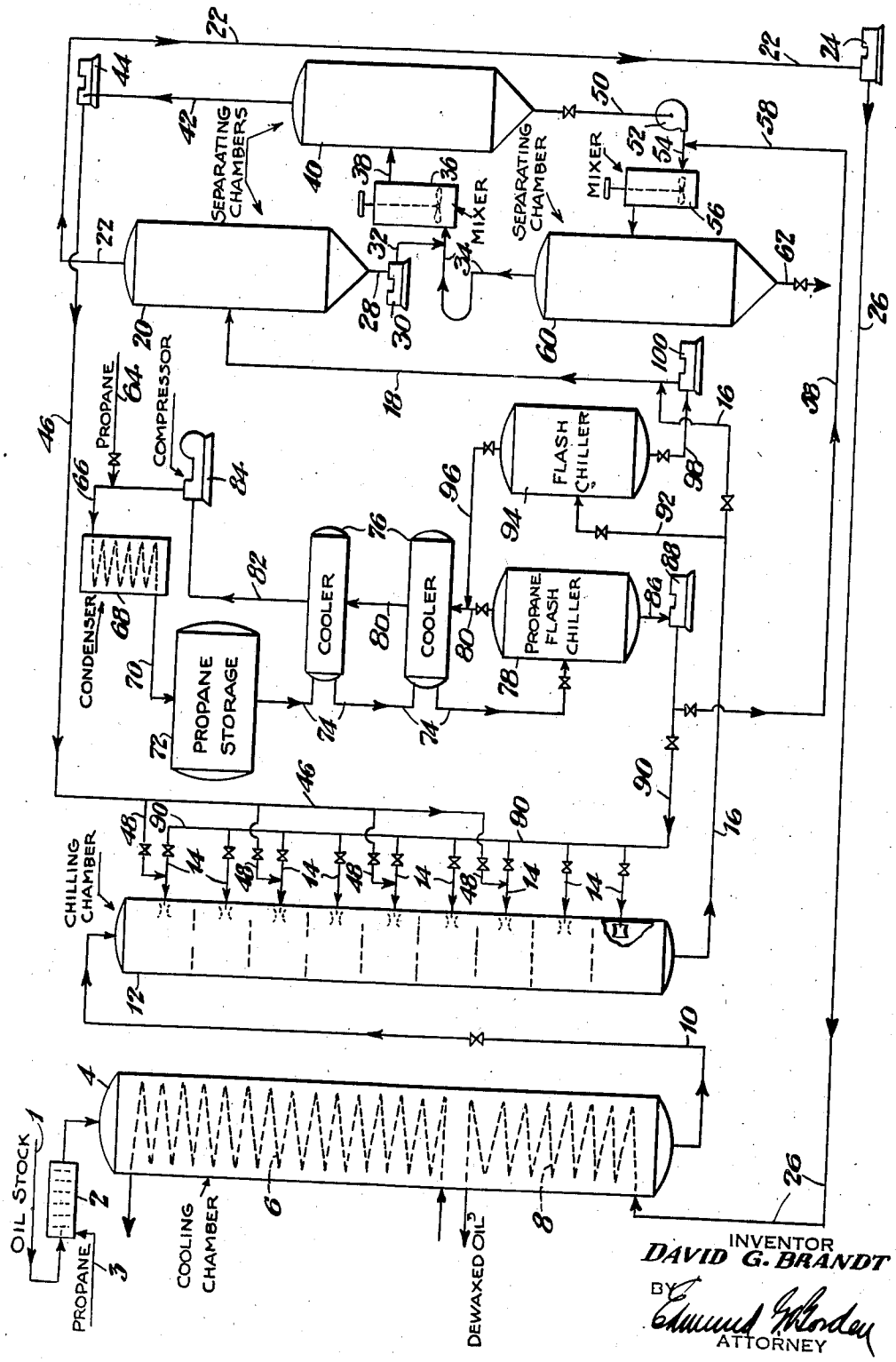
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PROCESS AND APPARATUS FOR DEWAXING PETROLEUM OILS

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PROCESS AND APPARATUS FOR DEWAXING PETROLEUM OILS

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This invention relates to a process for dewaxing petroleum oil stocks, and more particularly to a process in which a liquid normally gaseous hydrocarbon is used as a solvent and diluent.

A large number of different processes have been proposed for the dewaxing of petroleum lubricating oil stocks in which liquid propane or other similar hydrocarbon is employed as a diluent and internal direct refrigerant. In these processes the refrigeration and precipitation of wax is effected by vaporizing a portion of the liquid propane in which the oil stock is dissolved. A process of this general character is described in the applicant's pending application Serial No. 670,066, filed May 9, 1933, for an improvement in the "Art of dewaxing oils." In accordance with the disclosure of that application, the oil stock to be dewaxed is passed through a series of chilling chambers through which the diluted oil mixture is passed in series and portions of the liquid propane vaporized in each chamber to chill the oil mixture and precipitate the wax content thereof. In this process provision is made for introducing precooled propane into the oil mixture passing from one chilling chamber to the other, in order to make up for the vaporized propane and aid in chilling the oil mixture.

Dewaxing processes which involve the step of vaporizing a portion of the diluent in contact with the mixture being chilled have been reasonably successful, but the vaporization produces an intense agitation of the mixture, so that crytsal growth is prevented, and in some cases crystals which have been formed are broken up into smaller units. Oil stocks containing small crystals are much more difficult to handle in the wax separation stage than are stocks containing large crystals.

Accordingly, the primary object of the present invention is to provide an improved process in which the chilling operation to precipitate the wax content of the oil is carried out under conditions particularly adapted to the formation of large crystals and the maintenance of such crystal structures as are formed.

In general, the process of the present invention includes the steps of completely dissolving the oil stock to be dewaxed in a liquefied normally gaseous hydrocarbon such as propane, cooling the solution by indirect heat exchange to a temperature only slightly above the pour point of the oil stock or the point at which wax precipitation would commence, passing the cooled solution into a wax precipitating chamber into which sufficient precooled chilling agent including liquid propane is injected to effect the desired chilling of the mixture and precipitation of the wax content thereof, said injected chilling agent being comprised at least in part of a cold propane solution derived from the washing of the wax eventually obtained in accordance with the features of the process.

The process of the present invention comprises other features, objects, and advantages which will be apparent to those skilled in the art from the following more detailed description thereof, taken in connection with the accompanying drawing in which the single figure is a diagrammatic flow sheet of an apparatus particularly adapted for carrying out the features of the improved process and in which certain of the elements of the apparatus are shown in vertical position.

The petroleum oil stock to be dewaxed which may be an overhead wax distillate or a long residuum, and preferably relatively free from asphaltic constituents is preferably diluted with at least 30% to 50% of a liquefied normally gaseous hydrocarbon such as propane and completely brought into solution. This operation may require heating to a temperature of from 125° to 145° F.

The oil stock to be dewaxed is introduced into the apparatus shown in the drawing through a line 1, and passed into a mixer 2 in which it is dissolved in liquid propane introduced through a line 3. The resulting solution is passed through an indirect heat exchange chamber or tower 4 where it first passes in heat exchange with a cooling liquid such as water conducted through the coil 6, and then in heat exchange with a colder fluid such as the cold dewaxed oil produced by the process which is conducted through a heat exchange coil 8. The solution of oil stock passed through the chamber 4 is preferably cooled therein to a temperature just short of the temperature at which wax would start to precipitate, so that no wax is precipitated on the coils or the walls of the chamber 4.

The cooled solution of oil stock is conducted from the chamber 4 through a valved line 10 into a chilling chamber 12, wherein the oil stock passes through a series of chilling compartments separated only by baffle plates so that the oil stock passes in succession through the compartments. The oil mixture introduced into the chilling chamber 12 is preferably chilled to progressively lower temperatures, as it passes through the chamber by introducing an increment of precooled liquid propane from a plu-

rality of valved intake pipes 14 distributed along the chamber. The propane or other chilling agent injected from each of the pipes 14 is preferably introduced into the side of the chamber through an injection type of nozzle which prevents shock chilling by creating a flow of oil mixture past the nozzle and by producing a gentle circling or eddying action in the oil mixture in each compartment of the chamber. This insures thorough mixing of the injected cold chilling agent with the oil solution and prevents shock chilling of the oil, and by the time the oil has passed through the chamber, its wax content will have been completely precipitated to the extent desired to produce a stock of desired low pour point. The chilling effected in the chamber 12 may be sufficient to superchill the mixture to a sufficiently low temperature for separation of the precipitated wax. A temperature of minus 40° to minus 60° F. is sufficient for most petroleum lubricating oil stocks.

The cold mixture containing the precipitated wax is withdrawn from the chilling chamber 12 through a valved line 16, passed into a line 18, and conducted into a wax separating chamber 20. This wax separating chamber is preferably constructed like the separator shown in the drawings of the pending application Serial No. 670,066, referred to above. The separating chamber shown in this pending application is a jacketed chamber in the jacket of which liquid propane is vaporized to maintain a low temperature. The chamber itself is provided with a plurality of vertically spaced trays which slope toward the center of the chamber and which have central openings for the passage of settled wax. The trays are also of such a size that a free space is left between their outer edges and the inside wall of the separator for the upward passage of separated oil solution. Provision is made for introducing oil mixture containing precipitated wax at a point above each tray and near the center of the chamber so that the space between adjacent trays comprises a more or less individual settling zone. The settling chamber is also provided with sweeps above each tray for moving settled wax toward the center opening in the tray. Separated wax-free oil solution is discharged from the top of the settling chamber while the settled wax slurry is removed from the bottom of the chamber by a gear pump or other suitable means. In any case, the wax is settled out in the chamber 20, and the wax-free oil in solution in the liquid propane is withdrawn from the chamber through a line 22 and forced by means of a pump 24 and a line 26 through the cooling coil 8 mounted in the lower part of the cooling chamber 4, where the cold dewaxed oil solution is used as a cooling medium.

The pressure in the chamber 12 must be maintained sufficiently high to prevent vaporization of any of the propane at the highest temperatures of any of the materials therein. The pressure may be considerably reduced in the line 16, but sufficient pressure should be maintained to prevent vaporization of any of the diluent and provide for the flow of the oil mixture into the chamber 20, and the oil solution throughout the line 22. A superatmospheric pressure of from 10 to 25 lbs. is sufficient in the chamber 20.

The wax slurry separated out in the chamber 20 is removed from the conical bottom of the chamber through a line 28 and passed by means of a pump 30 and a line 32 into a line 34 where it is mixed with cold diluent. The wax slurry removed from the chamber 20 usually comprises about 25% wax, 25% oil, and about 50% of propane diluent. A considerable proportion of diluent is mixed with the slurry in the line 34 and the resulting mixture introduced into a mixing chamber 36 where a more thorough mingling of the constituents is accomplished by means of a rotary mixing element mounted in the chamber 36. The diluted wax slurry is conducted from the chamber 36 through a line 38 into a wax separating chamber 40 which may be of similar construction to that of the chamber 20.

The cold solution separated out in the chamber 40, and which contains a proportion of oil removed from the slurry is conducted through a line 42 and forced by means of a pump 44 through a line 46 and valved branch lines 48 into some of the injection lines 14, as shown in the drawing. This mixture containing the oil removed from the precipitated wax slurry is at an extremely low temperature and therefore suitable as a direct cooling medium for the precipitation of wax in the chamber 12. In fact this mixture may be utilized as the entire chilling means for precipitating wax in this chamber in accordance with the features of the present invention, and it may be introduced through each line 14.

The wax slurry separated out in the separating chamber 40 is withdrawn from the conical bottom thereof through a valved line 50 and passed by means of a pump 52 and a line 54 into a mixer 56 similar in construction to the mixer 36. The wax slurry removed from the chamber 40 contains about 70% of propane, 25% of wax, and about 5% of oil. This mixture is further diluted with extremely cold liquid propane introduced into the line 54 from a line 58 and thoroughly mixed with the slurry in the mixer 56. The diluted wax slurry is conducted from the mixer 56 into a final wax separating chamber 60 from which the separated wax substantially free of oil is removed through a valved line 62. The chamber 60 is constructed the same as the chamber 20.

The cold wash solution comprised largely of propane and a small proportion of oil is passed from the chamber 60 by the line 34 and used as the cold diluent for mixing with the wax slurry withdrawn from the chamber 20.

The propane or other liquefied normally gaseous hydrocarbon to be used in the process may be introduced into the system through a line 64, passed through a line 66, a condenser 68 and a line 70, into a liquid propane storage tank 72. The propane stored in the tank 72 is usually maintained at atmospheric temperature and at a sufficient pressure to maintain the propane in the liquid state. The cold propane used for precipitating the wax content of the oil and for washing the separated wax slurry is obtained by passing liquid propane from the storage tank 72 through lines 74 and coolers 76, into a propane flash chilling chamber 78. The propane is chilled by reducing the pressure upon the introduction of the propane into the chamber 78, so that a portion of the propane is vaporized and the remaining portion is retained in the liquid state and chilled to the desired low temperature.

The propane vapors formed in the chamber 78 are removed through a valved line 80, passed through coolers 76 in indirect heat exchange with the liquid propane from the storage tank 72, and then passed through a line 82 to a vacuum pump and compressor 84. The vaporization in the chiller 78 chills both the liquid and

vaporous propane, so that the relatively cold vapor conducted through the coolers 76 may be effectively utilized in cooling the liquid propane flowing to the chamber 78. Any desired pressure or vacuum may be maintained in the chamber 78 by means of the valve in lines 80, and the vacuum pump 84, so that the propane may be cooled to any desired low temperature of from minus 55° to minus 85° F.

The propane vapors picked up by the compressor 84 are placed under a high pressure and passed through the line 66, condensed in condenser 68, and the condensate is conducted through the line 70 into the propane storage 72.

The extremely cold liquid propane produced in the chamber 78 is withdrawn therefrom through a line 86, by means of a pump 88, and forced through a valved line 90 into the connecting lines 14 which are utilized for injecting the cold propane into the chamber 12 in the manner described above.

Cold liquid propane used for washing the wax slurry in chambers 60 and 40 is supplied from the valved line 58, as described above, which line connects directly into the line 90.

After the wax has been precipitated in the chamber 12, the resulting mixture may be further chilled in order to provide a suitable low temperature for wax separation by vaporizing a portion of the propane diluent under reduced pressure. This step may be effected by passing the mixture from the line 16 through a valved connecting line 92 into a flash chiller 94 where a suitably low pressure is maintained to effect the desired vaporization of propane and consequent chilling of the mixture. The vapor space of chamber 94 is connected with the low pressure or vacuum line 80 by means of a valved connecting pipe 96. The degree of pressure or of vacuum maintained in the chamber 94 is controlled by means of the valve in the line 96. The chilled mixture is withdrawn from the chiller 94 through a valved line 98 and a pump 100 and forced through the line 18 into the wax separating chamber 20 where the wax is separated in the manner described above.

Where the oil mixture can be chilled to sufficiently low temperatures in the chamber 12 without diluting the mixture excessively, the flash chamber 94 need not be used, but this chamber provides an effective means for lowering the temperature of the mixture containing the precipitated wax, so that a sufficiently low temperature mixture is provided for the wax separation operation. This supercooling of the mixture containing the precipitated wax will prevent the re-solution of wax from any slight rises in temperature which may occur during the separation operations.

The entire chilling in the chamber 12 is preferably effected with cold wash liquid from the chamber 40, but where this is insufficient, or for other reasons, it may be supplemented with cold solvent from flash chiller 78. All parts of the equipment in which low temperatures are involved are understood to be suitably insulated.

While the process of the present invention has been described in connection with the use of propane as the diluent, it is to be understood that other oil solvents of low specific gravity may be employed which are relatively poor solvents for petroleum waxes. Propane and other liquefied normally gaseous hydrocarbons having molecular weights below that of pentane are particularly suitable for the process.

Having thus described the invention in its preferred form, what is claimed as new is:

1. In the process of dewaxing petroleum lubricating oil stocks in which the oil stock to be dewaxed is diluted with liquid propane in sufficient quantity and at a temperature adapted to completely dissolve the oil stock and provide a solution which will be fluid and readily handled at temperatures as low as the point of wax precipitation, the improvement which comprises chilling the solution by passing the same through a series of connected enlarged chilling zones in each of which an extremely cold liquid diluent is introduced and mixed with the diluted oil mixture, maintaining the materials in said series of chilling zones at a sufficient pressure to prevent vaporization of any of the propane, introducing the cold diluent into each of said zones in a jetting action adapted to cause only gentle eddying currents in each of said zones to effect equilibrium between the oil mixture and the introduced dilutent therein without shock-chilling the oil, said diluent being introduced in sufficient quantity into said zones to precipitate the wax content of the oil desired to be removed therefrom to give a wax-free oil of predetermined pour point, separating the precipitated wax from the resulting chilled mixture, washing the separated wax with extremely cold liquid propane and utilizing the resulting wash liquid as the cold diluent introduced into said chilling zones.

2. The process of dewaxing petroleum lubricating oil stocks as defined by claim 1 in which the precipitated wax is settled from the chilled mixture containing the same to form a wax slurry, mixing a substantial proportion of a diluent comprising cold liquid propane with said slurry, and settling the resulting mixture to recover a solution comprising propane and oil washed from said wax slurry.

3. The process of dewaxing petroleum lubricating oil stocks as defined by claim 1 in which the precipitated wax is settled from the chilled mixture containing the same to form a wax slurry, mixing a substantial proportion of a diluent comprising cold liquid propane with said slurry, settling the resulting mixture to recover a solution comprises propane and oil and a second wax slurry, separating out said second wax slurry and mixing therewith a substantial proportion of extremely cold liquid propane, separating a substantially oil-free wax from the resulting solution of propane and oil, and mixing said last named solution with the wax slurry formed in the original wax settling step as said cold liquid propane diluent.

4. In the process of dewaxing petroleum lubricating oil stocks in which the oil stock to be dewaxed is diluted with a liquefied normally gaseous hydrocarbon which is liquid at low dewaxing temperature in sufficient quantity and under suitable conditions to completely dissolve the oil stock and provide a solution which flows readily at temperatures as low as the pour point of the oil stock, the improvement which comprises chilling the oil solution with a chilling medium and precipitating the entire wax content thereof desired to be removed therefrom in an enlarged elongated chilling zone in which a sufficient pressure is maintained to prevent vaporization of the liquid normally gaseous hydrocarbon, effecting the chilling of the oil solution in said zone by introducing thereinto at spaced points therealong a cold chilling medium, passing the resulting mixture from said zone into a wax settling

zone in which a wax slurry is formed containing the precipitated wax, some occluded oil, and liquid normally gaseous hydrocarbon diluent, recovering a wax-free oil having the desired pour point from said settling zone, mixing a substantial proportion of extremely cold liquid normally gaseous hydrocarbon with said slurry and settling the resulting mixture to produce a second wax slurry and a solution containing a relatively large proportion of liquefied normally gaseous hydrocarbon and a relatively small proportion of oil, and utilizing said solution as the chilling medium for effecting the precipitation of wax in said chilling zone by intimately mixing the solution with the oil stock introduced thereinto under conditions such that vaporization of the liquefied normally gaseous hydrocarbon is prevented.

5. The process of dewaxing petroleum oil stocks as defined by claim 4 in which the second wax slurry is mixed with a substantial proportion of extremely cold liquefied normally gaseous hydrocarbon and subjected to a settling operation, settling the wax from the resulting solution comprised mainly of said hydrocarbon and a small proportion of oil stock, and utilizing said solution as the liquefied normally gaseous hydrocarbon for mixing with the wax slurry formed in the first settling operation.

6. An apparatus for dewaxing petroleum lubricating oil stocks, which comprises a chilling chamber for precipitating wax in an oil solution introduced thereinto, said chamber comprising a series of relatively large interconnecting compartments each of which is provided with an injection means, a wax settling chamber for settling precipitated wax from a mixture containing the same, a wax washing chamber, means for introducing an oil solution to be dewaxed into said chilling chamber, means for passing an oil mixture containing precipitated wax from said chilling chamber into said wax settling chamber, means for passing wax slurry into said wax washing chamber, means for introducing a cold diluent washing liquid into said wax washing chamber, and means for passing cold wash liquid from said wax washing chamber and for introducing it into each compartment of said chilling chamber as the chiling medium for precipitating wax in the oil solution introduced into the chilling chamber.

7. In the process of dewaxing petroleum lubricating oil stocks in which the oil stock to be dewaxed is diluted with a liquid normally gaseous hydrocarbon which is liquid at low dewaxing temperatures in sufficient quantity and at a temperature adapted to completely dissolve the oil stock and provide a solution which will be fluid and readily handled at temperatures as low as the pour point of the stock, the improvement which comprises chilling the solution while passing the same through a series of connected enlarged chilling zones in an enlarged chamber by separately introducing into each zone an extremely cold liquid diluent which is mixed directly with the oil mixture in said zones, maintaining the materials in said enlarged chamber under sufficient pressure to prevent vaporization of any of said liquid hydrocarbon, introducing the cold diluent into each of said zones in a jetting action adapted to effect only gentle eddying currents in said zones thereby bringing the diluent and oil mixture into contact and temperature equilibrium in each of said zones, the cold diluent being introduced into each zone in such a manner as to avoid shock-chilling of the oil but in such quantity as to crystallize the wax content of the oil desired to be removed therefrom by the time the oil mixture has passed through said series of zones, separating the crystallized wax from the resulting chilled mixture, washing the separated wax with extremely cold liquid normally gaseous hydrocarbon, and utilizing the resulting wash liquid as the cold diluent for effecting the chilling of the oil mixture in said series of chilling zones.

8. The process of dewaxing petroleum lubricating oil stocks as defined by claim 1 in which said series of enlarged chilling zones are contained in an enlarged chamber divided by baffles forming said zones, and in which the oil mixture flows past said baffles in advancing through said series of zones.

9. In the process of dewaxing petroleum lubricating oil stocks in which the stock to be dewaxed is diluted with a liquid normally gaseous hydrocarbon which is liquid at low dewaxing temperatures in sufficient quantity and under suitable conditions to completely dissolve the oil stock in the hydrocarbon diluent and provide a solution which flows readily at temperatures as low as the pour point of the stock, the improvement which comprises introducing the diluted oil mixture into the top of an elongated chilling zone and flowing the oil mixture therethrough over a plurailty of spaced baffles to the bottom of the zone, injecting cold liquid normally gaseous hydrocarbon into said zone at spaced points along the length thereof to effect chilling of the oil mixture passing therethrough, the proportion of liquid normally gaseous hydrocarbon introduced at said points being such as to chill the oil mixture to progressively lower temperatures as it advances through said zone and to precipitate the wax content of the oil desired to be removed therefrom, maintaining a pressure in said zone sufficient to prevent vaporization of the injected chilling medium, withdrawing the resulting chilled oil mixture containing precipitated wax from the bottom of said zone, separating the precipitated wax from the withdrawn mixture, washing the separated wax with an extremely cold liquefied normally gaseous hydrocarbon, and utilizing the resulting wash liquid as the cold normally gaseous hydrocarbon injected into said zone.

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