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SOLVENT FRACTIONATION OF HYDROCARBON OILS

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My invention relates to the solvent fractionation of hydrocarbon oils, particularly to the solvent extraction of naphthas and still more particularly to the solvent fractionation of cracked naphthas, by means of certain new and superior solvent mixtures.

It is an object of my invention to provide processes utilizing new solvent mixtures for the solvent fractionation of hydrocarbon oils, particularly for the solvent fractionation of naphthas. Detailed objects of my invention will become apparent as the description thereof proceeds.

Phenol and other phenolic substances have been used or proposed for the solvent fractionation of lubricating oil stocks. These substances are not generally suitable to the solvent fractionation of lighter hydrocarbon oils such as naphthas and particularly cracked naphthas for reasons which will be brought out below. I have found that certain new combinations of solvents comprising at least one phenolic substance together with liquid ammonia are highly superior for the solvent fractionation of these light hydrocarbon oils.

The solvent fractionation of naphthas is important as a method of obtaining a fraction of high antiknock value, or in other words of high octane number, for use as a motor fuel or motor fuel component.

It is desirable that a solvent fractionation process should, if possible, be operated at ordinary atmospheric temperatures or at temperatures somewhat above atmospheric rather than at low temperatures since in the latter case expensive refrigeration is required. For this reason, the use of a phenolic substance, for instance cresylic acid, in the solvent fractionation of naphthas is not satisfactory since the miscibility temperature, i. e. the temperature at which two liquid phases commence to form, is generally such as to require considerable refrigeration. Thus, for instance, when 62% by volume of cracked heavy petroleum naphtha was dissolved in 38% of cresylic acid the solution was still clear when the temperature was lowered to 0° F. This indicates that a considerably lower temperature would be necessary in order to separate two liquid phases if any separation takes place at all. In contrast with this result, it was found that when 49% by volume of this same naphtha was mixed with 30% by volume of cresylic acid and 21% by volume of liquid ammonia the miscibility temperature was about 110° F. or in other words two liquid phases were present at temperatures

below 110° F. The addition of a larger amount of ammonia makes possible even higher miscibility temperatures. Thus, for instance, when 32% by volume of cracked heavy petroleum naphtha was dissolved in 19% by volume of cresylic acid and 49% by volume of liquid ammonia it was found that two layers existed, each in substantial volume, at 110° F., demonstrating that the miscibility temperature was considerably above this figure. As another example, a sample of cracked heavy petroleum naphtha was vigorously agitated with one-half its volume of liquid ammonia and one-half its volume of cresylic acid at 65° F. and it was found that two layers separated readily.

In any of these cases where two liquid layers are formed by the use of ammonia and a phenolic substance, the raffinate layer (usually the upper layer) contains the low octane number constituents of the original naphtha and the extract layer contains the bulk of the phenolic substance and the more valuable high octane number constituents of the original naphtha. Thus, for example, when one volume of cracked heavy naphtha derived from Mid-Continent crude oil was extracted with one-half volume of cresylic acid and one-half volume of liquid ammonia at 75° F., two liquid layers were formed. These were separated, the solvents were removed from the naphtha constituents and it was found that the extract fraction had an octane number of 94 as compared with an octane number of 62 for the original cracked heavy naphtha stock and an octane number of 48.5 for the raffinate fraction.

I prefer to conduct the extraction so as to produce an extract product with a knock rating above 70 octane number. By varying the conditions, degree of extraction, etc., I can produce by my process, gasolines having knock ratings up to 110 octane number, depending on the stock employed and the degree of extraction applied.

Various phenolic compounds can be used together with liquid ammonia in my process. As examples of these, I may mention phenol itself; the ortho, meta and para cresols; the mixed cresols, known as cresylic acid; the xylenols; phenolic products from wood tar distillation, known as wood tar acids; phenolic by-products from oil refining processes, for example the alkali extraction of cracked distillates; etc. Mixtures of these various phenolic substances can also be used.

Amounts of mixed solvent varying from one-half of the volume of the stock to be fractionated up to ten times the volume of the stock to be fractionated can suitably be used. In general, I

prefer, however, to keep the volumetric ratio of solvent to stock within the limits of from 1:1 to 5:1. The ratio of liquid ammonia to phenolic substance can also be varied within considerable limits depending on the results desired, the particular stock used, the temperature at which it is desired to operate, etc. In general, the greater the proportion of ammonia the higher will be the miscibility temperature. I may use from 10% by volume of liquid ammonia and 90% by volume of phenolic substance to 90% by volume of liquid ammonia and 10% by volume of phenolic substance. I prefer, however, to keep within the range of from 25% by volume of liquid ammonia and 75% by volume of phenolic substance to 25% by volume of liquid ammonia and 25% by volume of phenolic substance. Third components can also be added to the solvent mixture to increase selectivity or to render the solvent mixture either more or less miscible with the hydrocarbon oil. Thus, for instance, miscibility can be increased, if desired, by the addition of anhydrous ethanol or acetone.

It will be understood that my new solvent mixtures can be applied in any of the known types of solvent fractionation process. Thus, for example, the solvent mixture and stock can be heated above the miscibility temperature to form a homogeneous solution and then cooled to form two separate layers or phases and these can then be separated from each other and the solvent recovered from each of them. On the other hand, my process can be operated by co-agitating the solvent mixture and stock at a temperature below the miscibility temperature and then separating the two liquid phases, removing solvent, etc. The various types of countercurrent processes known to the art or which may hereafter be devised can also be used. Thus, for instance, the stock can be introduced at the bottom of a countercurrent extraction tower and the solvent mixture can be introduced at the top, the two liquids flowing countercurrent to each other at temperatures below the miscibility temperature, an extract phase being removed at the bottom and a raffinate phase at the top of the tower. When operated in a countercurrent system the two components of the solvent mixture can, if desired, be introduced at different points in the system. A stage countercurrent system can likewise be used.

Various methods can be employed for the removal of the solvents from the extract and raffinate phases. Thus, if the naphtha is sufficiently light a high boiling phenolic substance such as cresol or xylene can be separated by distilling off the naphtha and ammonia leaving the phenolic substance as a bottom. The ammonia can readily be separated from the naphtha by fractional distillation due to its low boiling point or by water washing, or it can be condensed along with the naphtha, in which case it will separate as a distinct layer or phase due to its almost complete immiscibility with the naphtha. On the other hand, if the naphtha being extracted is a heavy one and the phenolic substance used is phenol, the latter can be distilled off from the naphtha along with the ammonia. Another efficient method of removing the phenolic substance from the extract and/or raffinate portion of the naphtha is by the use of an excess of ammonia. The procedure according to this method is, in brief, to contact the extract or raffinate phase containing the phenolic substance with a large excess of liquid ammonia which will dissolve the phenolic substance away from the naphtha with-

out dissolving the naphtha. This can most efficiently be done in a tower or by other countercurrent extraction method. Water can be used in small quantities to aid phase separation.

The stock on which my process is operated is preferably a hydrocarbon material containing substantial amounts of material within the gasoline boiling point range. It may suitably be a crude gasoline or any type of naphtha, usually with a knock rating below 65 octane number. The process is, however, particularly adapted to the fractionation of heavy petroleum naphthas, i. e., materials consisting predominantly of hydrocarbons boiling between about 250° F. and about 400° F. Still more particularly, my process is adapted to fractionation of heavy petroleum naphthas produced by cracking processes and known as cracked heavy naphthas and still more particularly to cracked heavy petroleum naphthas produced by vapor phase cracking processes and containing high concentrations of olefinic hydrocarbons. Thus, for instance, a vapor phase cracked naphtha containing at least 25% of olefinic hydrocarbons and preferably at least 40% of olefinic hydrocarbons is a highly desirable charging stock for my process. The raffinate from my process can be returned to a cracking operation again to produce olefinic hydrocarbons and various types of combination processes involving solvent fractionation on the one hand and cracking on the other hand can be used. The term "cracking" as used herein also covers the so-called re-forming processes and the term "cracked naphtha" includes re-formed naphtha.

While I have described my invention in connection with certain specific embodiments and in connection with certain theories of operation, it will be understood that these are by way of illustration rather than by way of limitation, and I do not desire to restrict myself thereto except to the broadest valid interpretation of the appended claims in which I have set forth the novel features of my invention.

I claim:

1. A process for the solvent fractionation of a petroleum oil comprising contacting said oil with a substantial amount of at least one phenolic substance and a substantial amount of liquid ammonia.
2. A process according to claim 1 in which said at least one phenolic substance comprises cresylic acid.
3. A process according to claim 1 in which said oil consists predominantly of hydrocarbons boiling between about 250° F. and about 400° F.
4. A process according to claim 1 in which said oil is a cracked petroleum naphtha.
5. A process for the solvent fractionation of a cracked petroleum naphtha consisting predominantly of hydrocarbons boiling between about 250° F. and about 400° F., comprising contacting said cracked petroleum naphtha with a substantial amount of at least one phenolic substance and a substantial amount of liquid ammonia at a temperature below the miscibility temperature of the system thus formed, whereby raffinate and extract phases are formed, the extract phase containing hydrocarbons having an octane number of at least 70, and separating said extract and raffinate phases.
6. A process according to claim 5 in which said at least one phenolic substance is cresylic acid.
7. A process for the solvent fractionation of a cracked petroleum naphtha consisting predominantly of hydrocarbons boiling between

about 250° F. and about 400° F., comprising contacting said cracked petroleum naphtha with from 1 to 5 times its volume of a mixed solvent comprising from 25% to 75% by volume of at least one phenolic substance and from 25% to 75% by volume of liquid ammonia at a temperature below the miscibility temperature of the system thus formed, whereby raffinate and extract phases are formed, the extract phase containing hydrocarbons having an octane number of at least 70, and separating said extract and raffinate phases.

8. A process according to claim 7 in which said petroleum naphtha is a product of a vapor phase cracking operation.

9. A process according to claim 7 in which said at least one phenolic substance is cresylic acid.

10. A process according to claim 7 in which

said petroleum naphtha is a product of a vapor phase cracking operation and said at least one phenolic substance is cresylic acid.

11. A process for separating oil into fractions comprising extracting said oil with phenol or its homologues and ammonia to form a raffinate phase and an extract phase, and subsequently separating said phases.

12. A process for separating oil into fractions, comprising extracting said oil with cresylic acid and ammonia to form a raffinate phase and an extract phase, and subsequently separating said phases.

13. A process for separating oil into fractions comprising extracting said oil with phenol and ammonia to form a raffinate phase and an extract phase, and separating said phases.

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