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PROCESS OF FRACTIONATING MINERAL 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, and lubricating oils, which may or may not contain paraffin wax, into fractions of different properties by cooling the mixture to a temperature at which a portion thereof is solidified and separating the solidified portion from the liquid portion. The invention may, for example, be applied for separating various waxy substances from mineral oils, such as lubricating oils and fuel oils, and the like, to lower their pour points and/or their cloud points. It may, further, be applied to the manufacture of lubricating oil fractions of high viscosity index from the initial lubricating oil fractions which may or may not contain wax; or to the concentration of constituents of fuels for internal combustion engines which have superior anti-detonating properties, such as high octane gasoline or high cetene Diesel fuel; or to the concentration of burning oils of superior burning quality. This application is a continuation-in-part of our copending application Serial No. 65,843, filed February 26, 1936.

The removal of wax from mineral oil has in the past been effected by diluting the waxy oil with a dewaxing diluent primarily to lower the viscosity of the oil, chilling the resulting solutions to solidify the wax in a crystalline or amorphous form, and separating the latter from the oil diluent solution by any suitable means, such as filtration, cold settling, decanting, or centrifuging, depending on the nature of the wax, and its density. To improve the yield and lower the pour point of the dewaxed oil, it has more recently been proposed to employ as dewaxing diluents certain selective solvents, or mixtures of selective solvents with solubility enhancing agents, which selective dewaxing diluents or diluent mixtures not only reduce the viscosity of the oil solution but also exercise a selective solvent action between the oil and the wax, whereby the wax has a reduced solubility in the oil solution, and less oil is removed with the wax, while less wax remains dissolved in the oil. For example, a mixture of acetone and benzol has been employed as a solvent combination for this purpose.

Similar solvent mixtures have been employed to separate hydrocarbon fractions having melting points lower than that of paraffin wax by a similar process, employing lower temperatures such as temperatures between —20° and —130° C. In such selective solvent mixtures, one function of the selective solvent is to lower the solubility of the solidified higher melting constituent, such as solid wax, in the liquid phase. The selective solvents which are able to function in this manner are, however, generally not sufficiently miscible with the portion of the oil which is liquid at the dewaxing temperature, and it is often necessary to add another liquid which is miscible with the oil and with the selective solvent. The latter liquid is commonly known as the solubility enhancing agent.

In accordance with the present invention we have found that petroleum nitrogen bases are excellent diluents for fractionating processes of the type described wherein hydrocarbon mixtures are separated into portions having different freezing or solidification temperatures, and may be employed for dewaxing oil or for effecting a separation between hydrocarbons which are liquid at the solidification temperature of wax. The petroleum nitrogen bases may be employed either alone as single selective diluents, or as solubility enhancing agents in combination with other selective solvents. By "petroleum nitrogen bases" we mean the organic heterocyclic compounds containing nitrogen in the ring which are obtained by the acid extraction of various hydrocarbon distillates boiling within gasoline and kerosene range, i. e., boiling between about 115° C. and 330° C., and produced either by the straight or cracking distillation of petroleum crude oils, shale oil, coal tar, and similar hydrocarbon materials. We have found, moreover, that the petroleum heterocyclic nitrogen bases which contain heterocyclic nitrogen in aromatic rings are superior to nitrogen bases containing nitrogen in a naphthenic ring structure. For this reason, we prefer to obtain our petroleum nitrogen bases from cracked distillates, because acid and/or solvent extraction products from these distillates generally contain upwards of about 60% aromatic nitrogen bases, while the products derived from straight run kerosene may contain as little as 15% aromatic nitrogen bases and 85% naphthenic nitrogen bases.

The concentration of the nitrogen bases containing heterocyclic nitrogen in cracked distillates may be increased by mixing the charging stock prior to cracking with nitrogen gases derived from any source, and particularly with nitrogen bases obtained by acid extraction of crude oils or uncracked distillates. Thus, in the acid treatment of uncracked distillates, it is common to treat the acid sludge with a base such as ammonia to form ammonium sulfate and liberate the nitrogen bases. These liberated bases may be added to charging stock which is fed to cracking stills,

thereby improving the yield of cyclic compounds containing heterocyclic nitrogen, and particularly the aromatic nitrogen bases in the cracked distillate. Nitrogen bases derived from kerosene and similar straight run distillates may, however, be employed. In general, however, it is preferable to treat nitrogen bases which have been derived from uncracked distillates with hydrochloric acid and chloroform, as described by Perrin and Bailey in J. Am. Chem. Soc., vol. 55, pages 4136 et seq., (Oct., 1933) to concentrate the aromatic nitrogen bases.

The petroleum nitrogen bases which are to be employed according to the present invention may be obtained from cracked or uncracked distillates by any suitable extraction method employing either selective solvents or acids, or both, and it is understood that the methods described herein are exemplary only. According to one mode of extraction, the acid sludge, which is obtained by washing a light distillate (such as cracked gasoline or kerosene) with sulfuric acid of 83% to 97% concentration, may be neutralized with an alkaline medium, such as caustic soda or ammonia, and the nitrogen bases may be separated therefrom as the supernatant layer. If desired, the separated supernatant layer may be given a further extractive treatment to eliminate hydrocarbon oil.

According to another method, untreated distillate, such as raw cracked distillate, may be treated with an excess of a comparatively strong acid, such as sulfuric or hydrochloric, to yield an acid phase, which then may be separated from the distillate and neutralized as described above. From 1% to 20% of acid, based on the distillate, is generally satisfactory, although other quantities of acid may be employed. In the case of sulfuric acid, the concentration of the acid may range from 5% to 50%, but more dilute solutions may be employed. If so desired, the separated layer after neutralization with an alkaline medium may be subjected to additional treatment to separate any neutral hydrocarbon oil.

We may employ as our diluents the mixtures of nitrogen bases obtained as a result of the above described treatments or as a result of an extraction with selective solvents. It is often desirable, however, to treat these products further to concentrate their most valuable constituents, as described below.

The products obtained from cracked distillates by extraction with acids or other solvents may, for example, also be treated with hydrochloric acid and chloroform, or in any equivalent manner of treatment, to concentrate the aromatic nitrogen bases, which have been found to be particularly suitable for use as diluents for dewaxing and for the separation of hydrocarbons of lower melting points.

We have found, moreover, that the nitrogen bases which have low dissociation constants, i. e., those having dissociation constants lower than about 1×10^{-7} are superior to those having higher dissociation constants, and when a distillate contains a large proportion of nitrogen bases having high dissociation constants, such as aliphatic or naphthenic amines, it is often desirable to exclude them from the diluents which are used in the process. Various methods for concentrating the low dissociation constant bases may be employed. For example, the mixtures of nitrogen bases obtained according to any of the above described methods may be further treated with weak acids such as ovalic or acetic and to extract therefrom the bases having the highest dissociation constants; or the raw cracked or uncracked distillate may be treated first with such a weak acid to separate only the nitrogen bases having the highest dissociation constants, and the remaining parts of the distillate may then be treated with a stronger acid, as described above.

The most valuable petroleum nitrogen bases for dewaxing and for the other separations may also be concentrated by fractional distillation of either the raw distillate prior to solvent extraction or acid treatment, or of the extracted nitrogen bases. While petroleum nitrogen bases boiling with the above stated range may be employed, we occasionally prefer to employ those which boil within the range of 200° C. to 300° C., since the latter have solubility characteristics which are particularly suitable for our separations.

The nitrogen bases isolated by the acid treatment of cracked or uncracked distillates are believed to include substantial quantities of compounds of the homologous series represented by the following compounds: pyridine, quinoline, and isoquinoline, although pyridine, quinoline and isoquinoline themselves may not be present in substantial amounts. Many other types of nitrogen bases are, however, also present. Since the mixtures of nitrogen bases derived from these distillates are highly complex, and contain a great variety of different compounds, which may vary with the source of the initial cracking material, we do not limit our invention to any theory therein expressed concerning the composition of the nitrogen bases to be employed, but intend to include within the scope of our invention all nitrogen bases which are derived from the above described distillates by extraction with acids.

The petroleum nitrogen bases may be employed either alone or in combination with some highly selective solvents having a low solubility in oil such as selective solvents used for dewaxing oils. When mixed with such selective solvents, the petroleum nitrogen bases act as solubility enhancing agents and exercise some selective solvent action of their own. Among selective solvents which may be employed in combination with petroleum nitrogen bases are the following: Symmetrical and unsymmetrical aliphatic ketones, primary, secondary, and tertiary alcohols, aliphatic esters, aliphatic acids, hydroxy or keto-aliphatic acids, anhydrides of aliphatic acids, all preferably containing not more than about five carbon atoms in the molecule; halogenated derivatives of oxygenated aliphatic substances; and cyclic compounds containing oxygen or nitrogen in the ring and their halogenated and substituted derivatives. Specific examples of these substances are: acetone, ethyl methyl ketone, diacetone alcohol, methyl-formate, ethyl formate, methyl acetate, ethyl acetate, acetic acid, butyric acid, lactic acid, acetic anhydride, methyl carbonate, $\beta\beta'$-dichlorethyl ether, chlor-acetic acid, ethyl propyl and butyl alcohols, quinoline, pyridine, furfural, aniline, cresylic acid, triethanolamine, and nitrobenzene. Although we have enumerated a few specific selective solvents which are suitable for use as diluents for our process when used in conjunction with a solubility enhancing agent, it should be noted that our invention is not limited to this small group but that the petroleum nitrogen bases may be used with any other selective solvent which has the property of creating in the chilled hydrocarbon mixture-diluent system a condition in which the constituent having the higher solidifying tempera-

ture has a minimum solubility in the liquid phase. Thus, in the case of a dewaxing operation, the selective solvent lowers the solubility of the wax in the solution of oil and diluent.

Although our invention may be practiced with all types of selective solvents of the type described above, we prefer to employ a selective solvent which is itself a nitrogen base, and contains no alkyl side chain or only small alkyl side chains; i. e., alkyl side chains containing not over two carbon atoms. Examples of these preferred selective solvents are: pyridine, quinoline, isoquinoline, quinaldine, α picoline, β picoline, and lutidines. Such solvents possess a high selectivity between hydrocarbons solidifying at different temperatures, such as between wax and oil, but often are not sufficiently miscible with the fraction which is to be recovered in the liquid phase at the low temperatures employed. Thus, in dewaxing operations, they do not dissolve enough oil at the dewaxing temperature to permit effective dewaxing. The addition of petroleum nitrogen bases obtained in the above described manner increases their solvent power for the liquid portion of the chilled and partially solidified mixture, while preserving their selectivity.

The ratio of selective solvent to petroleum nitrogen bases may be varied within wide limits, and we may operate with pure petroleum nitrogen bases, or with any desired mixture of petroleum nitrogen bases and selective solvent. Suitable mixtures may, for example, consist of 50 parts by volume of petroleum nitrogen bases and 50 parts of selective solvent, although other ratios, such as 25/75 or 75/25 may be employed. For most efficient dewaxing operations, it is desirable that the diluent mixture have a high solvent power for the liquid hydrocarbons, i. e., for oil in the case of dewaxing and a low solvent power for hydrocarbons which are solid or semi-solid at the temperature employed for dewaxing, i. e., for wax in the case of dewaxing. The low solubility selective solvents, of which the nitrogen bases, and particularly quinoline and isoquinoline, are the preferred examples, are effective in lowering the solubility of the solid or semi-solid hydrocarbons in the liquid phase, while the petroleum nitrogen bases are effective in raising the solvent power of the selective solvent for liquid hydrocarbons.

When no petroleum nitrogen bases or an insufficient quantity of petroleum nitrogen bases are employed, the liquid hydrocarbons will not be completely dissolved in the selective solvent, and two liquid phases will be present in addition to the solid or semi-solid phase at the separating temperature. When operating under such conditions oils having very low pour points and lower-melting fractions of high purity are often obtained, but the yields are generally low. Such a result is often desirable when the solidified fraction is the most valuable product, as when it is desired to produce a paraffinic kerosene or gas oil or diesel fuels. Adding more petroleum nitrogen bases slightly increases the melting point or pour point of the liquid fraction, and increases the yield of this fraction considerably, this being desirable when the liquid fraction is the valuable product, as in dewaxing or in manufacturing gasoline of superior anti-detonating properties. In the latter situation, it will be advantageous to employ the minimum quantity of petroleum nitrogen bases which is required to cause the diluent and the liquid hydrocarbons to form a homogeneous liquid phase at the temperature at which the solid is separated from the liquid, although even slightly smaller or larger quantities of the petroleum nitrogen bases may be employed with good results. Actual dewaxing with various dewaxing mixtures has shown that most efficient wax separation is effected at or near the composition of the dewaxing diluent which corresponds to the transition between the one liquid phase and the two liquid phase conditions. Oil yields may be improved further by employing higher concentrations of nitrogen bases, but the pour points of the treated oils are slightly higher.

The dilution ratio, i. e., the volume ratio of initial oil to diluent or diluent mixture is determined by the viscosity of the oil-diluent solution at the separating temperature, and will depend upon the viscosity of the oil and of the diluent, and upon the dewaxing temperature. For example, dilution ratios of 2:1 to 1:8 have been found to be suitable.

As applied to the dewaxing of oils, the process may be operated, for example, by dissolving a wax bearing oil, such as paraffinous petroleum residues or distillates, lubricating oils, turbine oils, fuel oils, lignite tars, shale oils, low temperature tars, etc., in the petroleum nitrogen bases or in a dewaxing mixture containing a selective solvent and petroleum nitrogen bases, after which the wax is caused to separate out in a crystalline or amorphous state at a lower temperature, such as, for example, 10° C., 0° C., or −20° C., or lower, depending upon the desired pour point of the dewaxed oil and/or the desired melting point of the wax. The separation of the solidified wax may be carried out in any desired manner, although we have found filtration methods to be most suitable. Centrifuging, decantation, or cold settling may, however, often be employed, especially when the specific gravity of the selective solvent is such as to cause a sufficient difference between the densities of the oil phase and the precipitated wax. After the separation of the wax, the dewaxing solvents may be removed from the oil and from the wax by ordinary or vacuum distillation, or by any other method, such as washing with another solvent, which may be removed subsequently by distillation. Aqueous solutions of methanol or ethanol have been found to be suitable as washing solvents. The dewaxing may be carried out either as a continuous or a batch method.

It is desirable, but not essential, to produce a homogeneous oil-solvent system before chilling the oil to precipitate the wax. To achieve this, the dewaxing diluent may be added to the oil at an elevated temperature, or the mixture of oil and diluent may, after mixing, be heated. It is, moreover, often advantageous to heat the mixture to a temperature generally not above 150° C. and in most cases between 65° C. and 110° C. before chilling to improve the filtration rate.

Filter aids may likewise be employed during the filtration. Moreover, the dewaxing may be further improved by adding a pour point reducer, such as aluminum stearate, cracked residues, and the like to the oil in small quantities, generally not above 1%.

Under certain conditions, as when a moderately high pour point is permissible, and/or when, in a multiple stage process, it is desired to obtain high melting wax in the first stage, the precipitation of the wax may be effected at temperatures which are the same as or only slightly below normal. The oil filtrate may, if desired after further addition of dewaxing diluent, be further chilled to separate additional quantities of wax.

It is not necessary to mix all of the components of the diluent mixture before dissolving them in the oil. Thus, the petroleum nitrogen bases may be added first, and the requisite amount of the selective solvent or a solution of selective solvent containing petroleum nitrogen bases may be added separately. Although it is preferred to add the nitrogen bases to the oil prior to chilling, the present invention contemplates the addition of these bases at any stage, so as to be present when the solid wax is separated from the oil.

The same steps may be employed in the fractionations to effect separations between hydrocarbons which solidify at lower temperatures, the separation between the solid or semi-solid portion and the liquid portion being made at lower temperatures, e. g., between —20° C. and —130° C., as is well known in the art. (See U. S. Patent Nos. 1,980,649 and 2,108,629.) In these processes the more paraffinic or saturated hydrocarbons are recovered from the solidified fraction, while the more aromatic or less saturated hydrocarbons are recovered from the liquid fraction. Such low temperature fractionations may be applied to wax-free or to waxy oils, the wax being, in the latter case, solidified together with the more paraffinic hydrocarbons. If desired, waxy oils may be given a preliminary dewaxing treatment prior to being subjected to the low temperature treatment.

The effect of using petroleum nitrogen bases for dewaxing may be seen from the following examples which are not, however, to be regarded as restricting the scope of this specification:

Example I

A waxy lubricating oil of SAE 40 grade, prepared by solvent extraction of a Coalinga (San Joaquin Valley) lubricating distillate oil with SO_2 in conjunction with kerosene extract had a pour point of 65° F. (A. S. T. M. Method D97—34). This oil was mixed with 50% by volume of petroleum nitrogen bases obtained by sulfuric acid extraction of untreated pressure distillate, followed by neutralization and re-extraction to release hydrocarbon oil, and finally by fractional distillation to isolate the fraction boiling between 243 and 262° C. The diluted oil was chilled and filtered at 32° F., to produce an oil having a pour point of 40° F.

Example II

The same oil was mixed wtih 100% by volume of quinoline plus 30% petroleum nitrogen bases, obtained as described in Example I. On carrying out a similar dewaxing at 32° F. the pour point of the oil was reduced to 30° F.

In both examples the dewaxing diluent was removed from the oil by washing with methanol containing a small amount of water which was subsequently removed from the oil by heating under vacuum.

We claim as our invention:

1. A process for separating mineral oils containing several hydrocarbon components having different solidification temperatures, comprising the steps of chilling said oil to a separation temperature to solidify a component thereof, and separating said solidified component from a component having a lower solidification temperature in the presence of separating diluent containing petroleum nitrogen bases separated from a mineral oil distillate boiling between 115° C. and 330° C.

2. A process for separating mineral oils containing several hydrocarbon components having different solidification temperatures, comprising the steps of chilling said oil to a separation temperature between —20° C. and —130° C. to solidify a component thereof, and separating said solidified component from a component having a lower solidification temperature in the presence of separating diluent containing petroleum nitrogen bases separated from a mineral oil distillate boiling between 115° C. and 330° C.

3. A process for separating mineral oils containing several hydrocarbon components having different solidification temperatures, comprising the steps of chilling said oil to a separation temperature to solidify a component thereof, and separating said solidified component from a component having a lower solidification temperature in the presence of separating diluent containing petroleum nitrogen bases separated from a cracked mineral oil distillate boiling between 115° C. and 330° C.

4. A process for separating mineral oils containing several hydrocarbon components having different solidification temperatures, comprising the steps of chilling said oil to a separation temperature to solidify a component thereof, and separating said solidified component from a component having a lower solidification temperature in the presence of a diluent mixture containing petroleum nitrogen bases separated from a mineral oil distillate boiling between 115° C. and 330° C., and a selective solvent which has a relatively lower solvent power for said component having a lower solidification temperature and is completely miscible with said petroleum nitrogen bases at said separation temperatures.

5. The process according to claim 4 in which the selective solvent contains a nitrogen base consisting of a heterocyclic component containing nitrogen in the ring and being free from alkyl side chains containing more than 2 carbon atoms.

6. A process for dewaxing wax-bearing mineral oils, comprising the steps of chilling said oil to a dewaxing temperature to solidify wax, and separating the wax from the oil in the presence of a dewaxing diluent containing petroleum nitrogen bases, separated from a mineral oil distillate boiling between 115° C. and 330° C.

7. The process according to claim 6 in which the petroleum nitrogen bases have been extracted so as to employ in the dewaxing operation substantially only those nitrogen bases which have dissociation constants below 1×10^{-7}.

8. A process for dewaxing wax-bearing mineral oils, comprising the steps of chilling said oil to a dewaxing temperature to solidify wax, and separating the wax from the oil in the presence of a dewaxing diluent containing petroleum nitrogen bases obtained by extracting a mineral oil distillate boiling between 115° C. and 330° C. with an acid.

9. A process for dewaxing wax-bearing mineral oils, comprising the steps of chilling said oil to a dewaxing temperature to solidify wax, and separating the wax from the oil in the presence of a dewaxing diluent containing petroleum nitrogen bases, separated from a cracked mineral oil distillate boiling between 115° C. and 330° C.

10. A process for dewaxing wax-bearing mineral oils, comprising the steps of chilling said oil a dewaxing temperature to solidify wax, and separating the wax from the oil in the presence of a dewaxing diluent mixture containing petroleum nitrogen bases, separated from a mineral oil dis-

tillate boiling between 115° C. and 330° C. and a selective dewaxing solvent having a relatively lower solvent power for oil and completely miscible with said petroleum nitrogen bases at said dewaxing temperature.

11. A process for dewaxing wax-bearing mineral oils, comprising the steps of chilling said oil to a dewaxing temperature to solidify wax, and separating the wax from the oil in the presence of a dewaxing diluent mixture containing petroleum nitrogen bases, separated from a cracked mineral oil distillate boiling between 115° C. and 330° C. and a selective dewaxing solvent having a relatively lower solvent power for oil and miscible in all proportions with said petroleum nitrogen bases at said dewaxing temperature.

12. The process according to claim 11 in which the selective dewaxing solvent contains a nitrogen base consisting of a heterocyclic compound containing nitrogen in the ring and being free from alkyl side chains containing more than two carbon atoms.

13. The process according to claim 11 in which the quantity of petroleum nitrogen bases is not substantially greater than that required to cause the oil and the diluents to exist as a single liquid phase.

14. The process according to claim 11 in which the petroleum nitrogen bases have been extracted so as to employ in the dewaxing operation substantially only those nitrogen bases which have dissociation constants lower than 1×10^{-7}.

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