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DEWAXING HYDROCARBON OIL

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FIG. 1.

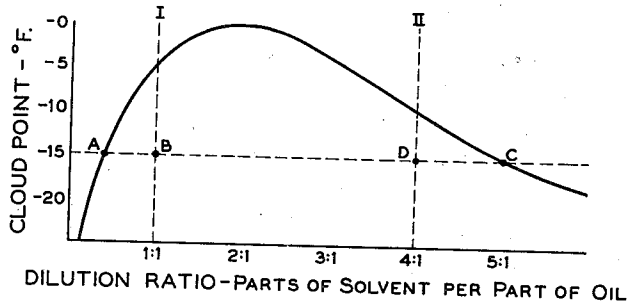
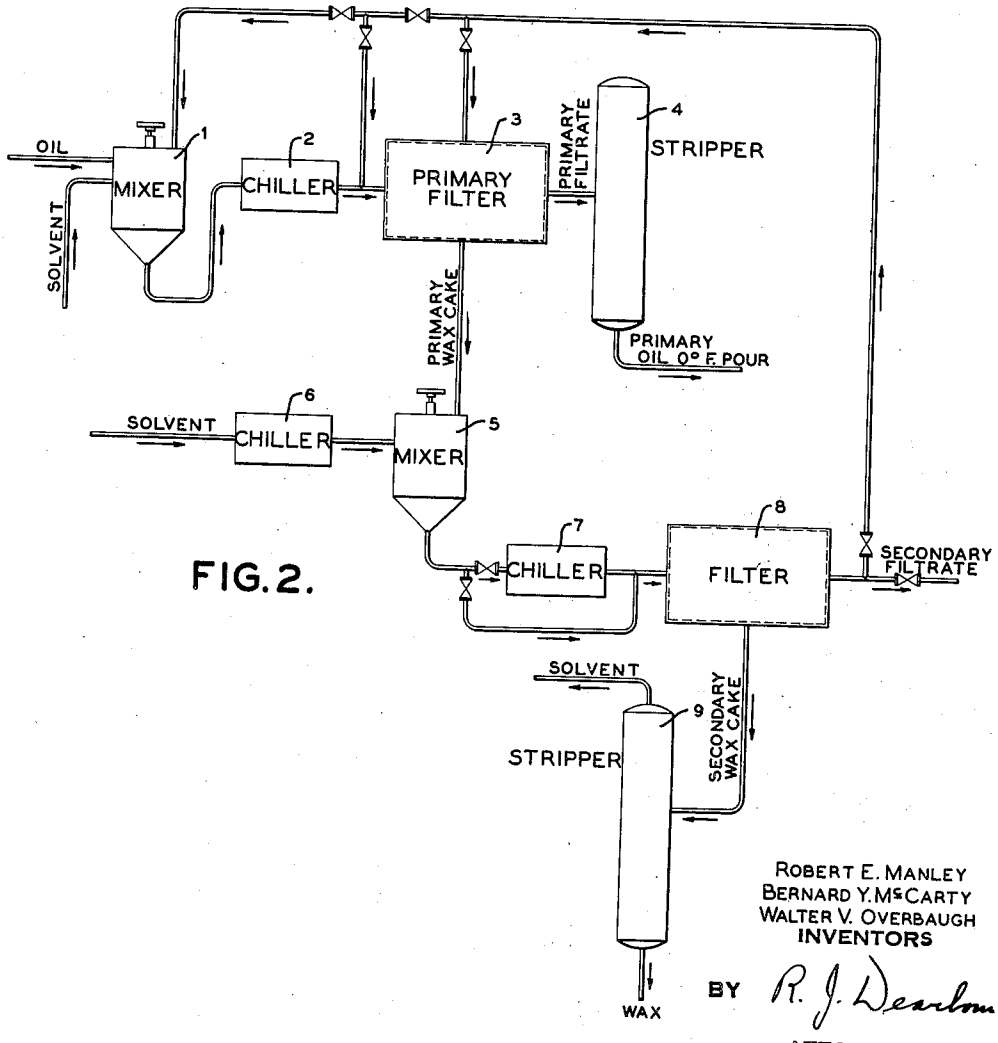


FIG. 2.



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DEWAXING HYDROCARBON OIL

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11 Claims. (Cl. 196—18)

This invention relates to a method of separating wax from oil, and particularly to a method of separating wax from wax-bearing mineral oil.

The invention broadly contemplates dewaxing wax-bearing hydrocarbon oil with a selective solvent under conditions of concentration, composition of solvent, and temperature of dewaxing such that the solid hydrocarbons can be removed from a cold mixture of solvent and oil by filtration at relatively rapid rates. The invention has reference to the dewaxing of mineral lubricating oil stocks to produce therefrom products of low pour test as, for example, having a pour test around 0° F. It has particular reference to the dewaxing of certain types of lubricating oil stock, as will be more fully explained.

In more detail, the invention comprises mixing the oil with a selective dewaxing solvent liquid in proportion such that upon chilling the mixture to around 0° F. and below, there is formed a liquid phase consisting essentially of the liquid hydrocarbons or oil and solvent, and a solid phase consisting essentially of solid hydrocarbons or wax, and such that upon chilling to a slightly lower temperature a small amount of a third phase is formed consisting of a mixture comprising hydrocarbons relatively lean in solvent and composed of oil associated with wax. It is desirable that this third phase be present in the form of small discrete particles of solid or semi-solid character which impart free-filtering characteristics to the chilled waxy mass.

The mixture of selective solvent and wax-bearing oil is chilled to the desired temperature to precipitate the solid hydrocarbons and a small amount of the above mentioned third phase. The chilled mixture containing the precipitated hydrocarbons is then filtered to produce a dewaxed filtrate and a filter cake of wax containing a small amount of oil, including oil forming a part of the above mentioned third phase.

The filter cake may be washed, in situ, with fresh solvent, in which case the wash solvent used may be at a temperature slightly above the temperature at which the wax-bearing mixture was filtered, the purpose of this washing being to remove the retained oil.

It is considered preferable, however, to remove the filter cake and subject it to a separate deoiling treatment. In this treatment, the cake is commingled with fresh solvent at a low temperature and then filtered, removing the wax as solid hydrocarbons in the form of a filter cake substantially free of oil. The filtrate resulting from this deoiling operation is advantageously recycled through the primary dewaxing apparatus. In such case, it is mixed with the fresh charge or with the mixture of fresh charge and solvent. In the case of certain wax-bearing fractions rich in wax, it is advantageous to incorporate a portion of the dewaxed filtrate in the charge to the filter. The recycling of oil of substantially the same grade as that being dewaxed has the effect of increasing the ratio of oil to wax, which causes a marked improvement in the yield of dewaxed oil in the filtering step, particularly in the case of certain types of charge stock. For this reason, it may be desirable to recycle the filtrate from the above described deoiling step through the initial filtering operation.

The selective solvent used in practicing the invention advantageously comprises a mixture of an oil solvent, such as benzol and toluol, and a wax anti-solvent, such as acetone and methyl ethyl ketone. Other anti-solvents, besides the aliphatic ketones, may be employed as, for example, sulphur dioxide, furfural, phenol, benzaldehyde, formates, acetates, etc. Likewise, other oil solvents may be used besides aromatic hydrocarbons as, for example, low-boiling aliphatic ethers, halogenated aliphatic hydrocarbons, such as propylene dichloride, and chlorinated aromatic hydrocarbons, such as chlorbenzene.

It has been discovered that, in the case of certain types of wax-bearing oil, by maintaining certain conditions of solvent composition, dilution ratio, and dewaxing temperature, it is possible to realize a substantial improvement in the rate at which the wax can be filtered from the chilled mixture. For example, it is possible to increase the filter rate by 10% to 30% from that normally obtaining while obtaining relatively high yields of dewaxed oil.

This improvement in filtration rate obtains where the solid hydrocarbons precipitated upon chilling contain a small amount of a third phase relatively lean in solvent and comprising hydrocarbon particles having a discrete or individually distinct crystalline character at the dewaxing temperature. These particles act as a filter-aid and appear to be a mixture of oil and wax. At any rate, the precipitated waxy mass is of a much more free-filtering character than when these particles are absent.

This third phase is distinct from the main body of wax-free oil dissolved in solvent, and it is distinct from the main body of solidified wax. On the other hand, it is to be contrasted with the type of third phase also relatively lean in solvent and which may be obtained under somewhat sim-

ilar conditions from certain types of oil particularly certain heavy residual lubricating oil fractions. The third phase, which may be formed in the case of the latter type of oil, is of a sticky character. It does not comprise particles of distinguishable crystalline character. For this reason, its presence actually impedes filtration.

Moreover, the type of third phase having the desired filter-aid characteristics is to be contrasted with the type of third phase which is relatively rich in solvent liquid and which occurs under certain other conditions of solvent composition and dosage for a particular stock. A third phase, rich in solvent, does not give the above mentioned improvement in filter rate.

The conditions which give rise to a third phase lean in solvent, and one rich in solvent, may be explained by reference to the curve shown in Figure 1 of the drawing showing the miscibility temperatures for a distillate lubricating oil fraction with different amounts of solvent. The distillate, for example, is one of about 100 Saybolt Universal seconds viscosity at 210° F., such as derived from a mixed-base crude which has been previously dewaxed to a pour test of around 0° to —5° F. The solvent consists of a mixture of equal parts by volume of methyl ethyl ketone and benzol. The benzol corresponds to the commercial grade of "90% Benzol."

The values represented by this curve are obtained by dissolving samples of the oil in different quantities of the solvent mixture, and gradually cooling the resulting solutions until the appearance of a cloud occurs. The temperature at which this cloud appears is the point at which there is incipient separation of oil from the solution.

It is possible to distinguish between a condition of incipient oil separation and incipient wax separation. The separation of wax from a solution of oil in solvent is noted as a translucent haze consisting of a fine flocky non-striating precipitate of crystalline wax, which redissolves only after considerable warming above the precipitation temperature. Oil separation, on the other hand, is evidenced by a sharp turbidity, or cloud, which forms striations on being agitated. This cloud dissolves more rapidly on reheating than does the wax cloud.

The area above the curve is the zone of complete miscibility between the oil and solvent mixture. The zone beneath or within the curve represents the zone in which the mixture exists in two liquid phases, disregarding the presence of any substantial amount of wax, which latter would constitute another and solid phase.

As indicated by the curve, the cloud point is relatively low with low dilution ratios and rapidly rises to a maximum with a dilution ratio of about two parts of solvent to one of oil. Thereafter, it decreases with increasing dilution ratios.

Considering Condition I, wherein one part of oil is dissolved in one part of solvent, separation into phases does not occur until cooling to a temperature of around —5° F. At a temperature around —15° F. the main body of oil and solvent will have a composition corresponding to the point "A", while the small amount of separated phase will have a composition corresponding to point "C"; that is, it will consist of a mixture of about five parts of solvent to one part of oil, and is therefore rich in solvent.

Under Condition II, however, where one part of oil is dissolved in four parts of solvent to begin with, separation into liquid phases begins at a temperature of around —7° or —8° F. At a temperature around —15° F., the composition of the main body of oil and solvent will correspond to point "C", while the separated phase will have a composition indicated by point "A". In other words, the separated phase is now lean in solvent.

Thus, the type of third phase formed under Condition II, and which is relatively lean in solvent, imparts the desired free-filtering characteristics to the filter cake on dewaxing, in accordance with the method of this invention.

This type of third phase, having the desired filter-aid characteristics, can be obtained in the case of distillate lubricating oil fractions of medium and heavy viscosity, for example, ranging from around 40 to 50 seconds to 100 or 120 seconds at 210° F. Saybolt Universal. Examples of such distillates are lubricating oils derived from Pennsylvania, Kettleman Hills, Mid-Continent, and Rodessa crudes. The process is applicable to the dewaxing of such distillates, either before or after solvent refining, to remove low viscosity index constituents.

It is applicable to residual fractions, provided the desired type of third phase is present, as may be the case with lighter residual fractions which contain a relatively large proportion of neutral oils.

In dewaxing a lubricating oil stock of the character illustrated by the curve referred to above, it is necessary to have a dilution ratio of greater than 2:1 in order to obtain the desired type of phase separation. With some stocks, the desired result may be obtained with a dilution ratio of only 1:1. The upper limit from a practical standpoint is about 5:1.

This process is thus applicable to the dewaxing of lubricating oil stocks which, when mixed with selective solvent under certain specified conditions, and chilled to the dewaxing temperature specified, form a small amount of third phase relatively lean in solvent, and comprising hydrocarbon particles having an individually distinct crystalline character.

Stated in more detail, the process is applicable to lubricating oil stocks of the type in question from which, when mixed with from one to five parts by volume of a methyl ethyl ketone-benzol mixture containing around 40% to 60% ketone, and the mixture chilled to a temperature of from 1° to 10° F. below the temperature at which incipient oil separation occurs, a small amount of a third phase is formed comprising hydrocarbons and solvent, containing not less than about 40% of hydrocarbons and amounting to around 1% to 10% by volume of the undiluted wax-bearing oil.

In order to further illustrate the invention, reference will now be made to Fig. 2 of the accompanying drawing.

Wax-bearing oil of the above type is conducted from a source not shown to a mixer 1 where it is mixed with solvent, also conducted from a source not shown. The solvent comprises a mixture of about 40% methyl ethyl ketone and 60% commercial benzol, and is mixed with the oil in the proportion of about four parts of solvent to one of oil.

The resulting mixture is then conducted to a chiller 2 wherein it is chilled to a temperature of around —10° F. The chilled mixture is then filtered in a continuous type of primary filter 3. This filter may be of the rotating drum type or of the rotating leaf type. The filtrate is drawn to a stripper 4 wherein the solvent is recovered for

reuse and a dewaxed oil having a pour test of around 0° F. is produced.

The primary wax cake containing some oil is then conducted to a mixer 5 wherein it is commingled with fresh solvent from a chiller 6. The solvent used may be in the proportion of a half to three parts of solvent to one part of wax cake.

From the mixer 5, the mixture may be conducted to a chiller 7, or it may be conducted directly to a secondary filter 8, wherein the wax is removed as a wax cake and the oil associated with the wax is removed along with the main body of solvent as a filtrate. The wax cake is drawn off to a stripper 9 to remove therefrom any remaining solvent and leave a wax substantially free from oil. The secondary filtrate is drawn off as indicated, and is returned, all or in part, to the mixer 1, previously mentioned, for recycling to the primary filtering operation. If desired, it may be mixed with the charge as it enters the primary filter 3.

A portion of this secondary filtrate may be returned to the cake discharge side of the primary filter 3 wherein it is used as a sluicing agent to facilitate removal of the primary cake from the primary filter. In this case, it is forced through jets against the filter surface carrying the filter cake, and this jetting action acts to dislodge the cake.

When operating in the above manner, the secondary filtrate produced from the filter 7 comprises around 1% to 8% of oil.

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. In the dewaxing of wax-bearing hydrocarbon oil consisting mainly of medium and heavy viscosity neutral lubricating oil to produce oil of around 0° F. pour wherein the wax is removed in solid form from a cold mixture of oil and solvent by filtration, the method comprising mixing the oil with a selective dewaxing solvent liquid in proportions such that upon chilling the mixture to around 0° F. there is formed a liquid phase comprising liquid hydrocarbons substantially free from solid hydrocarbons and a solid phase comprising solid hydrocarbons and such that upon chilling to a slightly lower temperature a small amount of a third phase is formed consisting of a mixture of petroleum hydrocarbons relatively lean in solvent, said mixture comprising oil associated with wax and in the form of discrete particles distinct from those of said liquid and solid phases, chilling the mixture to form a precipitate of solid hydrocarbons containing a small amount of said third phase, and filtering the mixture to remove the precipitated solid hydrocarbons in the presence of said third phase whereby the rate of filtration is substantially more rapid than in the absence of said third phase.

2. In the dewaxing of wax-bearing hydrocarbon oil consisting mainly of medium and heavy viscosity neutral lubricating oil to produce oil of around 0° F. pour wherein the wax is removed in solid form from a cold mixture of oil and solvent by filtration, the method comprising mixing the oil with a solvent for oil and an anti-solvent for wax in proportions such that upon chilling the mixture to around 0° F. there is formed a liquid phase comprising liquid hydrocarbons substantially free from solid hydrocarbons and a solid phase comprising solid hydrocarbons and such that upon chilling to a slightly lower temperature a small amount of a third phase is formed consisting of a mixture of petroleum hydrocarbons relatively lean in solvent, said mixture comprising oil associated with wax and in the form of discrete particles distinct from those of said liquid and solid phases, chilling the mixture to form a precipitate of solid hydrocarbons containing a small amount of said third phase, and filtering the mixture to remove the precipitated solid hydrocarbons in the presence of said third phase whereby the rate of filtration is substantially more rapid than in the absence of said third phase.

3. In the dewaxing of wax-bearing hydrocarbon oil consisting mainly of medium and heavy viscosity neutral lubricating oil to produce oil of around 0° F. pour wherein the wax is removed in solid form from a cold mixture of oil and solvent by filtration, the method comprising mixing the oil with a selective dewaxing solvent liquid in proportions such that upon chilling the mixture to around 0° F. there is formed a liquid phase comprising liquid hydrocarbons substantially free from solid hydrocarbons and a solid phase comprising solid hydrocarbons and such that upon chilling to a slightly lower temperature a small amount of a third phase is formed consisting of a mixture of petroleum hydrocarbons relatively lean in solvent, said mixture comprising oil associated with wax and in the form of discrete particles distinct from those of said liquid and solid phases, chilling the mixture to a temperature in the range 0° to −20° F. to form a precipitate of solid hydrocarbons containing a small amount of said third phase, said third phase containing oil and wax amounting to from 1% to about 10% of the wax-bearing oil charge, and filtering the mixture to remove the precipitated wax in the presence of said third phase whereby the rate of filtration is substantially more rapid than in the absence of said third phase.

4. In a dewaxing of wax-bearing mineral oil consisting mainly of medium and heavy viscosity neutral lubricating oil, the method comprising mixing the oil with a selective dewaxing solvent in proportions such that upon chilling the mixture to around 0° F. there is formed a liquid phase consisting essentially of liquid hydrocarbons dissolved in the main body of solvent and a solid phase comprising solid hydrocarbons and such that upon chilling to a slightly lower temperature a small amount of a third phase is formed consisting of petroleum hydrocarbons relatively lean in solvent, said mixture comprising oil associated with wax and in the form of discrete particles distinct from those of said liquid and solid phases, chilling the mixture to form a precipitate of solid hydrocarbons containing a small amount of said third phase, filtering the cold mixture to remove the precipitated solid hydrocarbons and third phase in the form of a filter cake, commingling the filter cake with a further quantity of cold solvent to dissolve the liquid hydrocarbons associated with the wax, and filtering the commingled mixture to produce a filtrate and a wax cake substantially free from oil.

5. The method according to claim 4 in which the filtrate obtained in the final filtration is mixed with fresh charge and recycled through the first filtering operation.

6. The method according to claim 4 in which a portion of the final filtrate is employed as a sluic-

ing agent to facilitate discharge of the filter cake from the filter in the initial filtering operation.

7. In a dewaxing of wax-bearing lubricating oil consisting mainly of neutral lubricating oil having a Saybolt Universal viscosity substantially above 50 seconds and around 100 seconds at 210° F. to produce oil of around 0° F. pour wherein wax is removed in solid form from a cold mixture of oil and solvent by filtering, the method comprising mixing the oil with a solvent comprising an aliphatic ketone and an aromatic hydrocarbon in proportion such that upon chilling the mixture to around 0° F. there is formed a liquid phase comprising liquid hydrocarbons substantially free from solid hydrocarbons and a solid phase comprising solid hydrocarbons and such that upon chilling to a slightly lower temperature a small amount of a third phase is formed consisting of a mixture of petroleum hydrocarbons relatively lean in solvent, said mixture comprising oil associated with wax and in the form of discrete particles distinct from those of said liquid and solid phases, chilling the mixture to a temperature in the range 0° to —20° F. to form a precipitate of solid hydrocarbons containing a small amount of said third phase, said third phase containing oil and wax amounting to from 1% to about 10% of the wax-bearing oil charge, and filtering the mixture to remove the precipitated wax in the presence of said third phase whereby the rate of filtration is substantially more rapid than in the absence of said third phase.

8. In a dewaxing of wax-bearing lubricating oil to produce oil of around 0° F. pour wherein wax is removed in a solid form from a cold mixture of oil and solvent by filtering, the method which comprises mixing the oil, consisting mainly of viscous neutral lubricating oil, with a selective dewaxing solvent liquid, comprising a mixture of a solvent for oil and an anti-solvent for wax in proportions such that upon chilling the mixture of wax-bearing oil and dewaxing solvent liquid to around 0° F. there is formed a liquid phase comprising liquid hydrocarbons relatively rich in solvent and substantially free from solid hydrocarbons and a solid phase comprising solid hydrocarbons and such that upon chilling to a slightly lower temperature a small amount of a third phase is formed consisting of a mixture of oil associated with wax, said mixture being relatively lean in solvent and in the form of discrete particles distinct from those of said liquid and solid phases, chilling the mixture to a temperature in the range 0° F. to —20° F. to form a precipitate of solid hydrocarbons containing a small amount of said third phase, said third phase containing oil and wax amounting to from 1% to about 10% of the wax-bearing oil charge, and filtering the mixture to remove the precipitated wax in the presence of said third phase whereby the rate of filtration is substantially more rapid than in the absence of said third phase.

9. A process for dewaxing a wax-bearing mineral oil of a character capable of forming, when mixed with a selective dewaxing solvent, a small amount of a third phase of mixed oil and wax in the form of small discrete particles of solid or semi-solid character at a dewaxing temperature, which comprises mixing the wax-bearing mineral oil with a solvent mixture of an oil solvent and a wax anti-solvent of such composition and in such proportions that upon chilling the mixture to a dewaxing temperature a small amount of said third phase material is formed which is of such character as to function as a filter-aid to materially improve filtration rates upon filtering of the chilled mixture, chilling the resulting mixture to dewaxing temperature, and then filtering in the pressure of said third phase to separate resulting precipitated material from filtrate oil.

10. A process for dewaxing a wax-bearing mineral oil, comprising the steps of mixing the oil with a dewaxing solvent liquid capable of causing the mixture to separate into three phases at a dewaxing temperature of around 0° F. and below, chilling the mixture to dewaxing temperature to precipitate wax constituents, forming a liquid phase comprising the bulk of the liquid hydrocarbons dissolved in the solvent, a solid phase comprising solidified hydrocarbons, and a small amount of a third phase relatively lean in solvent and relatively solid or semi-solid at the dewaxing temperature and which comprises oil associated with wax in the form of small discrete particles capable of imparting free-filtering qualtities to the solid phase, and separating the precipitated wax from the chilled mixture in the presence of said third phase.

11. A process for dewaxing a wax-bearing mineral oil, comprising the steps of mixing the oil with a dewaxing solvent liquid capable of causing the mixture to separate into three phases at a dewaxing temperature of around 0° F. and below, chilling the mixture to dewaxing temperature to precipitate wax constituents, forming a liquid phase comprising the bulk of the liquid hydrocarbons dissolved in the solvent, a solid phase comprising solidified hydrocarbons, and a small amount of a third phase relatively lean in solvent and relatively solid or semi-solid at the dewaxing temperature and which comprises oil associated with wax in the form of small discrete particles capable of imparting free-filtering qualities to the solid phase, and simultaneously filtering both said solid and third phases from the chilled liquid phase to produce a filter cake and a filtrate.

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