Aug. 28, 1951 K. A. FISCHER 2,565,489

PROCESS OF DEWAXING OF MINERAL AND TAR OILS

Filed June 22, 1948 2 Sheets-Sheet 1

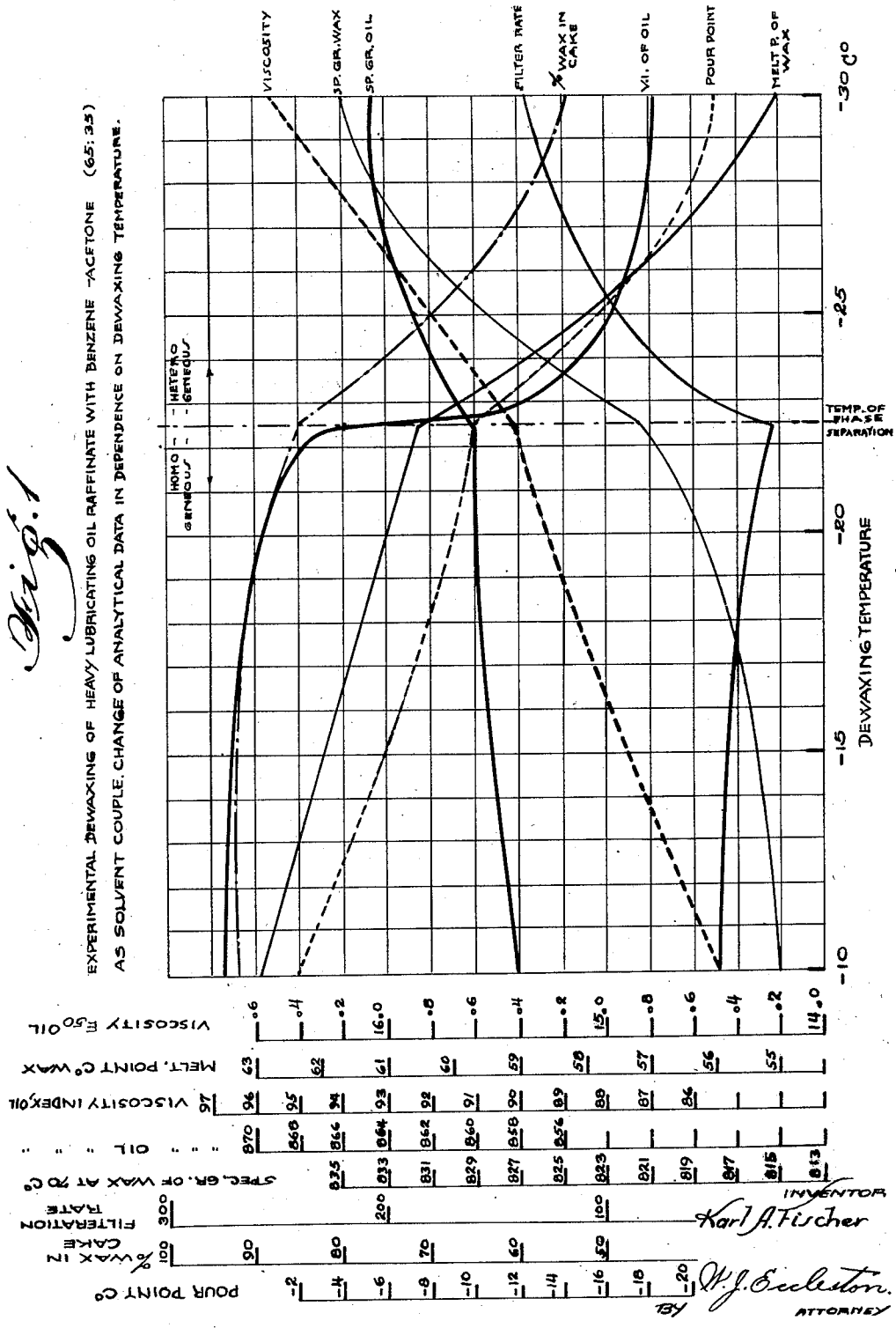


Fig. 1

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Fig. 2

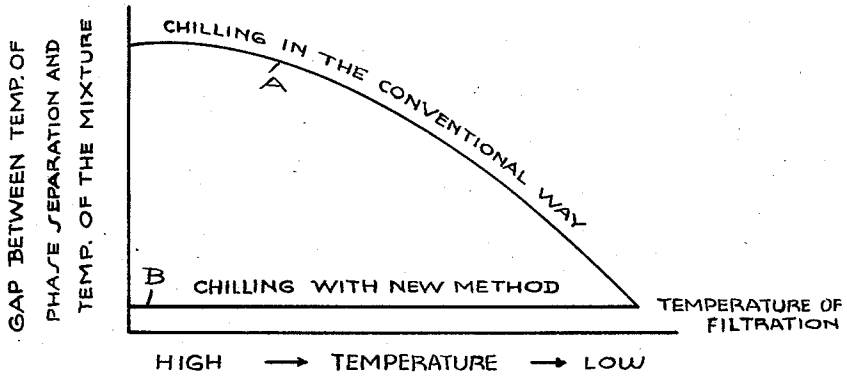
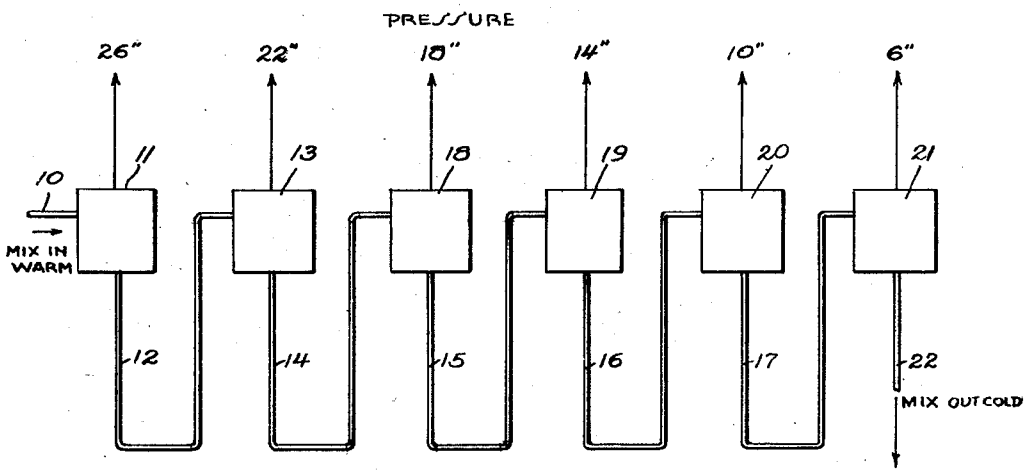


Fig. 3



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PROCESS OF DEWAXING OF MINERAL AND TAR OILS

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10 Claims. (Cl. 196—18)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

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The invention described herein, if patented, may be manufactured and used by or for the Government for governmental purposes without the payment to me of any royalty thereon.

This invention relates to an improved method or process for separating waxy components from mineral oils and tars. More particularly, the invention relates to an improved method for separating paraffin waxes from oils and tars by maintaining a substantially constant selectivity of diluting solvent to mineral oil components at any point of the temperature slant which is used in chilling. That is, the gap between temperature of liquid phase breakdown and existing temperature is kept constant throughout the entire chilling procedure.

Conventional procedures in oil-wax separation processes have been generally directed to the use of a solvent diluent or combination of diluents admixed with oils and utilizing either slow or rapid chilling to effect precipitation of wax material in crystalline form. The selection of diluents either in single or mixed form has been directed primarily towards obtaining a composition or compositions with a desired fixed selectivity at filtration temperature. That is, the removal of paraffin wax from mineral oils and tars is usually done by diluting the material with solvents or solvent combinations, which show selectivity at low temperature, chilling the mixtures to crystallize the wax and separating the solid wax by filtration or centrifuging.

Various methods of chilling oil compositions containing solvents and diluents, including vaporization of a solvent component of the mixture, with or without addition of a vaporizing agent, or indirect contact as by countercurrent flow of a cooling medium, and the like have been utilized without material regard to maintaining a strict selectivity relationship with respect to temperature drop.

In conjunction with the method of separating the waxy component from mineral oils and tars by the use of selective and non-selective agents, it has been discovered that oils of an improved quality and waxes of very little oil content may be obtained by maintaining throughout the normal chilling temperature a constant selectivity of solvent towards mineral oil at any existing temperature by counterbalancing the natural increase of solvent selectivity with dropping temperature through either gradually removing an added selective component or adding gradually a non-selective component.

It is therefore an object of this invention to

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provide an improved chilling process for separating wax from mineral oils and tars.

Another object of this invention provides a control method for improving the filtering of waxy components from oils and tars with maintenance of high quality oils and waxes.

An additional object of this invention is to provide by improved methods a process for separating wax from mineral and tar oils.

It is a further object of this invention to provide a method or process for separating wax from oils and tars by the combined use of selective and non-selective solvents, whereby a constant gap of phase breakdown temperature and existing temperature say e. g. 5° F. is maintained throughout the chilling process.

It is another object of this invention to provide a method or process for separating wax from oils and tars by the combined use of selective solvents, whereby a constant gap of phase breakdown temperature and existing temperature is maintained throughout the chilling process.

Further objects and advantages of this invention will be apparent from the accompanying description taken in conjunction with the following drawings, wherein;

Figure 1 is a graph illustrating the relative change in an oil composition upon phase breakdown;

Figure 2, an illustrative graph contrasting a conventional dewaxing method with that of the method disclosed herein; and,

Figure 3, a diagrammatic illustration of a six stage chilling unit for accomplishing the purposes of the method herein described.

In the specification the terms "selective" and "non-selective" are used in the conventional sense. The term "selective" is applied to liquids which have limited miscibility at room temperature or lower to petroleum hydrocarbons. Such selectivity increases generally with reducing temperature. The term "non-selective" is applied to liquids which have no selective solvent action on petroleum hydrocarbons at either elevated or reduced temperatures. Further, the relative proportions of solvents and non-solvents with respect to phase breakdown for dewaxing particular oils and tars are known in the trade and therefore the controls as hereinafter indicated are readily adaptable to accomplish the process by the methods as herein set forth.

With reference to the apparatus as illustrated in Figure 3 a lubricating oil distillate, for example, is diluted at elevated temperature, to within a few degrees of phase separation with,

for example, 300% dichloromethane and the required quantity of dichlorodifluoromethane, which may be in the amount of 50% more or less, dependent upon the particular oil, as understood in the trade. A mixture of this character is prepared in a conventional mixing vat (not shown) and is introduced through conduit 10 to a first stage chiller 11. When the homogeneous mixture of oil and diluents or solvents, prepared in the manner as indicated, is first introduced into chiller 11, it is in a relatively warm condition to afford a complete admixture between the components of the composition. In the chiller 11, pressure is reduced to substantially 26 inches atmospheric which permits proportional evaporation of the volatile fluorochlorinated methane constituent of the oil mixture causing the temperature of the oil composition to drop, for example, in the approximate amount of 6 degrees. Thereafter, the oil composition is conducted through conduit 12 to the second chiller 13 where atmospheric pressure is reduced to approximately 22 inches with further evaporation of the volatile components of the composition and subsequent further reduction in temperature approximately another 6 degrees. Thereafter, the cooled solution is conducted through conduits 14, 15, 16, and 17 to subsequent chilling stages 18, 19, 20 and 21 respectively with corresponding and equal reduction in atmospheric pressures to effect chilling in the same manner as in the 1st and 2nd stage chilling units. In a final chilling stage 21, maintained at substantially 6 inches atmospheric pressure, the oil composition drops to substantially —20° C. and thence flows through conduit 22 to a conventional wax filter or separating means (not shown).

In the chilling method above described the dichloromethane and the dichlorodifluoromethane is a highly selective combination which, as stated, is added in an amount to bring the mixture at elevated or room temperature close to the point of liquid phase separation, still keeping it in the homogeneous field. With the drop in temperature, say for example, in the 1st stage, the increased selectivity of the solvents towards the oil component is counterbalanced by the removal of part of the highly selective component upon evaporation at reduced pressure. As increasingly reduced pressures occur in successive stages additional dichlorodifluoromethane is withdrawn gradually in reducing percentages as selectivity becomes greater to avoid phase separation and to maintain substantially constant selectivity change controlled with the temperature change.

In the method as above described the apparatus may consist of from 6 to 12 chilling units with evaporative stages arranged to provide a temperature drop from room or elevated temperatures to —20° C. or less in the manner as known to the trade. For example, an 8 stage system is of general usage and the temperature drop for each stage depends upon the average overall pressure reduction in each unit to reduce the temperature from approximately 30° C. to —20° C. In a system of this character, utilizing controlled selectivity at any temperature, there is formed a wax crystalline structure of uniform size in a homogeneous oil solution which filtered readily. With the oil treated as above indicated and filtered by a standard filtration apparatus the wax was of commercial quality having very slight oil or almost no oil content and the oil had a —18° C. pour point.

Another method by which the constant selectivity at any temperature gap between phase breakdown and temperature drop may be maintained throughout the chilling process, is by progressive addition of a non-selective component. In this method the wax bearing oil is diluted with solvents of a highly selective character such as, organic acids, ketones, aldehydes, certain alcohols such as butyl, or amyl alcohol, and the like, fluorinated and chlorinated hydrocarbons, and other selective agents of this character known to the art, in amounts such as to be only a few degrees from phase separation at elevated or room temperature. Thereafter the mixture is chilled by conventional methods with the addition of a slightly selective or non-selective component in the nature of aliphatic and aromatic hydrocarbons as propane or benzene and the like, or amines, ketones, etc., and others as known to the trade, added in proportions of from 10% to 100%, which controls the selectivity continuously for any temperature. The relative value with respect to selectivity of solvent and/or non-solvent additions for different oils varies for each oil as recognized by trade knowledge and accordingly such expressions as used herein are broadly expressed to set forth the principles for using the process disclosed.

An example of a solvent mixture utilizing components of the above character is: Benzene and sulfurdioxide—the SO_2 as a highly selective component is added to oil in an amount just below liquid phase separation at room temperature. Chilling is effected in any conventional manner as with shell and tube chillers. As the temperature of the solvent and oil mixture is reduced benzene is injected into the mixture at regular intervals to keep the temperature gap between chiller temperature and temperature of liquid phase breakdown constant. Otherwise, with the benzene content constant, cooling by evaporation of sulfurdioxide may be utilized for a process as herein described, with subsequent additions, at intervals, of sulfurdioxide in gradually decreasing proportions of from 10% to 1%, or in amounts which keep the oil composition in the homogeneous field, and maintains the gap between temperature of liquid phase separation and temperature of the mixture at any time during the chilling process substantially constant.

The solvent couple benzene and acetone may be utilized with chlorinated and/or fluorinated hydrocarbons or sulfurdioxide with evaporation of the volatile selective component and/or addition of the non-selective components in the manner as herein described for keeping selectivity adjusted for any temperature. Likewise, other selective and non-selective solvents of the character known to the trade and utilizable in the manner as herein illustrated and described may be used for the purpose of dewaxing oils at relative and suitable dewaxing temperatures, e. g., dependent upon the pour point desired, by the methods as indicated.

As illustrated by Figure 1, the advantages of keeping an oil material in the homogeneous state during dewaxing is obvious. As indicated, when the line of phase separation is passed it is only filtration rate which increases rapidly, while all other data are changed most unfavorably. For example, the quality of oil and wax decrease with a sudden leap and the lower pour point of the oil is off-set with a substantial decrease of viscosity index.

In the graph of Figure 2, curved line A shows

selectivity changes or drops with decreasing temperatures in standard dewaxing processes, or as taught by indiscriminate general use of selective and non-selective solvents. Whereas, the line B is indicative of a substantially constant temperature gap between phase breakdown and existing temperature at any time during chilling as produced by practicing the method or process as herein disclosed.

By the process or method above described reliable and good results are obtained with less dewaxing efforts in separating waxes of high and low melting points from mineral and tar oils. Consequently, there is developed an advance in dewaxing methods. Further, by using the methods illustrated in this process dangers of local undercooling and damaging results from liquid phase breakdown are avoided.

Having thus described my improved process for dewaxing oils it will be readily apparent that the methods may be practiced in conventional equipment facilitating the production of improved waxes and oils.

I claim:

1. In the process of dewaxing oil by dissolving waxy oil in a combination of a selective and a non-selective solvent, followed by progressively chilling the solution and separating the wax from the chilled solution: the improvement comprising the step of progressively reducing the ratio of selective solvent to the remaining components of said solution during said chilling, said reduction being substantially proportional to the rate of progress of said chilling, so as to maintain said solution in a homogeneous state throughout the chilling process.

2. In the process of dewaxing oil by dissolving waxy oil in a combination of a selective and a non-selective solvent, followed by progressively chilling the solution and separating the wax from the chilled solution: the improvement comprising the step of progressively withdrawing portions of said selective solvent from said solution during said chilling, said withdrawals being substantially proportional to the rate of progress of said chilling, so as to maintain said solution in a homogeneous state throughout the chilling process.

3. In the process of dewaxing oil by dissolving waxy oil in a combination of a selective and non-selective solvent, followed by progressively chilling the solution and separating the wax from the chilled solution: the improvement comprising the step of progressively adding non-selective solvent to said solution during said chilling, said additions of non-selective solvent being at a rate to reduce the ratio of selective solvent to the remaining components of said solution substantially proportional to the rate of progress of said chilling, so as to maintain said solution in a homogeneous state throughout the chilling process.

4. In the process of dewaxing oil by dissolving waxy oil in a combination of a selective and a non-selective solvent, followed by progressively chilling the solution and separating the wax from the chilled solution: the improvement comprising the concurrent steps of progressively withdrawing portions of said selective solvent from said solution and progressively adding non-selective solvent to said solution during said chilling, said withdrawals and additions being at a rate to reduce the ratio of selective solvent to the remaining components of said solution substantially proportional to the rate of progress of said chilling, so as to maintain said solution in a homogeneous state during the chilling process.

5. The process of claim 2 wherein said withdrawals of selective solvent are carried out by evaporation under reduced pressure.

6. The process of claim 1, wherein said selective solvent is a halogenated hydrocarbon.

7. The process of claim 1 wherein said selective solvent is sulfur dioxide.

8. The process of claim 1 wherein said non-selective solvent is benzene.

9. A process of dewaxing oil comprising dissolving waxy oil in a solvent combination of dichloromethane and dichlorodifluoromethane, passing said solution through a series of chillers at progressively reduced pressures whereby portions of said dichlorodifluoromethane are evaporated from said solution in each chiller, controlling the rate of chilling and evaporating so as to maintain said solution in a homogeneous state throughout the chilling process, and separating the wax from the chilled solution.

10. A process of dewaxing oil, comprising dissolving waxy oil in a solvent combination of benzene and sulfur dioxide, progressively chilling said solution and injecting additional benzene into said solution at a plurality of regular intervals during said chilling and at a rate to reduce the ratio of sulfur dioxide to the remaining components of said solution substantially proportional to the rate of progress of said chilling whereby said solution is maintained in a homogeneous state throughout the chilling process, and separating the wax from the chilled solution.

KARL A. FISCHER.

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