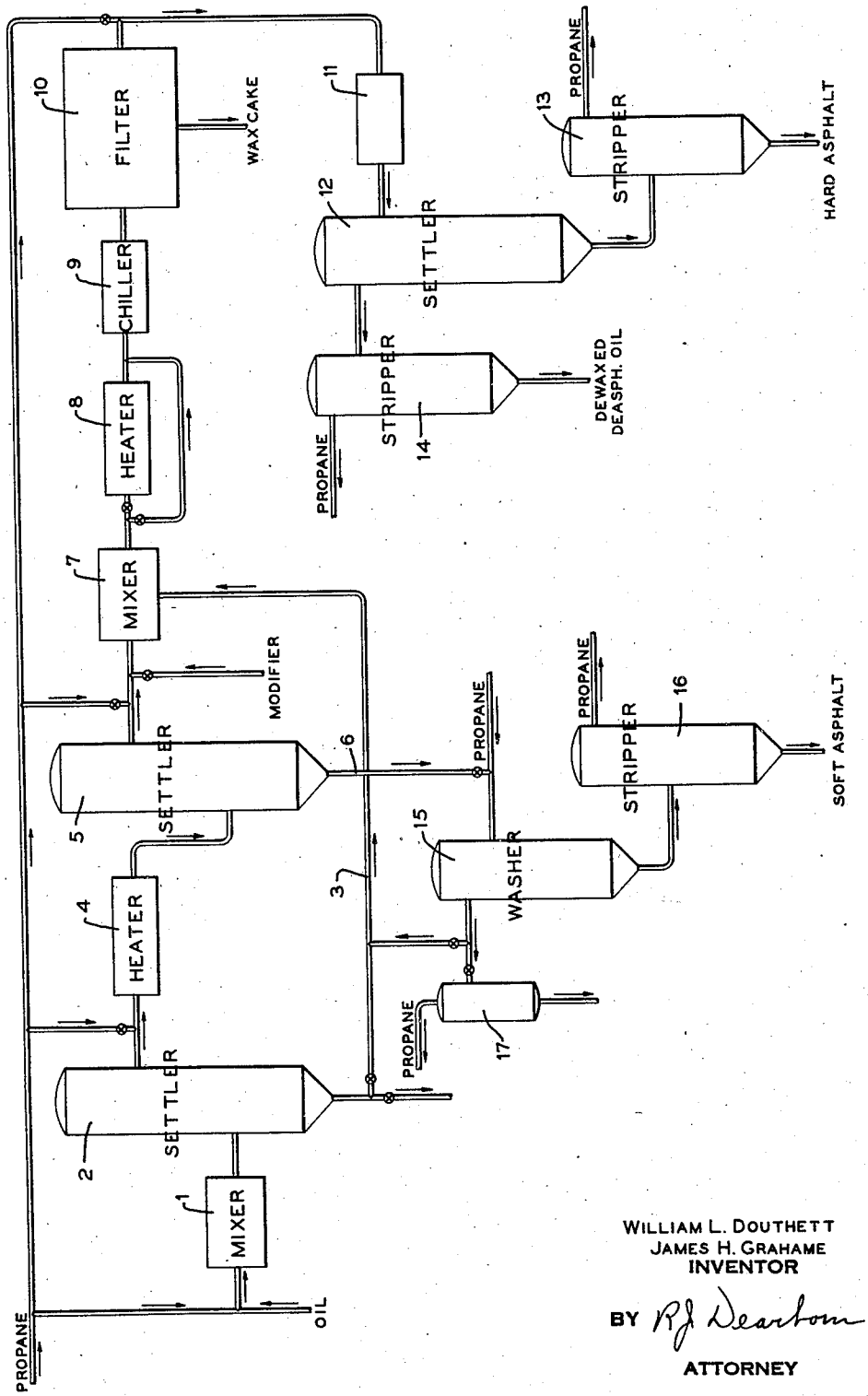
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REMOVING WAX AND ASPHALTIC CONSTITUENTS FROM OIL

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REMOVING WAX AND ASPHALTIC CONSTITUENTS FROM OIL

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This invention relates to a method of removing wax and asphaltic constituents from hydrocarbon oil, and particularly to the removal of such constituents from residual wax-bearing mineral oil.

The invention contemplates a method of refining wax-bearing oil containing relatively soft and relatively hard asphaltic constituents wherein the soft asphaltic constituents are removed, and the oil is then dewaxed in the presence of all or a portion of the relatively hard asphaltic constituents. These hard asphaltic constituents are removed along with the wax and are of such a nature that they aid in the separation of the wax from the oil, particularly where such separation is effected by filtration.

An object of the invention is to remove the soft asphalt from the wax-bearing oil prior to dewaxing, while taking advantage of the filter-aid properties of the hard asphaltic constituents of the oil in the subsequent dewaxing step. The soft asphaltic material contained in the oil may comprise a substantial proportion thereof, and since this material must be eliminated sooner or later, it is desirable to eliminate it prior to the dewaxing step so as to thereby increase the capacity of existing dewaxing equipment, and thus afford more economical operation.

In carrying out the process of this invention, a solvent, such as propane, is mixed with a wax-bearing residual oil such as derived from Mid-Continent crude for example. The ratio of propane to oil is such that the asphaltic material precipitated from the mixture at a temperature of around 80° to 100° F. comprises mainly the asphaltene type of constituent which tends to separate in hard granular form. The soft and resinous type of asphaltic material comprising, in many cases, the bulk of the asphalt content of the oil remains in solution along with the oil and wax. This solution is removed and modified to effect removal of the soft asphaltic and resinous material.

Modification of the solution may be accomplished by the addition of a further quantity of propane, and subjecting the resulting mixture to settling at a temperature of around 125° to 150° F. Under these conditions, the soft asphaltic and resinous material is removed.

To the remaining solution is added the precipitate containing hard granular asphalt removed in the preliminary operation. This mixture is then subjected to dewaxing in the conventional manner, involving chilling to a temperature of 0° F. to —40° F. and removing the resulting precipitate composed of wax and asphaltic material by filtration.

The dewaxed solution may still contain substantial amounts of asphaltic material, and in which case it is advantageously subjected to settling at a temperature of around 125° to 150° F. to remove any remaining asphaltic material as a precipitate.

Instead of propane, other liquefied normally gaseous hydrocarbons may be employed, such as ethane, propylene, butane, etc., or a light petroleum fraction composed of a mixture of such hydrocarbons.

It is also contemplated that the dewaxing step may be carried out in the presence of a suitable wax antisolvent liquid, such as acetone, methyl ethyl ketone, liquid sulphur dioxide, benzaldehyde. The anti-solvent liquid may be added to the solution of wax-bearing oil and light petroleum solvent subsequent to the removal of the soft asphalt fraction.

Where it is desired to subject the dewaxed oil to a further solvent refining step for the removal of low viscosity index constituents, advantage may be taken of the selective action of the wax anti-solvent liquid. That portion of the anti-solvent liquid remaining in the dewaxed solution may comprise a portion of the selective solvent mixture used in the subsequent solvent extraction of oil.

Heavy residual wax-bearing fractions, such as derived from Mid-Continent crude, contain large amounts of asphaltic and resinous material in addition to the wax. For example, such a residuum may contain around 12% to 18% by volume of paraffin wax, and around 30% to 40% by volume of tarry material.

This proportion of tar represents the portion of the oil removed in the acid layer obtained when about five parts of the residuum, diluted with an equal quantity of Stoddard solvent, are agitated with about one part of 93.2% sulphuric acid. This tarry material comprises constituents which are of the character of asphaltenes, and also constituents which are of a resinous nature.

The asphaltenes are less soluble in propane than the resinous material; that is, both the asphaltenes and resins will precipitate from a mixture of propane and oil containing them at a temperature of 130° to 150° F. But at lower temperatures, while the asphaltenes will precipitate from the same mixture, the resins will precipitate in correspondingly smaller amount. In other words, the lower the temperature, the more soluble the resinous material is in the sol-

vent. At low temperatures, such as prevail during dewaxing, practically all of the resinous type of asphaltic material may remain in solution.

It has been found that the asphaltene type of material which separates from a mixture of about one part of residuum and three to four parts of propane, at a temperature of around 90° F. and below, imparts free-filtering characteristics to the wax precipitated from such oil; that is, asphaltenes separate from such a mixture in a relatively dry, hard, granular form, and thus provide an effective, solid, inert filter-aid material for aiding in the filtration of the solidified wax from a mixture of wax-bearing oil and solvent.

When the wax is precipitated from the wax-bearing solution in the presence of these insoluble asphaltic constituents, the resulting precipitate is of a hard granular nature, and such that it can be removed by filtration at comparatively rapid rates. For example, the filtration rates may range from ten to a hundred times as rapid as those prevailing in the case where these asphaltic constituents are not present in the filter cake.

By proceeding in accordance with the process of this invention, the above mentioned hard granular asphaltene constituents desired as a filter-aid are segregated in a preliminary operation. Following this, the remainder of the asphaltic and resinous material comprising soft asphalt is removed, and thereafter the hard granular material preliminarily precipitated is mixed back with the wax-bearing solution from which the soft asphalt has been removed. In this way, the soft asphalt is eliminated prior to dewaxing, and the subsequent dewaxing is effected in the presence of the hard granular asphaltic constituents originally present in the oil.

When dewaxing a Mid-Continent type of residuum, satisfactory filtration rates have been obtained when the wax filter cake comprised about one part of asphaltic material to about three parts of wax. The asphaltic material thus present in the wax cake comprised about 2% to 5% of the total asphaltic matter contained in the residuum.

In order to more fully describe the process of the invention, reference will now be made to the accompanying drawing showing a flow diagram of the process. Cylinder stock residuum derived from Mid-Continent crude is drawn from a source not shown and introduced to a mixer 1. Liquefied propane, also from a source not shown, is introduced to the mixer 1 in the proportion of about four parts of propane to one part of oil.

The resulting mixture is then conducted to a settler 2 maintained at a temperature of around 80° to 100° F. The asphaltic material precipitated in this settler is withdrawn in the form of a slurry from the bottom thereof through a pipe 3 to which reference will be made later.

The solution of oil and propane in the upper portion of the settler 2 is withdrawn through the heating coil 4, and conducted to a settler 5. If necessary, a further quantity of propane may be mixed with the solution prior to passage through the heating coil 4. The solution is maintained in the settler 5 at a temperature of around 130° to 150° F. to cause precipitation of the soft and remaining asphaltic constituents of the oil. The precipitated matter is withdrawn from this settler through a pipe 6 to which reference will be made later.

The solution accumulating in the upper portion of the settler 5 is drawn off and conducted to a mixer 7 wherein it is mixed with the precipitated material removed from the settler 2 through the pipe 3 previously referred to. An additional quantity of propane may also be added to the solution at this point, if desired. From the mixer 7, the mixture is conducted through a heater 8 and a chiller 9. In the heater 8 the mixture may be heated to a temperature of around 150° to 190° F. prior to introduction to the chiller. Where it is desired to omit the heating step, the mixture may by-pass the heater and be conducted directly to the chiller 9.

The heating step is desirable where the wax-bearing solution contains either an artificial or a naturally-occurring wax crystal modifying substance. It has been found that when the solution does contain such substance, heating to an elevated temperature such as that mentioned, prior to chilling, promotes the modifying action of the substance upon the structure of the wax crystals precipitated from the solution during the subsequent chilling.

Heavy residual lubricating oil stocks usually contain naturally-occurring resinous constituents which possess the ability to modify the wax crystal structure. Less viscous oils are sometimes deficient in this respect, and therefore it is particularly desirable to add an artificial modifying substance, such as crude Montan wax, aluminum stearate, or a mixture thereof. In such case, the modifying substance may be incorporated in the wax-bearing solution prior to introduction of the solution to the mixer 7.

The chiller 9 is advantageously of the evaporative type wherein chilling is effected by vaporizing surplus propane from the wax-bearing solution undergoing chilling. On the other hand, the chiller may be of the more conventional type wherein the wax-bearing solution is chilled by passage in indirect heat exchange relationship with a refrigerant.

From the chiller 9, the solution is conducted at a temperature of around 0° to −50° F. to a filter 10 to effect removal of the wax.

The resulting dewaxed filtrate is conducted through a heating coil 11, and from there to a settler 12 wherein any remaining asphaltic matter is precipitated. This may be accomplished by maintaining the settler at a temperature in the range 125° to 130° F., either with or without the addition of a further quantity of propane. The precipitated material, mixed with some propane, is withdrawn from the bottom of this settler and conducted to a stripper 13 to remove the propane from the asphalt.

The solution accumulating in the top of the settler 12 is conducted to a stripper 14 wherein the propane is removed to produce a dewaxed deasphalted oil.

The soft asphalt which is withdrawn from the bottom of the settler 5 through the pipe 6 is conducted to a washer 15 wherein it may be washed with a further quantity of propane. This washer may be maintained at a temperature of 130° to 150° F., or at a temperature slightly above that maintained in the settler 5.

The resulting precipitated material is drawn off to a stripper 16 wherein the propane is removed, leaving the soft asphaltic material.

The solution collecting in the upper portion of the washer 15 may be withdrawn directly to a stripper 17 to effect removal of the propane and produce an oil product of intermediate character.

On the other hand, this solution may be conducted to the mixer 7, previously referred to, and therein mixed with the main body of solution for dewaxing.

While certain temperatures and temperature ranges have been specified with respect to the several operations described in the foregoing statement and description of the invention, it is contemplated that other temperature conditions may be employed, depending upon the nature of the oil undergoing treatment, and also upon the degree of the refining action required.

For example, in effecting separation of the hard granular asphaltic constituents, the temperatures may range from a point substantially below 80° F., to around 125° F. or even higher. While lower temperatures may be employed in this step, it is desirable to select a temperature above that at which any substantial amount of wax would precipitate from the solution along with the hard asphaltic constituents.

With respect to the second step, wherein the soft asphaltic constituents are removed, the temperatures may range from 125° to 180° F., for example.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of removing asphalt and wax from residual wax-bearing lubricating oil containing a relatively large amount of both soft and hard asphalt comprising mixing the oil with a liquefied normally gaseous hydrocarbon in such proportion that at a temperature of around 80° to 100° F., a small amount of hard granular asphalt is precipitated, maintaining the mixture at such temperature to precipitate a slurry of hard granular asphalt amounting to about 2% to 5% of the asphaltic content of the residuum and mixed with some solvent, removing the slurry, adding further solvent to the remaining solution, maintaining the solution at a slightly higher temperature sufficient to precipitate remaining asphaltic constituents, removing the asphaltic constituents so precipitated, thereby leaving a deasphalted solution, mixing the deasphalted solution with said slurry containing hard granular asphalt, chilling the mixture to a temperature of 0° F. and below to precipitate wax, and filtering the cold mixture to remove the wax in the presence of said hard granular asphalt.

2. The method according to claim 1 in which a small amount of a wax crystal regulator is incorporated in the mixture of oil, solvent and hard granular asphalt.

3. The method of removing asphalt and wax from residual wax-bearing lubricating oil containing a relatively large amount of both soft and hard asphalt comprising mixing the oil with a liquefied normally gaseous hydrocarbon in such proportion that at a temperature of around 80° to 100° F. a small amount of hard granular asphalt is precipitated, maintaining the mixture at such temperature to precipitate a slurry of hard granular asphalt amounting to about 2% to 5% of the asphaltic content of the residuum and mixed with some solvent, removing the slurry, adding further solvent to the remaining solution, maintaining the solution at a slightly higher temperature sufficient to precipitate remaining asphaltic constituents, removing the asphaltic constituents so precipitated thereby leaving a deasphalted solution, mixing the deasphalted solution with said slurry containing hard granular asphalt, incorporating in said mixture a small amount of a wax crystal regulator, heating the resulting mixture to a temperature in the range 150° to 190° F., chilling the mixture to a temperature of 0° F. and below to precipitate wax, and filtering the cold mixture to remove the wax in the presence of said hard granular asphalt.

4. The method of removing asphalt and wax from residual wax-bearing lubricating oil containing a relatively large amount of both soft and hard asphalt comprising mixing the oil with a liquefied normally gaseous hydrocarbon in such proportion that at a temperature of around 80° to 100° F., a small amount of hard granular asphalt is precipitated, while the bulk of the asphalt is retained in solution, precipitating from the mixture a small amount of hard granular asphalt in the form of a slurry mixed with some solvent, removing the slurry, maintaining the remaining mixture at a temperature of around 130° to 150° F., and while at such temperature precipitating remaining asphaltic constituents, removing the asphaltic constituents so precipitated, thereby producing a deasphalted solution, mixing the deasphalted solution with said slurry containing hard granular asphalt, chilling this mixture to precipitate wax and filtering the chilled mixture to remove the wax in the presence of said hard granular asphalt.

5. The method of removing asphalt and wax from residual wax-bearing lubricating oil containing a relatively large amount of both soft and hard asphalt comprising mixing the oil with a liquefied normally gaseous hydrocarbon, maintaining the mixture at a temperature of around 80° to 100° F. sufficient to precipitate a slurry of hard granular asphalt amounting to about 2 to 5% of the asphaltic content of the residuum and mixed with some solvent, removing the slurry, maintaining the remaining solution at a temperature of around 130° F. and above sufficient to precipitate remaining asphaltic constituents, removing the asphaltic constituents so precipitated, thereby producing a deasphalted solution, mixing the deasphalted solution with said slurry containing hard granular asphalt, chilling the mixture to precipitate wax, and filtering the cold mixture to remove the wax in the presence of said hard granular asphalt.

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