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RECOVERY OF NAPHTHALENE AND HOMOLOGUES FROM PETROLEUM PRODUCTS

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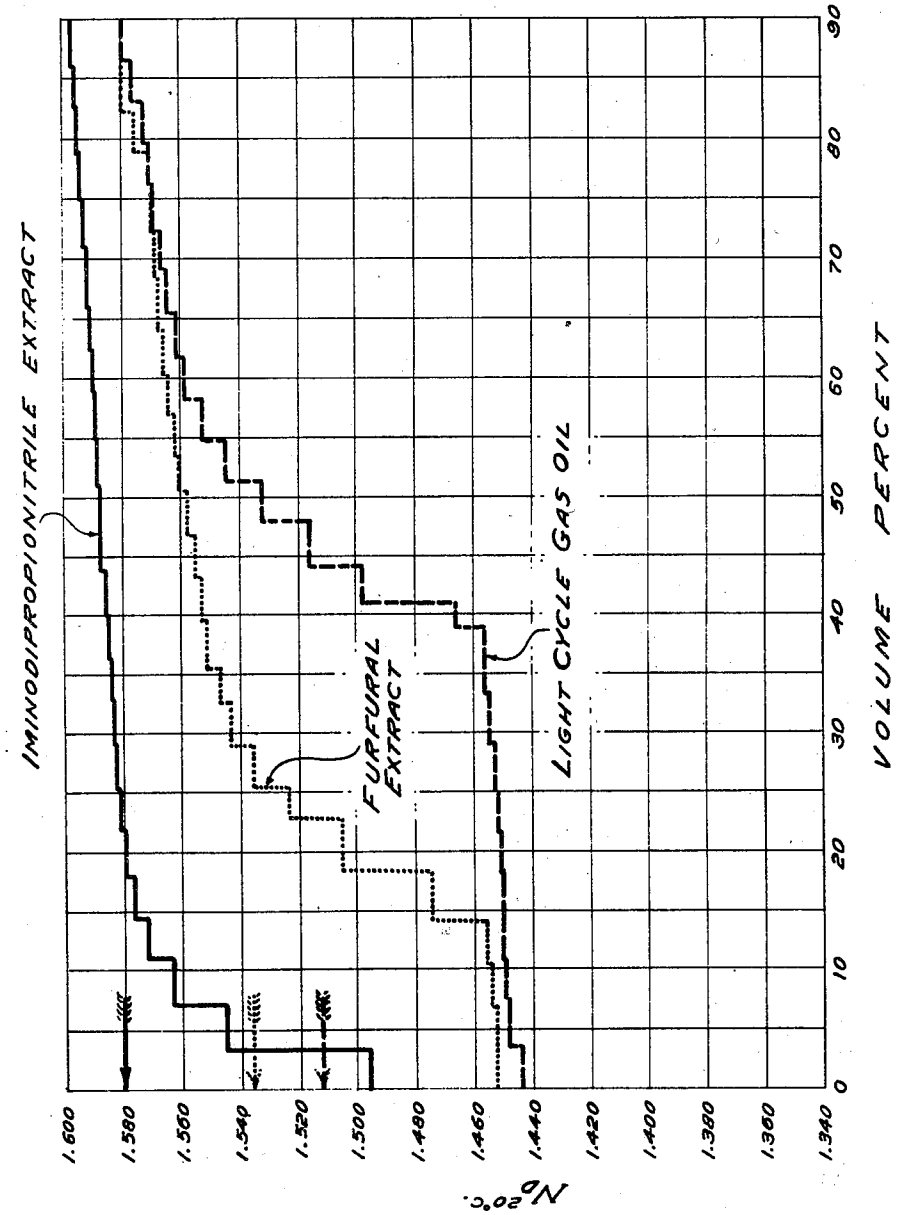


FIG. 1.

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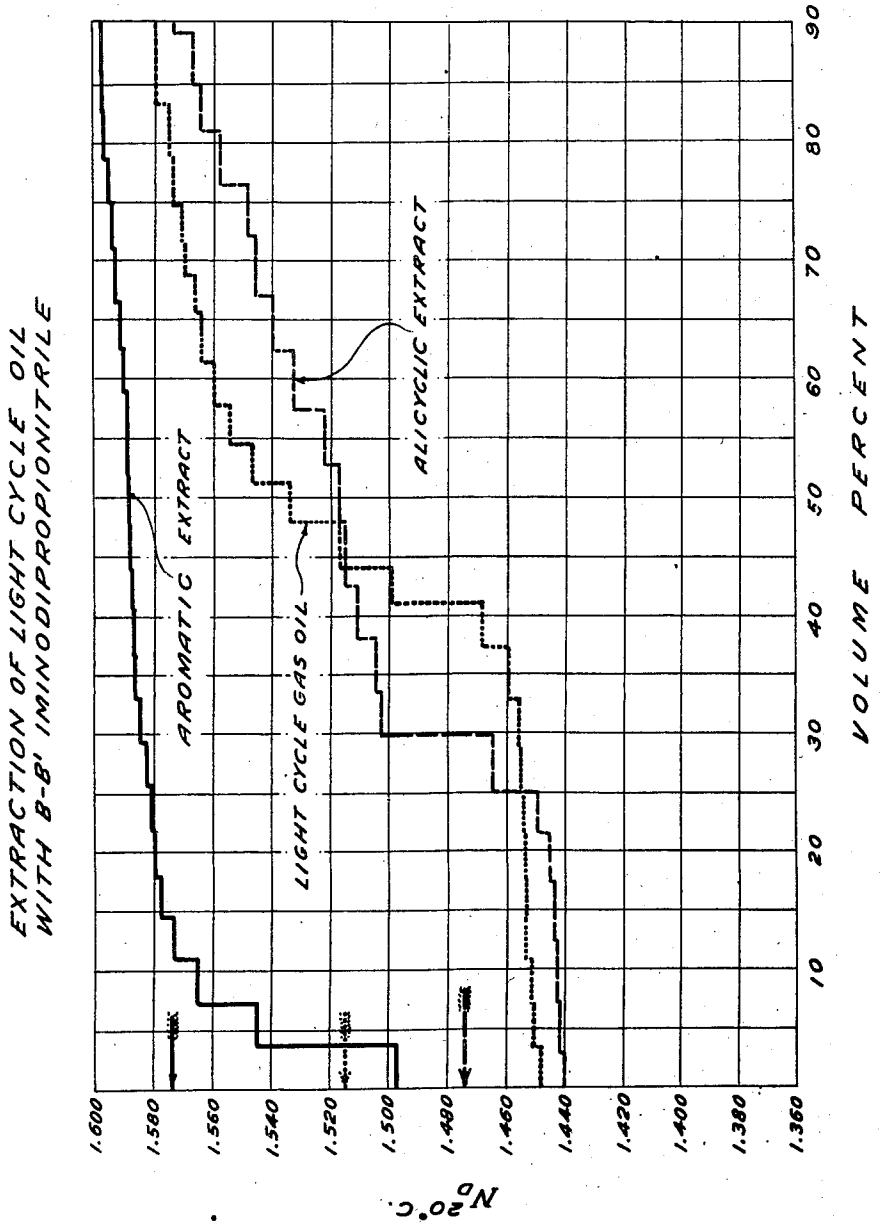


Fig. 2.

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RECOVERY OF NAPHTHALENE AND HOMOLOGUES FROM PETROLEUM PRODUCTS

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6 Claims. (Cl. 260—674)

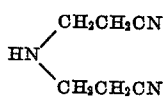
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This invention relates to a process of recovering condensed nuclei aromatic compounds from petroleum products containing the same, and more particularly the recovery of naphthalene and its homologues.

In the catalytic cracking of petroleum, there are produced fractions which contain various amounts of condensed nuclei aromatics which fractions are often referred to as light cycle gas oils from the fact that the fraction can be recycled through a catalytic process if necessary. This fraction usually has an aromatic content which will vary from about 1% to 30% or more. The aromatics of the fraction are predominantly condensed nuclei compounds, for the most part naphthalene and its homologues. In most cases the content of naphthalene and its homologues is at least 50% and sometimes as high as 80% or slightly more. Petroleum products from somewhat different cracking cycles are also known which contain aromatics although the light cycle gas oil is the largest available source having substantial content of naphthalene and its homologues.

Various methods have been used in the past to produce concentrates containing higher proportions of aromatics from the petroleum products of the type referred to above. One of the best known involves the use of wet furfural as a selective solvent for aromatics. While furfural has been practically used, its selectivity leaves much to be desired and particularly when used with a raw material having a high aromatic content. In such cases, the selectivity drops off more sharply.

The present invention is based on the discovery that iminodipropionitrile having the formula



possesses an extraordinarily high selective solvent action for condensed nuclei aromatics such as naphthalene and its homologues. The selectivity is so high that even with raw materials having high content of naphthalene, non-aromatic hydrocarbons are practically immiscible at room temperature.

The process of the present invention can be used to separate naphthalenes from petroleum products containing them in widely varying proportions from very lean products having as low as 1% of aromatics up to relatively richer products which have 30 or more per cent aromatics.

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The wide applicability of the process to a large number of petroleum products is an important practical advantage.

Another advantage of the process of the present invention is that the selectiveness of the solvent is not dependent on the presence of water as is the case with furfural. This does not mean that absolutely anhydrous conditions are essential as small amounts of water do not adversely affect the separation. It is, however, not necessary to have any particular water content and this lack of critical composition makes the practical operating control much simpler.

An additional advantage of the present invention is the high overall efficiency based on the solvent. The negligible solubility in non-aromatic hydrocarbons makes the recovery problem very simple. In some cases, the amount of iminodipropionitrile in the non-aromatic fraction may be so low that it can be neglected, but if it is desired to recover it, the recovery presents no problem as treatment with water removes any traces of iminodipropionitrile from the non-aromatic raffinate and the recovery from the water layer is simple because the iminodipropionitrile does not have any material vapor pressure below the boiling point of water. A complete separation by distillation is, therefore, a simple matter.

The recovery of the naphthalenes from the iminodipropionitrile extract is simple. Typical methods are vacuum distillation, steam stripping, and separation by means of water. In the latter two cases the negligible volatility of the iminodipropionitrile makes the recovery of the solvent from the associated water easy.

The process of the present invention can be used with a wide range of petroleum products containing varying contents of condensed nuclei aromatics. The composition of the aromatics recovered depends, of course, on the source. If it is desired to obtain a high proportion of naphthalene itself, petroleum products may be sharply fractionated so that the naphthalene is not associated with large amounts of homologues. On the other hand, in many cases it is preferable to use the process of the present invention to separate a product which is a mixture of naphthalene and its homologues, the separation of the different aromatics being effected in a later stage.

Where the reduced pressure distillation method is used in isolating the naphthalene from other iminodipropionitrile extracts, this may be carried out if desired as a fractional distillation in order to produce a product which is substantially free from non-aromatic hydrocarbons. This renders

further purification of the naphthalene very simple and is of special interest where the naphthalene is to be transformed into a product of very high purity for use in the dyestuff industry. The thorough removal of non-aromatic hydrocarbons is particularly useful as they present a serious problem for separation when fractional distillation processes are used. Many of the typical non-aromatic hydrocarbons, such as, for example, n-dodecane, tend to form azeotropes with the naphthalenes which defeats fractional distillation.

While it is an important advantage of the present invention that the solubility of naphthalenes in iminodipropionitrile is not materially increased by high temperatures, even up to 200° C., the solubility of alicyclic compounds does become quite extensive at higher temperatures. At 125° C. most alicyclic compounds, such as, for example, hydrogenated naphthalenes, are quite soluble in iminodipropionitrile and the solubility is still high at about 100° C. The solubility becomes sufficiently great to be a material factor at about 40–50° C. This differential solubility of the alicyclics at various temperatures may be utilized to effect a three-product separation. Thus, for example, the petroleum product may be extracted with iminodipropionitrile at 100° C., or higher, the two layers separated and the extract cooled, for example, to room temperature. This will separate out from the extract practically all of the alicyclic compounds which can be recovered by separation, the aromatics remaining in solution at room temperature being then recovered in the usual manner.

Another way of using the differential solubility of alicyclics with temperature is to extract first at room temperature, producing an extract containing only the aromatics. The two layers are separated and the raffinate can then be extracted with iminodipropionitrile at a high temperature such as 100–125° C., in order to obtain a hot extract containing the major portion of the alicyclic compounds in the raffinate. After separation of the two layers, the alicyclics may be removed from the extract by cooling, treatment with water, or other means.

The invention will be described in connection with the following specific examples which are typical and in connection with the drawings in which:

Fig. 1 is a series of chromatographic adsorption curves comparing the adsorption of furfural with that of iminodipropionitrile, and

Fig. 2 is a similar set of chromatographic adsorption curves showing aromatic and alicyclic extracts.

Example 1

A light cycle gas oil from Texas crude having a 30% aromatic content, of which approximately 80% was naphthalene and homologues, was divided into three portions. One portion was subjected to a differential chromatographic adsorption by adsorping a unit quantity in silica gel and progressively driving it out with methyl alcohol as a desorbing liquid. The refractive indices of the successive portions desorbed were measured and the results plotted in the usual chromatographic graph which is shown in dashed lines on Fig. 1. A dashed arrow indicates the refractive index of the starting material.

A second portion of the light cycle gas oil was treated at 1.25 volumes of wet furfural to produce an extract and a raffinate. The furfural was then removed from the aromatic extract by the customary bisulfite solution, the aromatics dried and subjected to the same chromatographic adsorption and desorption in silica gel as described above in conjunction with the starting material. A chromatographic curve was obtained and is shown in dotted lines on the drawing. The refractive index of the aromatic extract before chromatographic treatment is shown by the dotted arrow.

A third sample of the gas oil was subjected to a single stage extraction with an equal volume of iminodipropionitrile producing an aromatic extract and a raffinate, and the aromatic extract after separation was washed with water to remove the solvent, dried, and subjected to chromatographic adsorption and desorption as described above. The chromatographic curve is shown on the drawings in full lines, the refractive index of the extract as a whole being indicated by the full line arrow.

On the chromatographic curves, material having a refractive index below 1.5 is aliphatic and for the most part paraffins. Between a refractive index of 1.50 and 1.56 the products are predominantly alicyclic and above 1.56 they are predominantly aromatic. A small amount of highly alkylated benzenes appear in the broad range of the refractive indices typical of the alicyclics.

It will be noted that the aromatics constituted 30% of the original gas oil and the aliphatics about 45%. Furfural extraction produced a product in which the aliphatic content was reduced only to about 18 to 20%, the aromatic content being raised to about 50%, leaving almost 30% of contaminating alicyclics.

The process of the present invention using iminodipropionitrile produced an extract in which the non-aromatics have been reduced to about 7%, and the aliphatics are not more than about 4%. In other words, almost all of the aliphatics, such as dodecane, have been removed, thus eliminating any purification problem due to azeotrope formation. The alicyclics are present in equally small amounts and their removal is a simple matter. Losses of iminodipropionitrile in the raffinate are negligible as it is present only in traces. The amount is so small that it is not essential to recover it.

Example 2

The relative solubilities of aliphatics and naphthalene in iminodipropionitrile was tested as follows.

A 50–50 mixture of naphthalene and iminodipropionitrile was prepared. This product forms a completely homogeneous liquid at 69° C. With lower contents of naphthalene, homogeneous liquids are obtainable at temperatures ranging down to room temperature and below.

When an equal mixture of n-dodecane and iminodipropionitrile was heated at 55° C., complete separation into layers resulted and on dilution of the iminodipropionitrile with water only traces of dodecane could be observed.

An equal mixture of n-dodecane and iminodipropionitrile was heated to 200° C. Even at this temperature there was no appreciable solubility of the dodecane in the nitrile.

Example 3

Light cycle gas oil was fractionally distilled to produce a fraction containing substantially naphthalene as its aromatic content. This fraction had a crystallizing point of 32.6° C. and had

a naphthalene content of about 20%. The product was subjected to a single stage extraction with an equal volume of iminodipropionitrile at room temperature and the solvent layer steam stripped. A naphthalene was obtained having a crystallizing point of 58.9° C. which represents a naphthalene content of approximately 60%.

Example 4

The effect of various concentractions of methyl naphthalenes in a mixture, the non-aromatic portion of which was mainly n-dodecane, was determined. The methyl naphthalene which had a high content of the alpha isomer had a refractive index of 1.6142, the dodecane 1.4211. Four mixtures were prepared containing 2%, 25%, 50%, and 75% methyl naphthalene. These were then subjected to a single stage extraction with iminodipropionitrile as described in Example 1, producing a raffinate and an extract from which the methyl naphthalenes were removed. The following table shows the refractive indices of the original mixture of raffinate and methyl naphthalenes recovered from the extract.

Methyl Naphthalene	N_D^{20} Mixture	N_D^{20} Raffinate	N_D^{20} Extract
2 percent	1.4251	1.4213	1.6115
25 percent	1.4704	1.4543	1.6102
50 percent	1.5130	1.4870	1.6120
75 percent	1.5660	1.5279	1.6110

It will be noted that the reduction of the dodecane was just as complete with the mixture containing the enormous proportion of 75% of methyl naphthalene, far in excess of any petroleum fraction, but, of course, there are limits to the amount of methyl naphthalene which can be extracted with the relatively small volume of iminodipropionitrile. This is reflected in the index of the raffinate which shows that when there was more than 50% methyl naphthalene, some of the naphthalene could not be dissolved in the small amount of iminodipropionitrile used, but even in this case the reduction of the dodecane was just as complete.

Example 5

A sample of light cycle gas oil having a refractive index of 1.5138 was extracted at 125° C. with an equal volume of iminodipropionitrile. Two layers were produced and separated, yielding a raffinate with a refractive index of 1.4995; in other words, one which contains substantially only aliphatics, and an extract. The extract was then cooled to room temperature, a separate layer formed which was recovered by separation and had a refractive index of 1.5246. In other words, this product was substantially alicyclics. The iminodipropionitrile solution was then treated with water to recover the hydrocarbons which had a refractive index of 1.5782. These were substantially all aromatics. The alicyclic product obtained by cooling the hot iminodipropionitrile extract amounted to about 4–5% of the weight of the gas oil, whereas the aromatics were about 11%.

Example 6

Light cycle gas oil of Example 5 was subjected to an extraction with an equal amount of iminodipropionitrile at room temperature. The extract and raffinate were separated and the hydrocarbons recovered from the extract as described in the preceding example. They showed

a refractive index of 1.5761 and were, therefore, substantially all aromatics.

The raffinate from the room temperature extraction was then extracted with an equal volume of iminodipropionitrile at 125° C. to produce an extract and a second raffinate which were separated, the raffinate had a refractive index of 1.4750, and thus was substantially aliphatic in nature. The extract was then cooled to room temperature, a hydrocarbon separated out and was recovered and showed a refractive index of 1.5152. It was, therefore, mainly alicyclic. At room temperature, the iminodipropionitrile extract still contained a small amount of hydrocarbon which was removed as described in the preceding example and showed a refractive index of 1.5643. In other words, it was a mixture of alicyclics and aromatics with the latter predominating.

Chromatographic adsorption curves of the aromatic and alicyclic extracts described in Figs. 5 and 6, are shown in Fig. 2 of the drawings. It will be apparent that the aromatic extract was substantially free from aliphatic constituents and that the alicyclic extract shows a marked enrichment in alicyclic material over the original light cycle gas oil.

Example 7

A petroleum product was used as the test material, containing about 25% of tetrahydronaphthalene having a refractive index of 1.5414; 25% of alphamethylnaphthalene having a refractive index of 1.614; and 50% of aliphatic hydrocarbons predominantly n-dodecane having a refractive index of 1.4272. This mixture was extracted at room temperature with an equal volume of iminodipropionitrile. The extract and raffinate were separated and the hydrocarbons recovered from the extract as described above. They had a refractive index of 1.5762 and, therefore, showed a high content of aromatics.

The raffinate was then extracted at 125° C. with an equal volume of iminodipropionitrile. The two layers were separated, one being a second raffinate having a refractive index of 1.4632 and being substantially aliphatic in nature. The extract was slowly cooled. Turbidity began to be noticeable at about 100° C. and at 40–50° C. the major portion of the tetrahydronaphthalene had separated out leaving a small amount of extract from which the hydrocarbon was removed in the usual manner and possessed a refractive index of 1.5616. It was thus a mixture of alphamethylnaphthalene and tetrahydronaphthalene.

It will be noted that when it is desired to separate the alicyclics from aromatics in a hot iminodipropionitrile extract, the cooling should preferably be continued to 40–50° C. as at temperatures above this point, the solubility of the alicyclics is quite appreciable.

We claim:

1. The method of recovering condensed nuclei aromatics and alicyclics from petroleum products containing the same in admixture with aliphatic hydrocarbons which comprises extracting the mixture with iminodipropionitrile at a temperature of at least about 100° C. to produce raffinate and extract layers, separating the layers, cooling the extract to a temperature not above 40–50° C. whereby alicyclics separate, recovering the separated liquids and recovering the condensed nuclei aromatics from the remaining solution.

2. The method of recovering condensed nuclei

aromatics and alicyclics from petroleum products containing the same in admixture with aliphatic hydrocarbons which comprises extracting the mixture with iminodipropionitrile at room temperature to produce raffinate and extract layers, separating the layers, recovering the condensed nuclei aromatics from the extract, extracting the raffinate with iminodipropionitrile at a temperature at least as high as 100° C. to produce raffinate and extract layers, separating the layers and recovering alicyclic compounds from the extracts.

3. The method of recovering naphthalenes and hydrogenated naphthalenes from petroleum products containing the same in admixture with aliphatic hydrocarbons which comprises extracting the mixture with iminodipropionitrile at a temperature of at least about 100° C. to produce raffinate and extract layers, separating the layers, cooling the extract to a temperature not above 40–50° C. whereby hydrogenated naphthalenes separate, recovering the separated liquids and recovering the naphthalenes from the remaining solution.

4. The method of recovering naphthalenes and hydrogenated naphthalenes from petroleum products containing the same in admixture with aliphatic hydrocarbons which comprises extracting the mixture with iminodipropionitrile at room temperature to produce raffinate and extract layers, separating the layers, recovering the naphthalenes from the extract, extracting the raffinate with iminodipropionitrile at a temperature at least as high as 100° C. to produce raffinate and extract layers, separating the layers and recovering hydrogenated naphthalenes from the extract.

5. The method of recovering naphthalene and hydrogenated naphthalenes from petroleum products containing the same in admixture with aliphatic hydrocarbons which comprises extracting the mixture with iminodipropionitrile at a temperature of at least 100° C. to produce raffinate and extract layers, separating the layers, cooling the extract to a temperature not above 40–50° C. whereby hydrogenated naphthalenes separate, recovering the separated liquids and recovering the naphthalene from the remaining solution.

6. The method of recovering naphthalene and hydrogenated naphthalenes from petroleum products containing the same in admixture with aliphatic hydrocarbons which comprises extracting the mixture with iminodipropionitrile at room temperature to produce raffinate and extract layers, separating the layers, recovering the naphthalenes from the extract, extracting the raffinate with iminodipropionitrile at a temperature at least as high as 100° C. to produce raffinate and extract layers, separating the layers and recovering hydrogenated naphthalenes from the extract.

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