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SOLVENT REFINING OF PETROLEUM PRODUCTS

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Our invention relates to the separation of petroleum products by selective solvents into valuable fractions, and more particularly to the separation of crude petroleum by fractional extraction with certain novel and highly selective solvents.

It has for its general objects the isolation and recovery of useful fractions of petroleum products; and more particularly the production by fractional extraction of products composed principally of naphthenes and aromatic substances; and the production of lubricants and lubricating oils of any desired quality, irrespective of the source of the crude petroleum; high efficiency in the extraction thereof; simplification of methods; and economies in processing by avoidance of waste both of the material treated and of the materials used in such treatment.

With the foregoing and other and further objects in view, as hereinafter more particularly pointed out, our invention concerns, and in part consists in, the discovery that a certain class of substances have higher selective solubility values as to the unsaturates and the aromatic and naphthenic hydrocarbon constituents of crude petroleum than any of the known selective solvents heretofore used in th solvent extraction of such hydrocarbons.

It is known that petroleum products contain three principal groups of hydrocarbon saturates; namely, paraffins, naphthenes and aromatics, of which the paraffins are least reactive and the aromatics most reactive; that such reactivity depends upon their polarity, the naphthenes and aromatics being polar and the paraffins non-polar. It is further known that the solubilities of these groups in polar solvents vary directly as the polarities of these groups, the paraffins being comparatively insoluble in polar solvents, and the aromatics most soluble therein.

While it is thus known that the solubility of hydrocarbon groups in polar solvents corresponds with the polarity of the group, we have further discovered that the index of the selective solubility potential of a solvent is its dipole moment; and that selective solubility values of the polar solvents vary directly as their dipole moments. Such polar solvents as have been heretofore employed in selective solvent refining of petroleum hydrocarbons are severally characterized by relatively low dipole moments; that is below 4.3 Debyes. (cf. Transactions of the Faraday Society, appendix to vol. 30 of 1934: A Table of Dipole Moments.)

We have found the characteristic of an optimum selective solvent for separation of crude petroleum by fractional extraction into a desired lubricant fraction and a residual fraction to be a high dipole moment, by which term as used herein is meant a moment at least higher than 4.5 D., measured in solution. The suitability of substances having high dipole moments is dependent also upon certain other factors; for example, some of these substances are impracticable as solvents because they crystallize before two phases form; others, because they have too high a boiling point. Hence further essential or highly desirable qualifications for such optimum solvent are:

1. A low melting point, preferably under 50° C.

2. A low boiling point, preferably under 300° C.; and

3. Ability to produce, or capacity to form, a two-phase liquid system at a temperature above the melting point of the solvent.

4. A negative reaction effect upon the desired oil product; that is to say, the solvent must neither alter nor change nor affect that quality of the oil sought, such as lubricity; nor may it have any harmful reactive effect thereon or interactive effect therewith tending to degrade that quality.

5. A specific gravity such that there may be the widest difference between it and that of the desired fraction.

6. Recoverability; and the more readily recoverable the solvent is, the more preferable it becomes.

7. Low solubility in water.

We have discovered that polar solvents of high dipole moment possessing the foregoing characteristics are superior to any known solvent in efficiency of extraction and simplicity of application. Examples of such high dipole moment solvents, possessing in high degree all the functional qualifications above pointed out as essential or desirable, are ortho-nitroanisole and ortho-methoxybenzonitrile, whose dipole moments are, respectively, 4.8 and 4.7. As illustrating the functional qualifications, those of ortho-nitroanisole are typical. Its characteristics are: melting point 9° C.; boiling point 277° C.; specific gravity 1.27; and solubility in water 0.169 g. in 100 cc. of H_2O at 30° C.

The like pertinent characteristics of ortho-methoxybenzonitrile are: melting point, 24.5° C.; boiling point, 260° C. at 762 mm. of Hg.; specific gravity at 15° C., liquid 1.095, solid 1.237; and solubility in water, 0.183 g. in 100 cc. of H_2O at 26° C.

As stated, the high dipole moment solvents are highly selective. By a highly selective solvent, as herein used, is meant a polar solvent of a power of selectivity, from a yield standpoint, superior to that of nitrobenzene. Nitrobenzene is the most polar selective solvent now in use. It was selected as a standard of comparison with high dipole moment selective solvents as typified by ortho-nitroanisole under the test conditions governing the obtaining of the data compiled in the table given in Industrial and Engineering Chemistry, vol. 23, at page 757, in order to demonstrate a high dipole moment to be the controlling factor in the function of selectivity. To obtain comparative data when the quality of the oils produced were equal, and the yields of raffinate were equal, it was necessary to use various solvent oil ratios. Such comparison resulted in a yield of the same quality of oil, but of 18% greater amount from Mid-Continent distillate with ortho-nitroanisole; and from Pennsylvania distillate, for a yield of the same quality of oil, an increase of 13% greater in amount with ortho-nitroanisole. With equal yields, Mid-Continent oil refined with ortho-nitroanisole was 15 points higher in viscosity index than the index figure obtained when nitrobenzene was the solvent used. Thus while nitrobenzene has a greater solvent power than orthonitroanisole, the latter is more selective than the former.

Features of especial advantage and utility which accrue from the use of high dipole moment solvents, as shown by comparisons with nitrobenzene and most other polar solvents heretofore used are that the former can be used at far higher temperatures. This is particularly advantageous when large quantities of oil are being refined. The use at high temperature cuts down the viscosity of the oil, thereby permitting higher flow rates through pipes, faster settling, and greater heat conductivities. The rate of settling also depends upon the specific gravity. Ortho-nitroanisole is denser than nitrobenzene, so that from both standpoints the former is superior. In addition, no refrigerating units are required when ortho-nitroanisole is employed; nor is any departure from atmospheric pressure required for its optimum operability. High, super or sub-normal pressures or vacuum are neither required nor in normal practice even useful, and apparatus therefor is dispensed with. Thus high dipole moment solvents have the advantages over low dipole moment solvents that they afford a greater yield; or for equal yields, a better quality oil; also a notable time saving in processing, due to their employment of higher working temperatures.

Thus the use of highly selective solvents, i. e., those having a dipole moment above 4.5 D., permits a more rapid and finer separation with less equipment.

Our invention further consists in the useful application of our discovery of the highly selective capacity of those solvents characterized by high dipole moments to any suitable process of solvent refining of lubricating oils to which it may be adapted, with such simplification of steps and apparatus as are thereby made possible, as more particularly hereinafter defined and claimed.

The method of treatment with the described class of high polar solvents as typified by ortho-nitroanisole in the extraction of a petroleum hydrocarbon lubricating oil, varies with such primary factors as: the lubricant product desired; the yield thereof sought; the character of the lubricating fraction to be processed, and its viscosity index; the temperature at which the process is to be carried out; the method of contacting; and the pressure, which is hereinafter assumed to be atmospheric, unless otherwise stated.

The choice of a lubricant depends upon the use to which it is to be put. Paraffinic lubricants are preferable for internal combustion engines, and especially for automobiles, because comparison of a paraffinic oil with a naphthenic oil of the same viscosity at 210° F. shows the following differences:

1. The viscosity of the paraffinic oil at 100° F. will be lower than that of the naphthenic oil.

2. The paraffinic oil will be less volatile than the naphthenic oil.

3. The paraffinic oil will be higher in molecular weight than the naphthenic oil.

4. The paraffinic oil will be more resistant to oxidation than the naphthenic oil.

5. The paraffinic oil will be more efficacious in preventing wear than the naphthenic oil and less paraffinic oil will be consumed if the two oils are used in an internal combustion engine under identical conditions.

As the primary function of a lubricant is to minimize metallic friction, the advantage of using a paraffinic lubricant may be understood from the above comparison.

Crude lubricating oil varies in its paraffinicity. As a general rule, crude oil from Pennsylvania is more paraffinic than oil derived from Mid-Continent sources. Mid-Continent oil is between Pennsylvania oil and Coastal oil in quality.

In order to produce lubricants from Mid-Continent oil which equal in quality those produced from Pennsylvania sources, it is necessary to increase the percentage of paraffinic constituents. This may be done in the following manner:

The oil and the highly selective solvent are intimately mixed. A certain amount of the oil dissolves in the solvent. A small amount of the solvent dissolves in the oil. The agitation is stopped and it is found that two liquid phases are present, an oil phase and a solvent phase. The solvent phase, including the oil dissolved in it, is heavier than the oil phase. It settles to the bottom. The oil phase forms above it. By means of a separatory funnel or other mechanical devices, the two phases are separated.

Each phase is then subjected to a vacuum distillation. The solvent is more volatile than the oil and it is distilled off. In this manner, the original oil is split up into two fractions: One, that oil which formed the oil phase and in which a small amount of solvent was dissolved but was removed by the distillation. This oil, without any dissolved solvent, is termed the raffinate. Two, that oil which dissolved in the solvent and was in the solvent phase. This oil, with the solvent removed, is termed the extract.

The raffinate is more paraffinic than the original oil. The extract is more naphthenic than the original oil. The function of the selective solvent is evident. It has the ability to dissolve naphthenic oil, but it does not dissolve paraffinic oil. In this way, lubricants of any desired quality may be made irrespective of the source of the crude. No oil is lost and no chemicals are wasted, as the solvent is completely recovered.

The above description is the simplest way by which our process for refining lubricating oil may be carried out. On a commercial scale, a

continuous counter-current method of contacting oil and solvent is usually employed. This may take various forms, such as a series of mixers and settlers, or pipe contactors or baffles used in conjunction with settlers. Another method is the use of a packed tower, solvent being admitted at the top and oil at the bottom. The solvent phase is removed at the bottom, the oil phase at the top. Either these or other usual apparatus may be used in our process by adaptations which will be plain to oil-refining engineers.

Our high-dipole moment solvents may be used with other selective solvents or with hydrocarbons which dissolve oil in order to get the benefit of a stripping operation. Such hydrocarbons are propane, butane, pentane, light naphtha, gasoline, etc.

By similar steps as in the simplified process above described, light hydrocarbons may be improved; for example, products such as the gasolines with higher octane numbers may be obtained without the use of cracking.

Both of the high-dipole moment solvents exampled can be used at relatively high temperatures. The optimum temperature at which they should be employed depends upon the nature of the oil being processed. The miscibility temperature varies with the viscosity and the quality of the oil. In one case, with an oil having a viscosity of 260 Saybolt Universal seconds at 100° F. and a viscosity index of about 58, the miscibility temperature with ortho-nitroanisole using equal volumes of oil and solvent was 266° F. It should be emphasized that there are many advantages in processing lubricating oils at the relatively high temperatures made operatively possible by the properties of this particular solvent, which advantages, in varying degrees, are common to all the high dipole moment solvents.

While the applicability of these high dipole moment selective solvents to the refining of lubricating oils and to the production of high-grade lubricants has been more particularly described, we do not thereby intend to be understood as limiting the availability of these solvents thereto, since our discovery equally relates to their employment in the separation of other desirable petroleum products from concomitant undesirables. Thus our discovery broadly contemplates the utilization of the described class of highly selective solvents in the separation of petroleum products into useful fractions; and essentially includes refining with this class of high dipole moment solvents, not only those particular components desired, which may be associated with the paraffinic fraction of petroleum, but also such other particular components desired, which may be associated with the aromatic and naphthenic fractions of petroleum.

Having thus described our invention, we claim:

1. In the process of solvent refining of petroleum containing polar and non-polar hydrocarbon groups, the step consisting in separating said groups by extracting the petroleum with ortho-methoxybenzonitrile.

2. The process of solvent refining of petroleum containing polar and non-polar hydrocarbon groups which consists in contacting said petroleum with ortho-methoxybenzonitrile, whereby the said groups pass into liquid phase composed of an oil phase and a solvent phase; and fractionally distilling the oil phase and the solvent phase independently.

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