove more desirable to remove them by acid treating or other means before the dewaxing.

While any suitable means may be used to separate the wax or wax-asphalt precipitate from the blend, settling, filtration and a combination of the two have been employed. The conditions for settling are favorable due to the low viscosity of the flux. Some waxes settle in a few hours' time to a sludge containing as much as 30% dry wax. In these cases decantation of the supernatant liquor, and extraction of dissolved oil from the sludge by mixing it with a succession of diluent washes, will give a practically complete separation of the oil from the wax. The solid fraction so separated will contain not more than 10% of "oil", as distinguished from "wax", in that it is made up of compounds having melting points below 0° F.

In other cases separation by settling may be too slow or not complete. Filtration of the sludge may be employed in this case, followed by washing the wax in the press with cold diluent. For a given blend, the pour point of the oil recovered by settling and decantation will be the same as that recovered by filtration.

Since very rapid chilling by "auto-refrigeration" may be effected without resultant "shock", my process lends itself to continuous operation in contra-distinction to other dewaxing processes which are by their nature batch processes. The essential feature of the continuous operation consists of a series of self cooled chillers operating at successively lower temperature and pressure levels. While it is possible to carry out the cooling in one step, multiple stage chilling is more desirable from the point of the control of the process. The wax is separated by settling and washing although filtration may also be employed. In a variation of the process the washed wax sludge is continuously pumped to a recovery still to remove the light hydrocarbons therefrom. The dewaxed oil solution and the propane extract from the washers are separated into propane and dewaxed oil by distillation under pressure. The dewaxed oil may then be stripped with steam, or any other method to correct the flash. In the multiple stage chilling of the continuous operation, the growth of the crystals may be controlled as to form in that the more desirable plate type of crystals which form in the first stage serve as nuclei for the smaller needles and other types which may come out in subsequent stages. It is also possible to chill a fraction of the total flux in one stage and use it for seeding the whole flux which may be chilled in successive stages. Such an operation would require a small chiller in parallel to the large multi-stage chillers. The concentration of the dilutent may be varied over wide limits from chiller to chiller in a multi-stage unit, although the control of the operation is simpler when the concentration of of the diluent is not varied.

Referring to Fig. 2, numeral **1** designates the storage tank for the oil to be dewaxed, **2** an overhead feed barrel for the oil, **3** the propane or other liquid hydrocarbon storage tanks, **4** and **5** the proportioning pumps for the oil and propane. The oil-propane mixture is passed through a steam heated mixer **6** and line **7** to the heat exchanger **8** in which the mixture is cooled and then discharged into the first chiller **9**. The temperature of **9** is lowered by venting propane through valved line **10**, compressing the propane vapors in the three-stage compressor **11**, cooling the propane in cooler **12** and returning it through line **13** in admixture with the oil-propane mixture from line **7** to the chiller. The chilled flux is transferred through line **14** to the second chiller **15** which is again further chilled by venting propane vapors through valved line **16** to the intake valve of rotary vacuum pump **17**, then compressing the vapors in the two-stage compressor **18**, condensing them in condenser **19**, and returning the liquid propane through the flash cooler and vapor separator **20** and to the chiller **15**. Uncondensed vapors are recycled from separator **20** to compressor **18** and condenser **19**. The vapors may be withdrawn after leaving condenser **19** by means of valve line **60** and returned to condenser **12**. The flux is then transferred from chiller **15** to the final chiller **21** which is again cooled by venting propane vapors through line **22**, and the finally chilled flux then passes into the settling tank **23**. Propane may be added

to the flux upon withdrawal from chiller 15 prior to its entrance into chiller 21. The dewaxed oil and propane mixture is drawn off from the settling tank through line 24 and passes by means of pump 25 through the heat exchanger 8 and line 26 to the steam preheater 27 and thence to the fractionating column 28 of propane recovery still 29. The latter is heated by closed steam coil 30. The light hydrocarbon solvent is distilled overhead, condensed in water condenser 31 and returned through overhead accumulators 32 and line 33 to the storage tanks 3. The oil residue from still 29 is further heated in steam preheater 34 and finally stripped from any remaining light ends in stripping still 35 by steam admitted through steam line 36. The stripped dewaxed oil is then cooled in cooler 37 and passed to accumulators 38 and thence to the storage tank (not shown).

The wax sludge from settling tank 23 is pumped by means of pump 39 and line 40 through the washer drum 41 in counter-current with propane admitted from "auto-refrigeration" chiller 42 through line 43. The washed wax sludge is then pumped by 44 through line 45 and steam preheater 46 to the column 47 of the wax stripping still 48. The stripped wax is removed therefrom through bottoms line 49 and the propane vapors after condensation in water condenser 50 are passed through accumulators 51 and 52 and lines 53 and 33 to the propane storage tank. Column 47 is provided with water reflux coils 54. Pressure equalizing line 55 is provided between the propane storage tanks and the overhead accumulators 32.

The reflux obtained in gasoline stabilizers and containing a large proportion of propane may serve as the light solvent in the process. The stabilizer reflux may be taken directly from tank wagons (not shown) by line 56 and passed by rotary pump 57 together with aqueous caustic soda solution from tank 58 to the washing column 59. The washed stabilized reflux is transferred from column 59 to the container 60 and hence into the storage tanks 3.

The operation may be conducted in a manner in which a small chiller is parallel to the large multi-stage chillers. In this manner of operating, a small fraction of the total flux is used for seeding the whole flux and is chilled in the small parallel chiller. For example, a small fraction of the mixture may be removed from line 7 by means of line 62 and chilled in the small parallel chiller 66. Portions of this chilled mixture containing small wax crystals are introduced into the feed lines of chillers 9, 15 and 21 by means of lines 65, 64 and 63 respectively. Propane is removed from the chiller 66 by means of line 67 and introduced in the propane line 16.

The following example will illustrate my process:

A flux containing 65% of a diluent having 121° A. P. I. gravity at 60° F. and 35% of a Mid-Continent overhead stock of 87 Saybolt viscosity at 210° F. and 113° F. pour point, was chilled at 10° F./hr. by "auto-refrigeration" to —40° F. After settling for 4 hours, 72% of the total volume was supernatant and was decanted from the sludge. This decanted liquor contained 0° F. pour lubricating equivalent to 72.6% of the original stock charged. Filtration and washing of the sludge yielded an additional 9.2% of 0° F. pour lubricating oil and 18.4% of wax of melting point of 130° F. by the A. S. T. M. method. The stock employed in the above experiment if dewaxed by chilling in a naphtha flux and centrifuging, yields only 68% oil of 0° F. pour. Inspection of the above data on light hydrocarbon dewaxing shows that the sludge liquor is much less concentrated in oil than that which was decanted. This definitely shows a selective adsorption of the diluent such as propane on the surface of the crystals. On the other hand, where these crystals are formed in a heavier naphtha flux they adsorb oil which is consequently lost when the wax is removed by centrifuging.

My invention is not to be limited by any theory or by the particulars given for illustration, but only by the appended claims in which it is my intention to claim all novelty inherent in my process.

I claim:

1. A process for separating wax from wax-containing oil which comprises diluting the oil with a liquefied normally gaseous hydrocarbon solvent, cooling the mixture to successively lower wax separation temperatures in a plurality of separate chambers by reducing the pressure to successively lower levels in each chamber, separating the precipitated wax from the oil-solvent mixture in the last chamber and removing the solvent from the dewaxed oil.

2. A method according to claim 1 in which the solvent is a hydrocarbon of 4 carbon atoms.

3. A method according to claim 1 in which the solvent is a mixture of hydrocarbons of 2 and 3 carbon atoms.

4. A method according to claim 1 in which the solvent is a liquefied hydrocarbon which has a vapor pressure higher than that of butane and lower than that of ethane.

5. A method for separating wax from wax-containing oil which comprises diluting the oil with a liquefied normally gaseous hydrocarbon, chilling the mixture to successively lower wax separation temperatures in a plurality of separate stages, effecting the chilling at least partially by evaporation of a portion of the diluent, maintaining the ratio of diluent to flux substantially constant in each stage by condensing and recycling to the chillers that portion of the diluent which is evaporated, and separating the wax from the oil.

6. A method for separating wax from wax-containing oil which comprises diluting the oil with a liquefied normally gaseous hydrocarbon, separately chilling a portion of the diluted mixture to a temperature at which a small amount of wax is caused to precipitate, adding this chilled portion to the remainder of the diluted mixture, chilling the same to a successively lower wax separation in a plurality of separate expansion stages, removing the wax so caused to precipitate, and recovering wax free oil.

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