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PROCESS FOR FRACTIONATING HYDRO-CARBON OILS

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This invention relates to a process for the separation of hydrocarbon mixtures, such as mineral oils, particularly gasoline, kerosene, gas oil, which are substantially free from paraffin wax, into fractions of different properties and melting points by cooling the mixture to solidify at least a portion of the mixture, and separating the lower melting components from the deeply cooled mixture with the aid of a solvent. More particularly, the present invention is concerned with the separation of low melting fractions from higher melting fractions which, however, have melting points below that of paraffin wax.

It is already known to separate paraffin wax in the solid state from hydrocarbon oils, particularly from lubricating oils, by cooling the wax-bearing oil after the addition of diluents, and filtering the solidified wax from the liquid solution of oil and diluent. Further, it is known to separate hydrocarbon fractions having melting points lower than that of paraffin wax by a similar process, employing lower temperatures, such as a temperature between -45° and -130° C.

Finally, it has already been proposed to carry out the dewaxing of lubricating oil by separately cooling the wax-bearing oil and the diluent to the dewaxing temperature, and then mixing the chilled diluent and the chilled oil, after which the paraffin wax which has been crystallized is separated from the liquid oil and diluent solution by mechanical means.

In accordance with the present invention it was found that the separation of low melting fractions from a mixture which is normally liquid, i. e., which is liquid at -20° C., and which may or may not contain small amounts of wax, can be carried out more economically and with greater ease of operation by cooling the normally liquid mixture substantially in the absence of a diluent to a temperature sufficiently low to solidify at least certain hydrocarbons having melting points lower than paraffin wax and produce a partially or entirely solid mass of extremely low mobility, and lixiviating the resulting mass with a solvent in which the lower melting fractions of the mixture are more readily soluble than the higher melting fraction, the lixiviation being carried out at a temperature at which at least one fraction melting below paraffin wax is solid. The lixiviation temperature may be varied, depending upon the nature of the hydrocarbon mixture being treated, and the yield and properties of the desired fractions, and will fall within the range: -35° C. to -125° C.

The solvent may be cooled prior to lixiviation

to the same temperature as the deeply-cooled hydrocarbon mixture, or to a somewhat lower temperature; or the hydrocarbon mixture may be cooled to a temperature below that at which the lixiviation is to occur, and the solvent may be only slightly cooled, or not cooled at all, so that the desired low temperature is reached upon lixiviating the former by the latter.

One advantage of the present process lies in the saving of a considerable amount of cold. Thus, when the hydrocarbon mixture and solvent are mixed prior to cooling, large quantities of solvent are required to produce a mobile and filterable mass, e. g., several volumes of solvent for one volume of initial hydrocarbon mixture to be fractionated. This requirement of a large quantity of solvent is due to the formation of unfilterable or difficultly filterable gelatinous masses when insufficient quantities of solvent are used. Such large quantities of solvent necessitate a large supply of cold, not only because a greater quantity of solvent has to be chilled, but also because a deeper cooling is necessary to cause the separation of an equal quantity of solids from the initial mixture. The last requirement may be due to the dissolution of appreciable amounts of hydrocarbons in the solvent which would be solid in the absence of the solvent.

When employing the process according to the present invention smaller quantities of solvent may be employed. For example, from one quarter to one and a half volumes of solvent to one volume of initial mixture may be employed in most cases, although my invention is not restricted to this specific range.

If desired, several fractions with successively decreasing melting points may be separated from a hydrocarbon mixture by evaporating the solvent from the liquid remaining after the separation of the first fraction, and subsequently subjecting the said liquid to a still deeper cooling to solidify at least one more fraction, and then lixiviating the recooled mass anew with the same or another solvent.

It is often desirable to treat initial mixtures containing hydrocarbons of closely similar boiling temperatures. Thus, a petroleum fraction may be fractionally distilled to produce fractions having boiling temperature ranges of 15° to 75° C., or less, and these narrow boiling fractions may then be treated in the manner described above.

The separation effected according to the present invention is—when no high melting cyclic hydrocarbons are present—a separation between

saturated aliphatic hydrocarbons with straight chains and a higher melting point on the one hand and saturated aliphatic hydrocarbons with branched chains, unsaturated aliphatic and cyclic hydrocarbons on the other hand. Such a separation is of importance in the manufacture of nearly all the principal petroleum products: for lubricating oils because the saturated aliphatic hydrocarbons with straight chains, boiling in the lubricating oil range, according to the present views are most suitable for lubrication (high viscosity index, slight formation of sludge, etc.); for gas oil because the saturated aliphatic hydrocarbons with straight chains, boiling in the gas oil range, have the highest cetene number and therefore excel as Diesel engine fuel; for kerosene because the saturated aliphatic hydrocarbons with straight chains, boiling in the kerosene range, have the smallest tendency to soot, and finally for gasoline because as a result of this process the gasoline can be split up into fractions of varying octane numbers.

The solvents which, in applying the process according to the invention, are used for the lixiviation of the deeply-cooled, entirely or partly solid hydrocarbons must be either non-polar or only slightly polar. Of course, they should be liquid in the presence of the oil at the low temperatures employed in the process. Thus, for instance, hydrocarbons, or mixtures thereof, such as gasoline fractions, toluene, further chlorinated hydrocarbons, such as ethylene chloride and the like, ethers, esters, etc. with a low melting point may be considered as solvents.

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Example

A gas oil having a spec. gr. 20/4 of 0.903, a pour point of $-11^{\circ}\text{C}.$, and an aromatic content of 40% by volume, was cooled to $-60^{\circ}\text{C}.$ To the semi-solid vaseline-like paste thus obtained there was added—in several portions—in all 70% by volume of toluene, likewise cooled to $-60^{\circ}\text{C}.$, without mixing too intensively. The resulting mass was then filtered at $-60^{\circ}\text{C}.$, yielding more than 40% of a filter-cake which could be easily separated with a spec. gr. 20/4 of 0.874, a pour point $+1^{\circ}\text{C}.$ and an aromatic content of 30% by volume. The filtrate had a pour point of $-57^{\circ}\text{C}.$, a spec. gr. 20/4 of 0.924 and an aromatic content of 50% by vol.

When the same gas oil is initially mixed with a similar volume of toluene and then chilled to $-60^{\circ}\text{C}.$, a mass is obtained which filters much more slowly and finally yields a jelly-like filter cake still containing a considerable quantity of liquid that belongs in the filtrate.

I claim as my invention:

1. A process for separating hydrocarbon fractions having melting points below that of paraffin

wax and contained in a hydrocarbon mixture liquid at $-20^{\circ}\text{C}.$, comprising the steps of chilling said mixture substantially in the absence of a diluent to a temperature below $-35^{\circ}\text{C}.$ to solidify at least a portion of the hydrocarbons having melting points below that of paraffin wax and form an unfiltrable mass of low mobility, adding to the said mass an amount of a liquid solvent in which the lower melting hydrocarbons are more readily dissolved than the higher melting hydrocarbons, said solvent being liquid at the temperature of the filtration, and filtering the resulting mixture to separate the undissolved solid hydrocarbons from the solvent and dissolved lower melting hydrocarbons at a rate of filtration which is greater than that of the same hydrocarbon mixture, when this is mixed with the same amount of said solvent while in the liquid state, chilled to the same temperature and filtered under identical conditions.

2. The process according to claim 1, in which the solvent is precooled to substantially the same temperature as the hydrocarbon mixture prior to lixiviation.

3. The process according to claim 1, in which the lixiviation temperature is between -35° and $-125^{\circ}\text{C}.$

4. The process according to claim 1, in which the mass of low mobility is entirely solid.

5. The process according to claim 1, in which the initial mixture has a boiling range not substantially over $75^{\circ}\text{C}.$

6. The process according to claim 1, in which the initial mixture is gasoline.

7. The process according to claim 1, in which the initial mixture is gas oil.

8. The process according to claim 1 in which the solvent is added to the mass of low mobility without thorough mixing.

9. A process for separating hydrocarbon fractions having melting points lower than that of paraffin wax and contained in hydrocarbon mixtures liquid at $-20^{\circ}\text{C}.$, comprising the steps of chilling said mixture substantially in the absence of a diluent to a temperature below $-35^{\circ}\text{C}.$ to form a mass of low mobility, adding to said mass a liquid solvent in which the lower melting hydrocarbons are more readily dissolved than the higher melting hydrocarbons and filtering the resulting mixture at a temperature between $-35^{\circ}\text{C}.$ and $-125^{\circ}\text{C}.$ to separate undissolved solid hydrocarbons from the solvent and lower melting hydrocarbons dissolved therein, said solvent being liquid at the filtration temperature.

10. The process according to claim 9 in which the solvent is a hydrocarbon.

11. The process according to claim 9 in which the solvent is toluene.

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