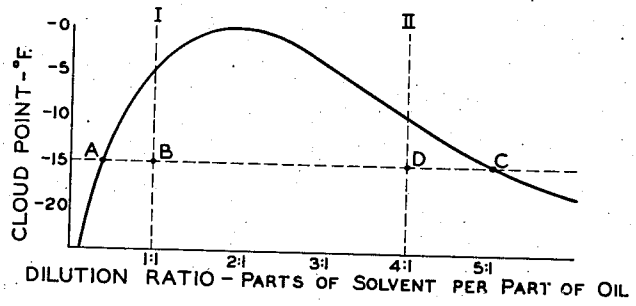
June 6, 1939. H. H. GROSS 2,161,569

DEWAXING HYDROCARBON OIL

Filed Feb. 19, 1938

FIG. 1.



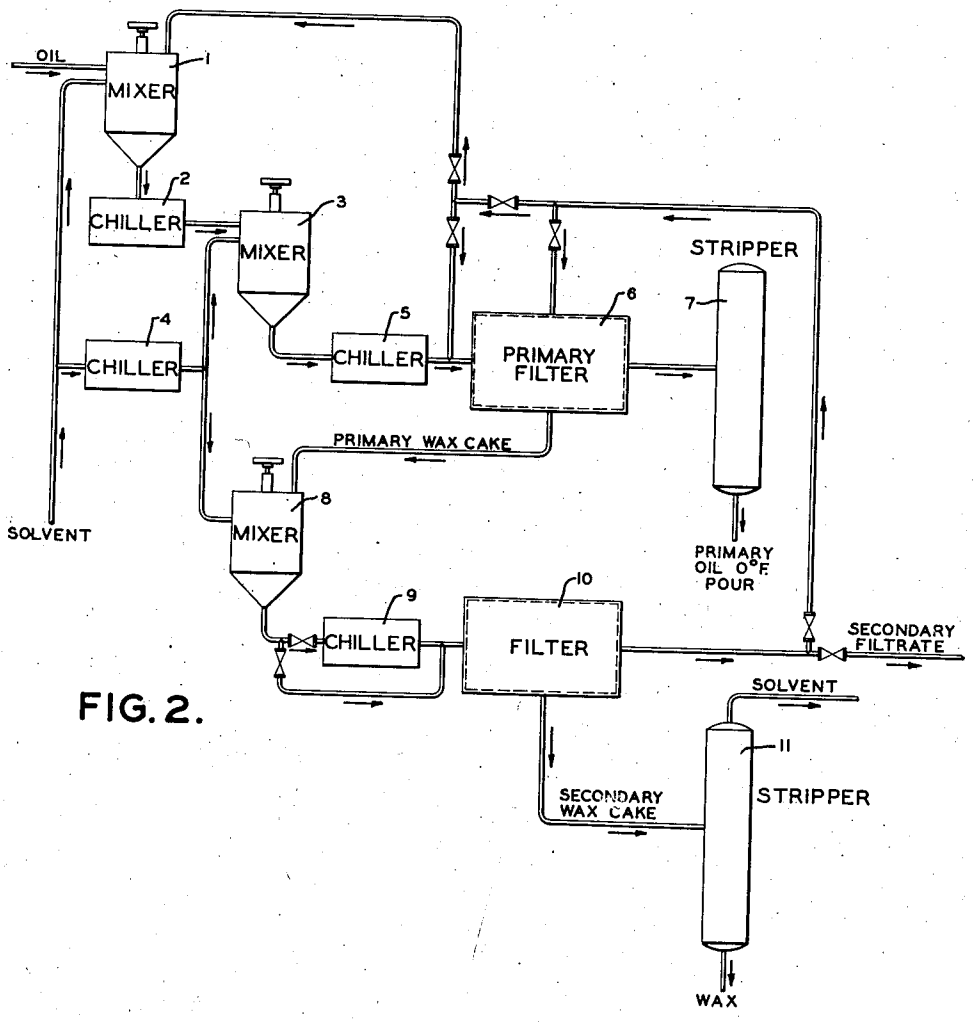


FIG. 2.

HOWARD H. GROSS
INVENTOR
BY R. J. Dearborn
Daniel Stryker

ATTORNEYS

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DEWAXING HYDROCARBON OIL

Howard H. Gross, Beacon, N. Y., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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5 Claims. (Cl. 196—18)

This invention relates to a method of dewaxing hydrocarbon oil, and particularly to a method of separating wax from wax-bearing mineral lubricating 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 to produce a relatively high yield of dewaxed oil.

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 of around 0° F. and below. 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 wax-bearing oil with a relatively small proportion of selective dewaxing solvent liquid. For example, the oil is mixed with about one to two parts by volume of the solvent, depending upon the character of the oil. This mixture is then chilled to about the dewaxing temperature and to a temperature just above that at which liquid hydrocarbons begin to separate from the mixture. To this chilled mixture, a further quantity of solvent in a prechilled condition is added so that, at a temperature of 0° F., the solvent contained in the entire mixture has substantially complete selective action as between liquid and solid hydrocarbons.

At about this temperature, there occurs formation of a liquid phase comprising liquid hydrocarbons substantially free from solid hydrocarbons, and a solid phase comprising solid hydrocarbons.

The mixture of diluted charge and prechilled solvent is chilled to a slightly lower temperature to cause separation of a third phase consisting of a mixture comprising petroleum 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. This final chilling is usually to a temperature of about 6 to 8° F. lower than the temperature at which incipient oil separation ocurs.

It has been discovered that, in the case of certain types of wax-bearing oil, by having a small amount of this third phase material present during dewaxing, the rate at which the precipitated solid hydrocarbons can be removed from the chilled mixture by filtration is very substantially increased. For example, the filter rate may be increased by 10 to 30% from that normally obtaining in the conventional dewaxing procedure.

This improvement in filtration rate obtains where the precipitated solid hydrocarbons contain a small amount of this third phase, which is relatively lean in solvent and comprises 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. The resulting precipitated waxy mass is of a much more free-filtering character than when these particles are absent.

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 such as sulphur dioxide, furfural, phenol, benzaldehyde, formates, acetates, etc.

Likewise, other oil solvents may be used besides aromatic hydrocarbons, such as low-boiling aliphatic ethers, halogenated aliphatic hydrocarbons, for example, propylene dichloride and chlorinated aromatic hydrocarbons such as chlorbenzene.

The process is applicable to lubricating oil stocks which, when mixed with from one to five parts by volume of a methyl ethyl ketone—benzol mixture containing around 40–60% 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 petroleum hydrocarbons and amounting to around 1% to 10% by volume of the undiluted wax-bearing oil. Lubricating oil stocks of the type in question comprise distillate lubricating oil fractions of medium and heavy viscosity, for example, ranging from around 40 to 50 seconds to 100 or 120 seconds Saybolt Universal at 210° F. Examples of such distillates are those derived from Pennsylvania, Kettleman Hills, Mid-Continent and Rodessa crudes. The process is particularly applicable to the dewaxing of lubricating oil stocks which have been previously refined by solvent extraction to remove the low viscosity index constituents.

It is applicable also 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.

The third phase material previously mentioned 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 similar conditions from certain types of oil, particularly certain heavy residiual 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 lean 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 desired 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 and showing the miscibility temperatures for a distillate lubricating oil fraction with different amounts of solvent.

The distillate is one of about 100 Saybolt Universal seconds viscosity at 210° F. such as derived from a mixed-base crude 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 commercial benzol known as "90% benzol".

The values represented by this curve are obtained by dissolving samples of 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 is characterized by 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 that 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 part of oil. Thereafter, it decreases with increasing dilution ratios.

Thus, in 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 of 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 the 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 of 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, 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.

While a substantial increase in filtration rate is realized by dewaxing in the presence of this third phase, nevertheless the maximum yield of dewaxed oil is not realized in a single stage filtering operation. This is due in part at least to the intentional removal of part of the oil with the wax in the form of the third phase.

It is, therefore, necessary to treat the resulting filter cake with further solvent in order to recover the oil associated with the wax.

I have found that this reduction in yield of dewaxed oil can be offset, in substantial measure, by modifying the procedure with respect to chilling. Instead of mixing all the solvent with the wax-bearing oil initially, only a small proportion of the solvent is initially mixed with the charge, sufficient to render the mixture relatively fluid at a temperature of around 0° F.

For example, in the conventional procedure, where the wax-bearing oil would be mixed with from two to four parts of selective solvent, in the procedure of my invention the wax-bearing oil is initially mixed with about one to two parts by volume of the selective solvent.

This initial mixture is chilled to about —5° F. or to a temperature just above that at which oil separation occurs. Thereafter, an additional quantity of the solvent prechilled to about —5° F. is added to bring the dilution ratio up to the desired amount so that at around 0° F. the solvent will have substantially complete selective action as between wax and oil.

This mixture is then chilled to a slightly lower temperature, for example, around —15° F., to cause formation of the third phase in a relatively small amount. Thereafter, the chilled mixture is filtered in the presence of this third phase.

Chilling the wax-bearing oil in the presence of a small proportion of the selective solvent results in substantially higher yields of dewaxed oil although this is frequently accompanied by a reduction in filtration rates, unless provision is made for increasing the filtration rate by dewaxing in the presence of a filter-aid comprising the third phase material described above.

Accordingly, the invention involves chilling wax-bearing oil in the presence of a relatively small proportion of selective dewaxing solvent to enhance the yield of dewaxed oil, and separating the wax from the chilled mixture of oil and solvent in the presence of the above described filter-aid material to thereby enhance the rate of filtration.

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

A wax distillate of about 70 seconds viscosity at 210° F. Saybolt Universal, derived from Mid-Continent crude, and previously refined by solvent extraction, is conducted to a mixer 1. It is there mixed with a selective solvent comprising a mix-

ture of about equal parts of methyl ethyl ketone and commercial benzol. The solvent is added in the proportion of about one to two parts of solvent to one part of oil.

This mixture is conducted through a chiller 2 wherein it is chilled to about —5° F. From this chiller, it is introduced to a mixer 3 and there mixed with additional solvent of the same composition which has been chilled to about —5° F. in a chiller 4. This solvent is added to bring the dilution ratio up to about four parts of solvent to one part of oil.

This mixture is then passed through a chiller 5 wherein it is chilled to a temperature of around —15° F., which is about 6 to 8° below the temperature at which oil begins to separate from the solution.

The chilled mixture is then charged to a continuous rotary filter 6. The resulting filtrate is drawn off to a stripper 7 wherein the solvent is recovered for re-use, and a dewaxed oil having a pour test of around 0 to —5° F. is produced.

The primary wax cake containing some oil is then conducted to a mixer 8 wherein it is commingled with fresh solvent from the chiller 4. The solvent used may be in the proportion of one-half to three parts of solvent to one part of wax cake.

From the mixer 8, the mixture is conducted to a chiller 9 where it may be conducted directly to a secondary filter 10 wherein the wax is removed as a wax cake, and the oil associated with the wax is removed along with the solvent as a filtrate.

The wax cake is drawn off to a stripper 11 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 for recycling to the primary filtering operation. If desired, it may be mixed with the charge as it enters the primary filter 6.

A portion of this secondary filtrate may be returned to the cake discharge side of the primary filter 6 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 10 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.

I claim:

1. In the dewaxing of wax-bearing hydrocarbon oil to produce oil of around 0° F. pour, the method comprising mixing the oil with a small proportion of selective dewaxing solvent sufficient to render the mixture relatively fluid at the dewaxing temperature, chilling the mixture to a temperature of at least as low as about 0° F. just above that at which liquid hydrocarbons would begin to separate from the mixture, adding prechilled solvent at susbtantially this same temperature to the chilled mixture such that at a temperature of around 0° F. the solvent contained in the entire mixture has susbtantially complete selective action as between liquid and solid hydrocarbons, forming a precipitate of solid hydrocarbons, chilling this mixture to a slightly lower temperature to cause separation of a small amount of a third phase consisting of a mixture of petroleum hydrocarbons relatively lean in solvent and having a crystalline character, and separating the solid hydrocarbons from the chilled mixture in the presence of said small amount of third phase material.

2. The method according to claim 1 in which the wax-bearing oil is initially mixed with about one to two parts by volume of selective dewaxing solvent.

3. The method according to claim 1 in which the mixture of diluted charge and prechilled solvent liquid is chilled to a temperature of around 6 to 8° F. below the mixing temperature to cause separation of a small amount of a third phase consisting of a mixture of petroleum hydrocarbons relatively lean in solvent and having a crystalline character prior to filtering.

4. In the dewaxing of wax-bearing hydrocarbon oil to produce oil of around 0° F. pour, the method comprising mixing the oil with a small proportion of selective dewaxing solvent having the essential selective action of a mixture of methyl ethyl ketone and benzol containing around 40 to 60% of ketone sufficient to render the mixture relatively fluid at the dewaxing temperature, chilling the mixture to a temperature of at least as low as about 0° F. just above that at which liquid hydrocarbons would begin to separate from the mixture, adding prechilled solvent at substantially this same temperature to the chilled mixture such that at a temperature of around 0° F. the solvent contained in the entire mixture has substantially complete selective action as between liquid and solid hydrocarbons, forming a liquid phase comprising liquid hydrocarbons substantially free from solid hydrocarbons, and a solid phase comprising solid hydrocarbons, chilling this mixture to a slightly lower temperature such that a small amount of a third phase is formed consisting of a mixture of petroleum hydrocarbons relatively lean in solvent and having a crystalline character, and separating the solid hydrocarbons from the chilled mixture in the presence of said third phase.

5. In the dewaxing of wax-bearing hydrocarbon oil to produce oil of around 0° F. pour, the method comprising mixing the oil with about one to two parts by volume of selective solvent comprising a mixture of methyl ethyl ketone and benzol containing around 40 to 60% of ketone, chilling the mixture to a temperature of around 0° F., mixing therewith a further quantity of solvent prechilled to about 0° F. and such that at this temperature the solvent mixture has substantially complete selective action as between liquid and solid hydrocarbons, forming a liquid phase comprising liquid hydrocarbons and a solid phase comprising solid hydrocarbons, chilling this mixture to a slightly lower temperature such that a small amount of a third phase is formed consisting of a mixture of petroleum hydrocarbons relatively lean in solvent and having a crystalline character, and filtering the solid hydrocarbons from the chilled mixture in the presence of said third phase.

HOWARD H. GROSS.