

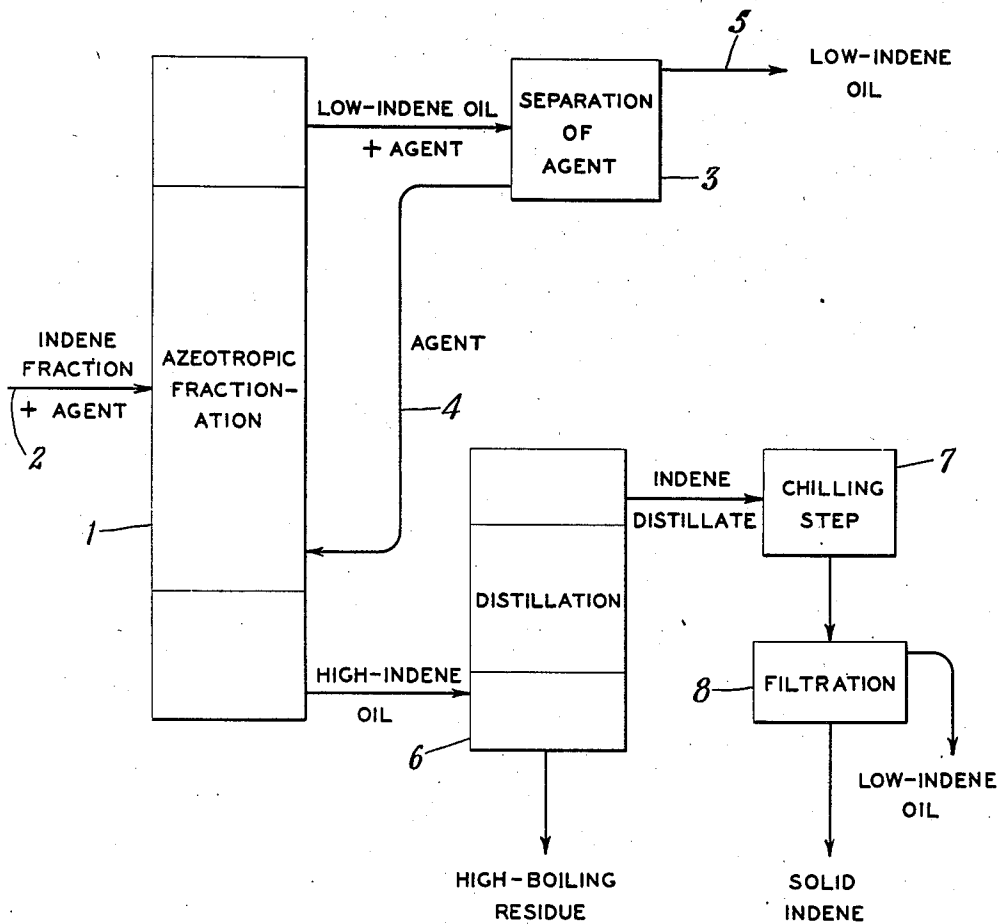
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PROCESS FOR THE PRODUCTION OF HIGH-INDENE-CONTENT HYDROCARBON OILS

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PROCESS FOR THE PRODUCTION OF HIGH-INDENE-CONTENT HYDROCARBON OILS

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This invention relates to the production and purification of indene-containing oils and more particularly to the production of hydrocarbon oils of a high indene content from hydrocarbon oils of relatively low indene content.

Indene has heretofore been recovered from crude indene-containing hydrocarbon oils by treating them with substances such as sodium amide or potassium hydroxide whereby the alkali metal compound combines with the indene to produce a compound which separates from the hydrocarbon oils. The indene is then recovered from the compound thus formed by hydrolysis. Indene has also been recovered from indene-containing hydrocarbon oils by fractionating the oils to obtain a fraction having an indene content of about 80% and then cooling the fraction to temperatures of about -25°C . to cause the indene to freeze and separate from the oils. Fractionation of indene-containing hydrocarbon oils by the usual distillation methods, no matter how carefully conducted, fails to produce oils of an indene content substantially higher than 80–81% for the reason that many of the oils contained in crude indene-containing hydrocarbon oils have practically the same boiling point as indene and therefore cannot be separated therefrom by ordinary fractionation. None of the above methods of obtaining indene have been found to be commercially satisfactory from an economic viewpoint.

It is an object of this invention to provide a simple and inexpensive method of obtaining oils of high indene content from oils of relatively low indene content. Other objects of this invention will appear from the following detailed description thereof.

As above indicated, indene-containing oils of commerce such as those obtained from coal tar oils, drip oils, carburetted water-gas tar oils, oil-gas-tar oils, and light oils removed by scrubbers in coal gas and water-gas operations contain a number of non-indene oils such as tri- and tetramethylbenzenes and other alkylated benzenes and also paraffinic hydrocarbons, which have in the mixtures in question substantially the same distillation temperatures as indene and which therefore cannot be separated from indene by ordinary fractional distillation. As a result of extensive development work in this field I have made the surprising discovery that indene may be separated from such non-indene oils by distilling the indene-containing hydrocarbon oil in the presence of an agent capable of forming azeotropes with indene and the non-indene oils contained in the hydrocarbon oil; I have found that indene and the non-indene oils form azeotropes of the minimum-boiling type; i. e., the azeotropes distill at temperatures lower than the distillation temperatures of any of the azeotrope

constituents, and that the indene azeotropes and the indene have substantially higher distillation temperatures than the distillation temperatures of the non-indene azeotropes; thus separation by distillation of the indene and the indene azeotropes from the non-indene azeotropes may be effected. This discovery is indeed surprising because the close chemical relationship existing between the constituents of the indene-containing hydrocarbon oil and the fact that indene and the non-indene oils have substantially the same distillation temperatures would not lead a chemist to expect that the addition of a single agent to the complex mixture of hydrocarbons would effect the formation of azeotropes such that on distillation substantially all of the non-indene azeotropes distill off, leaving an oil of high indene content in the still. As contrasted with the 80% indene content of oils produced by ordinary fractionation, the process of this invention makes possible the production of substantially pure indene—up to 98% or more—by a fractional distillation process. Throughout the specification and claims the term "agent" is intended to refer to those substances added to the hydrocarbon oil of relatively low indene content to form azeotropes with indene and the non-indene oils contained therein.

In the course of my development work, I have observed that certain organic compounds are particularly suitable for use as agents in the recovery of indene from crude indene-containing hydrocarbon oils by the process of my invention. I have found that these compounds possess the following characteristics:

(1) They are distillable without substantial decomposition within the range of from about 145° to about 220°C . at atmospheric pressure.

(2) They are miscible at the temperatures at which distillation is carried out with indene-containing hydrocarbon oils.

(3) They do not react chemically to any permanent or substantial degree with indene or other substances present in crude indene-containing hydrocarbon oils; furthermore, they do not cause the indene present in the crude indene-containing oils to polymerize on distillation to any undesirable degree.

(4) They contain a radical which renders the compounds relatively strongly polar as compared with indene and other substances present in crude indene-containing hydrocarbon oils and which makes the compounds soluble in water or in aqueous solutions of acids or bases. Among such radicals may be mentioned $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$ and the aromatic heterocyclic nitrogen radical containing pyridinic nitrogen such as is found in pyridine, quinoline, etc.

(5) They are separable from the non-indene oils distilled from the crude indene-containing

hydrocarbon oil in accordance with my invention by gravity or by a simple extraction with water or an aqueous solution of an acid or base.

In the following table several compounds are listed having the above characteristics and which I have found to be extremely suitable for use as agents in the practice of my invention:

Compound	Polar group	Soluble in—	Boiling point °C.
Phenol	—OH	H ₂ O, aq. alkali	183
Ethylene glycol	—OH	H ₂ O	197
Propylene glycol	—OH	H ₂ O	187.4
Diethylene glycol mono-methyl ether	—OH	H ₂ O	193.2
o-Chlorophenol	—OH	Aq. alkali	174-175
o-Cresol	—OH	Aq. alkali	191
Butyric acid	—COOH	H ₂ O	163.5
Aniline	—NH ₂	Aq. acid	184.4
Monoethanol amine	(—OH) (—NH ₂)	H ₂ O	172
Pyridine base fractions from tar	Pyridinic nitrogen	Aq. acid	171-181

Indene-containing hydrocarbon oils, as is well known, may be obtained by fractional distillation of coal tar oils, drip oils, carburetted water-gas tar oils, oil-gas-tar oils, and light oils recovered in coal gas and water-gas operations. In accordance with this invention, the indene-containing oils are mixed with an agent which will form azeotropes with the constituents of the oils and the mixture is then fractionally distilled to effect the separation of the non-indene azeotropes from the indene and the indene azeotrope. Distillation may be carried out under a partial vacuum if desired, thus permitting greater heat economy without affecting the efficiency of the separation of indene and non-indene oils. It should be noted, however, the ratio of hydrocarbon oil to agent in the azeotrope may change slightly at reduced pressures, generally increasing. Since the agents used in accordance with this invention form minimum-boiling azeotropic mixtures, it has been found desirable, before the addition of the agent, to subject the indene-containing oils to be treated according to the invention to ordinary fractional distillation in order to remove non-indene oils of a substantially different boiling range from indene, particularly those of substantially higher boiling range than indene. The removal of these oils reduces the amount of agent required for the distillation, minimizes contamination of the high-indene-content product by azeotropes formed of the agent and the higher boiling non-indene oils, and increases the yield of indene by reducing the volume of material which must be distilled, thus lessening the amount of indene carried into the distillate.

The amount of agent added to the indene-containing hydrocarbon oil should be regulated so that there will not be an undue amount remaining in the still residue when fractional distillation is discontinued. However, there should be enough of the agent present so that the azeotropic ratio of agent to non-indene oils in the distillate will be maintained throughout the fractionation. The entire amount of agent may be added to the indene-containing hydrocarbon oil before fractionation; or the agent may be added gradually in a continuous or intermittent fashion during the course of the fractionation.

At the beginning of the fractionation the distillate consists almost entirely of the azeotropic mixture of the non-indene oils and agent, but as fractionation proceeds and the temperature approaches the distillation temperature of the

indene azeotrope, the indene content of the distillate increases. The course of the fractionation may be followed by taking samples of the distillate and testing them for their indene content. The point at which fractionation is discontinued depends upon the indene content of the hydrocarbon oil being treated, the desired indene content of the final product and the efficiency of the agent used in separating the indene and non-indene oils. Thus the lower the indene content of the hydrocarbon oil being treated and the higher the desired indene content of the final product, the longer fractionation of the oil must be continued; while the higher the separation efficiency of the agent, the shorter will be the time necessary to obtain a hydrocarbon oil of the desired indene content. Obviously the longer fractionation is continued, the smaller will be the yield of the desired high-indene-content hydrocarbon oil. If desired, fractionation may be continued until substantially the entire indene content charge has been distilled, thereby recovering from the last distillate cut an oil containing about 98% indene. Fractionation of the mixture, however, is ordinarily discontinued when the indene content of the distillate shows the still residue contains about 89% to 95% indene (exclusive of the agent, if any) and the still residue is distilled straight, i. e. without fractionation, obtaining thereby the desired high-indene-content hydrocarbon oil.

The distillate recovered during the course of the fractionation contains the agent added to the indene-containing oil and also varying amounts of indene, in addition to the non-indene oils. It may be treated in any suitable manner, e. g. extraction or decantation, to effect recovery of the agent for reuse. The distillate oil fractions, which contain appreciable quantities of indene, may be then recycled through the above-described process to recover the indene contained therein, agent being added as necessary; or it may be treated in the ordinary manner with sulfuric acid to polymerize the indene and obtain hydrocarbon oils for solvent purposes and the like.

The accompanying drawing is a flow diagram illustrating a preferred method of carrying out the process of my invention.

Reference numeral 1 indicates an azeotropic fractional distillation operation in which a mixture of azeotropic agent and a close-cut indene fraction, e. g. a drip oil high-flash naphtha fraction of boiling range 176°-183° C., enter the process as indicated at 2 and are subjected to azeotropic distillation. As above indicated, the overhead product consists primarily of an azeotrope of the agent and non-indene components of the oil. This mixture is treated as indicated at 3 to separate the agent from the oil. As above indicated, in the case of a number of agents, such as glycol compounds, the separation may be brought about merely by cooling the mixture to room temperature and decanting; the separated agent may then be returned to the azeotropic fractionation step as indicated at 4. The low indene oil from which the agent has been separated is withdrawn as indicated at 5. As above stated, fractions of this oil may contain appreciable quantities of indene and may therefore be recirculated in the process or treated by other means to recover indene contained therein.

The high indene oil withdrawn as residue from the azeotropic fractionation may contain traces of azeotropic agent which may be removed as

above indicated. The high indene oil is then subjected to distillation as indicated at 6 to produce an indene distillation which may contain up to about 98% indene. The high-boiling residue which contains some indene may be treated to recover the indene contained therein. The indene distillate may be further subjected to a chilling operation indicated at 7 as hereinafter described, and the solid indene thus formed may be separated by filtration as indicated at 8. The filtrate from this operation may be reworked to recover indene contained therein.

The following examples are illustrative of the practice of this invention. Amounts are given in parts by volume. The indene percentages were calculated from the relation of the specific gravity of the oil to that of a similar oil of known indene content.

Example 1.—500 parts of drip oil high-flash naphtha of a boiling range from 176° to 183° C., a specific gravity at 22° C. of 0.957 and an indene content of 78% were mixed with 125 parts of phenol. This mixture was then fractionated in a 32-ball 7-foot column. Distillate cuts of 50 parts each were tested to determine their specific gravity, the phenol was then removed by washing with alkali, the ratio of distillate oil to phenol calculated, and the specific gravity of the phenol-free distillate oil determined. From the specific gravity of the phenol-free oil, its indene content was calculated. The following table shows the results of these tests:

Parts of distillate	Column temp.	Sp. gr. of distillate cut at 22° C. (inc. phenol)	Ratio distillate oil/phenol	Sp. gr. of phenol-free distillate oil at 22° C.	Indene distillate oil
	°C.				Percent
0.....	150				
10.....	170				
30.....	170.5				
40.....	170.5				
50.....	171	0.948	63/37	0.866	20
60.....	171.5				
80.....	171.8				
90.....	172				
100.....	172	0.952	63/37	0.886	32.5
110.....	172.2				
130.....	172.5				
150.....	172.5	0.975	62/38	0.915	51
160.....	172.8				
170.....	173				
200.....	173	0.988	62/38	0.933	62
210.....	173				
230.....	173.5				
250.....	173.5	0.997	62/38	0.947	71
260.....	173.5				
290.....	173.5				
300.....	173.8	1.006	62/38	0.965	83
305.....	173.8	(No determinations made of these fractions because of small size of fractions)			
310.....	174.5				
320.....	175.5				
325.....	176.5				

Fractionation was discontinued after 325 parts of distillate had been recovered and the still residue was then distilled straight, yielding, after removal of the small amount of phenol contained therein, 270 parts of an oil of specific gravity of 0.983 at 22° C. and an indene content of 94%. By this method for every 100 parts of crude high-flash naphtha, approximately 44 parts of an oil containing 55% indene and 54 parts of an oil containing 94% indene were obtained.

When the same oil was fractionated in the same column at the same rate without the use of phenol, it was impossible to obtain an oil of higher indene content than about 81% thereby.

Example 2.—500 parts of a crude carbolic oil

high-flash naphtha cut boiling from 178° to 183° C., having a specific gravity of 0.951 at 22° C. and an indene content of 68%, were mixed with 125 parts of phenol, the mixture was fractionated as in Example 1, with the following results:

Parts of distillate	Column temp.	Sp. gr. of distillate cut at 22° C. (inc. phenol)	Ratio distillate oil/phenol	Sp. gr. of phenol-free distillate oil at 22° C.	Indene distillate oil
	°C.				Percent
0.....	164				
10.....	167				
20.....	168				
30.....	168.5				
50.....	168.5	0.945	68/32	0.894	23
60.....	168.7				
90.....	169				
100.....	169.5	0.951	69/31	0.897	25
110.....	170				
140.....	170				
150.....	170.5	0.960	68/32	0.906	32
160.....	170.5				
180.....	171				
190.....	171				
200.....	171.5	0.971	66/34	0.920	43
210.....	171.5				
220.....	172				
250.....	172	0.980	64/36	0.934	54
260.....	172.2				
280.....	172.5				
300.....	172.8	0.991	64/36	0.946	65
310.....	173				
330.....	174				
350.....	175	0.995	64/36	0.960	75
360.....	176				
370.....	177				
380.....	177.5				
390.....	178				
400.....	178	0.978	96/4	0.972	84

Fractionation was discontinued after 400 parts of distillate had been recovered. The still residue was then distilled straight, yielding, after removal of the small amount of phenol contained therein, 220 parts of an oil of specific gravity at 22° C. of 0.980, and having an indene content of 91%.

Example 3.—500 parts of crude carbolic oil high-flash naphtha, boiling from 181° to 183° C., having a specific gravity of 0.958 at 22° C. and an indene content of 74% were mixed with 150 parts of phenol and the mixture was fractionated in a packed column at a pressure of about 280 mm. mercury. Distillate cuts were tested by washing the cuts with alkali to remove the phenol, calculating the ratio of distillate oil to phenol, and then determining the specific gravity of the distillate oil. From the specific gravity of the phenol-free oil, its indene content was calculated. The following table shows the results of these tests:

Parts of distillate	Column temp.	Ratio distillate oil/phenol	Sp. gr. of distillate oil at 22° C.	Indene distillate oil
	°C.			Percent
0.....	138			
10.....	138.5			
20.....	138.5			
30.....	139			
65.....	139	62/31	0.886	17
75.....	140			
130.....	140	75/25	0.917	40
140.....	140			
150.....	141			
195.....	141	75/25	0.956	72
200.....	141			
210.....	141.5			
255.....	141.5	75/25	0.970	82

Fractionation was discontinued after 255 parts of distillate had been recovered and the still residue was then distilled straight, yielding, after removal of the remaining phenol contained therein, 305 parts of an oil of specific gravity of 0.983 at 22° C., and an indene content of 92%. Thus for every 100 parts of crude high-flash naphtha containing 74% indene, approximately 37 parts of an oil containing 52% indene and about 61 parts of an oil containing 92% indene were obtained.

Example 4.—500 parts of a drip oil high-flash naphtha fraction boiling from 176° to 183° C., having a specific gravity of 0.948 at 22° C. and an indene content of 70% were mixed with 110 parts of ethylene glycol, and the mixture was fractionally distilled in a 32-ball 7-foot column. The glycol separated from the distillate oil when cooled to 22° C. Distillate cuts of 70 parts each were tested by permitting the glycol to separate from the distillate oil, washing the oil with water to remove traces of glycol, drying, and then determining the specific gravity of the oil. The small amounts of hydrocarbon oils remaining in the glycol were separated by dilution with water and the glycol reused. The following table shows the results of these tests:

Parts of distillate	Column temp.	Ratio distillate oil-glycol	Sp. gr. of glycol-free distillate oil at 22° C.	Indene distillate oil
	° C.			Percent
0.....	90			
10.....	156			
20.....	158			
30.....	159			
40.....	159.5			
50.....	160			
60.....	160			
70.....	160	71/29	0.908	47
80.....	160.5			
90.....	161			
100.....	161			
110.....	162			
120.....	162	67/33	0.918	53
140.....	162			
150.....	162			
210.....	162	70/30	0.928	61
220.....	162			
230.....	162.5			
290.....	162.5	70/30	0.938	67
300.....	162.5			
330.....	162.5			
340.....	163			
350.....	163	70/30	0.946	71
360.....	163			
420.....	163	73/27	0.953	77

Fractional distillation was discontinued after 420 parts of distillate had been recovered and the still residue was then distilled straight, yielding, after separation of the glycol contained therein, 187 parts of an oil of specific gravity at 22° C. of 0.977 and an indene content of 91.5%.

Example 5.—500 parts of a drip oil high-flash naphtha fraction boiling from 176° to 183° C., with a specific gravity of 0.948 at 22° C. and an indene content of 70%, were mixed with 110 parts of propylene glycol, and the mixture was then fractionally distilled in a 32-ball 7-foot column. The glycol separated from the distillate oil when cooled to 22° C. Distillate cuts of 70 parts each were tested by permitting the glycol to separate from the distillate oil, washing the oil with water to remove traces of glycol, drying, and then determining the specific gravity of

the oil. The following table shows the results of these tests:

Parts of distillate	Column temp.	Ratio distillate oil-glycol	Sp. gr. of glycol-free distillate oil at 22° C.	Indene distillate oil
	° C.			Percent
0.....	Moisture			
10.....	158			
20.....	158			
30.....	159.5			
40.....	160			
70.....	160	74/26	0.900	42
80.....	161			
120.....	161			
140.....	161	75/25	0.903	44
150.....	161			
200.....	161			
210.....	161.5	73/27	0.913	49
220.....	161.5			
240.....	162			
270.....	162			
280.....	162.5	73/27	0.927	58.5
290.....	163			
350.....	163	72/28	0.946	71
360.....	164			
370.....	164			
380.....	166			
390.....	169			
410.....	169			
420.....	175	67/33	0.972	87.5

Fractionation was discontinued after 420 parts of distillate had been recovered and the still residue was then distilled straight, yielding, after separation of the small amount of glycol contained therein, 180 parts of an oil of specific gravity at 22° C. of 0.982 and containing 95% indene. By combining the last cut, i. e. the cut from 350–420 parts, with the straight distillate and separating glycol therefrom, 225 parts of a hydrocarbon oil containing 93.5% indene were obtained.

Example 6.—500 parts of a drip oil high-flash naphtha fraction boiling from 176° to 183° C., having a specific gravity of 0.948 at 22° C. and an indene content of 70% were mixed with 100 parts of diethylene glycol mono-methyl ether and the mixture was then fractionally distilled in a 32-ball 7-foot column. The glycol ether separated from the hydrocarbon oil in the distillate when cooled to 22° C. Distillate cuts of 70 parts each were tested by permitting the glycol ether to separate from the hydrocarbon oil, washing the oil with water to remove traces of the glycol ether, drying, and then determining the specific gravity of the oil. The following table shows the results of these tests:

Parts of distillate	Column temp.	Ratio distillate oil-glycol ether	Sp. gr. of glycol-ether-free distillate oil at 22° C.	Indene distillate oil
	° C.			Percent
0.....	Moisture			
10.....	155			
20.....	156			
30.....	158			
40.....	159			
50.....	160			
60.....	160			
70.....	161	80/20	0.903	44
80.....	161			
90.....	161			
100.....	166			
110.....	171			
120.....	172			
130.....	172.5			
140.....	172.5	79/21	0.915	52

Parts of distillate	Column temp.	Ratio distillate oil/glycol ether	Sp. gr. of glycol-ether-free distillate oil at 22° C.	Indene distillate oil
	° C.			Percent
150.....	172.5			
160.....	173			
210.....	173	79/21	0.927	59
220.....	174			
250.....	174			
280.....	174	79/21	0.940	68
290.....	174			
300.....	174			
310.....	175			
350.....	175	79/21	0.952	75
360.....	175			
390.....	175			
400.....	176			
420.....	176	82/18	0.962	81

Fractionation was discontinued after 420 parts of distillate had been recovered and the still residue was then distilled straight, yielding, after separation of the small amount of glycol ether contained therein, 156 parts of a hydrocarbon oil having a specific gravity of 0.980 at 22° C. and containing 92% indene.

Example 7.—500 parts of a carbolic oil high-flash naphtha cut boiling from 178° to 183° C., having a specific gravity of 0.951 at 22° C. and an indene content of 68%, were mixed with 175 parts of o-chlorphenol and the mixture was then fractionally distilled in a 32-ball 7-foot column. Distillate cuts of 50 parts each were tested to determine their specific gravity, the chlorphenol was then removed by washing with alkali, the ratio of distillate oil to chlorphenol calculated, and the specific gravity of the chlorphenol-free distillate oil determined. An additional 50 and 125 parts of o-chlorphenol were charged into the still after 200 and 300 parts of distillate respectively had been collected. The following table shows the results of these tests:

Parts of distillate	Column temp.	Sp. gr. of distillate cut (including o-chlorphenol) at 22° C.	Ratio distillate oil/chlorphenol	Sp. gr. of chlorphenol-free distillate oil at 22° C.	Indene distillate oil
	° C.				Percent
0.....	169.6				
50.....	174.3	1.072	44/56	0.880	11
100.....	174.4	1.091	46/54	0.890	19
150.....	175.5	1.092	46/54	0.922	45
200.....	175.7	1.092	46/54	0.927	49

An additional 50 parts of o-chlorphenol were charged to the still at this point, and fractionation continued.

250.....	174.7	1.101	42/58	0.927	49
300.....	175.3	1.108	34/66	0.921	44

An additional 125 parts of o-chlorphenol were charged to the still at this point, and fractionation continued.

350.....	175.0	1.120	34/66	0.914	38
415.....	175.1	1.128	34/66	0.934	54

Fractionation was discontinued after 415 parts of distillate had been recovered. The still residue was then washed with alkali to remove residual chlorphenol and distilled straight, yielding 198 parts of an oil of specific gravity of 0.980 at 22° C. and an indene content of 90%.

Example 8.—500 parts of a carbolic oil high-flash naphtha cut boiling from 178° to 183° C., having a specific gravity of 0.951 at 22° C. and

an indene content of 68%, were mixed with 350 parts of o-chlorphenol and the mixture fractionated in a 32-ball 7-foot column. Distillate cuts of 100 parts each were tested to determine their specific gravity, the chlorphenol was then removed by washing with alkali, the ratio of distillate oil to chlorphenol calculated, and the specific gravity of the chlorphenol-free distillate oil determined. The following table shows the results of these tests:

Parts of distillate	Column temp.	Sp. gr. of distillate cut (including o-chlorphenol) at 22° C.	Ratio distillate oil/chlorphenol	Sp. gr. of chlorphenol-free distillate oil at 22° C.	Indene distillate oil
	° C.				Percent
0.....	171.2				
100.....	173.9	1.090	38/62	0.869	3
200.....	174.4	1.099	36/64	0.892	21
300.....	175.1	1.121	35/65	0.915	39
400.....	175.7	1.133	37/63	0.944	62

An additional 150 parts of o-chlorphenol were added to the still charge at this point, and fractionation continued.

500.....	175.7	1.152	30/70	0.945	63
600.....	175.7	1.153	32/68	0.956	72
700.....	176.9	1.140	40/60	0.969	81

Fractionation was discontinued after 700 parts of distillate had been recovered. The still residue was then washed with alkali to remove residual o-chlorphenol and distilled straight, yielding 172 parts of an oil of specific gravity at 22° C. of 0.982 and an indene content of 92%.

Example 9.—500 parts of a drip oil high-flash naphtha fraction boiling from 176° to 183° C., having a specific gravity of 0.957 at 22° C. and an indene content of 78% were mixed with 125 parts of aniline, and the mixture fractionally distilled in a 32-ball 7-foot column. Distillate cuts were tested by washing with dilute hydrochloric acid and water to remove the aniline, and then determining the specific gravity of the distillate oil, with the following results:

Parts of distillate	Column temp.	Ratio distillate oil/aniline	Sp. gr. of aniline-free distillate oil at 22° C.	Indene distillate oil
	° C.			Percent
0.....	168			
10.....	171			
20.....	172.5			
30.....	173			
40.....	173			
50.....	173.5	66/34	0.887	33
60.....	173.5			
80.....	174			
100.....	174	66/34	0.905	44.5
120.....	174.2			
140.....	174.5			
150.....	174.5	66/34	0.918	53
170.....	174.8			
190.....	175			
200.....	175	66/34	0.935	63
220.....	175			
250.....	175	66/34	0.947	71
270.....	175.5			
290.....	175.5			
300.....	176	66/34	0.958	79
330.....	176			
350.....	176			
370.....	177	74/26	0.972	87

Fractionation was discontinued after 370 parts of distillate had been recovered and the still residue was then distilled straight, yielding, after removal

of the small amount of aniline contained therein, 195 parts of a hydrocarbon oil of specific gravity 0.981 at 22° C. and containing 92.5% indene.

Example 10.—500 parts of a carbolic oil high-flash naphtha cut boiling from 178° to 183° C., having a specific gravity of 0.951 at 22° C. and an indene content of 68%, were mixed with 200 parts of a tar base fraction boiling from 170° to 186.5° C. and containing pyridine bases and about 48% aniline, and the mixture was then fractionally distilled in a 32-ball 7-foot column. Distillate cuts of 100 parts each were tested to determine their specific gravity, tar bases were then removed by washing with hydrochloric acid, the ratio of distillate oil to tar base fraction calculated, and the specific gravity of the tar base-free oil determined. The following table shows the results of these tests:

Parts of distillate	Column temp.	Sp. gr. of distillate cut (including tar bases) at 22° C.	Ratio distillate oil/tar base	Sp. gr. of tar base-free distillate oil at 22° C.	Indene distillate oil
	°C.				Percent
0.....	150.0				25
100.....	176.8	0.933	65/35	0.904	41
200.....	177.5	0.946	65/35	0.918	55
300.....	178.4	0.955	65/35	0.935	75
400.....	179.6	0.969	70/30	0.960	84
500.....	180.8	0.977	78/22	0.973	

Fractionation was discontinued after 500 parts of distillate had been recovered. The still residue was washed with hydrochloric acid to remove residual tar bases and distilled straight, yielding 121 parts of an oil of specific gravity of 0.986 at 22° C. and an indene content of 95%.

Example 11.—500 parts of a drip oil high-flash naphtha fraction, boiling from 176° to 183° C., having a specific gravity of 0.948 at 22° C. and an indene content of 70%, were mixed with 100 parts of mono-ethanol amine and the mixture was fractionally distilled in a 32-ball 7-foot column. The amine separated from the distillate oil when cooled to 22° C. Distillate cuts were examined by permitting the amine to separate from the distillate oil and then determining the specific gravity of the oil. The following table shows the results of these tests:

Parts of distillate	Column temp.	Ratio distillate oil/ethanol-amine	Sp. gr. of ethanol-amine-free distillate oil at 22° C.	Indene distillate oil
	°C.			Percent
0.....	98			
10.....	145			
20.....	149			
30.....	144.5			
40.....	150			
50.....	150			
60.....	151			
70.....	151	58/42	0.868	21.5
80.....	151			
90.....	151.5			
100.....	151.5			
110.....	152			
120.....	152			
130.....	152.5			
140.....	152.5	61/39	0.884	32
150.....	153			
160.....	153.5			
170.....	153.5	65/35	0.928	59
180.....	168			
190.....	168			
200.....	176.5			
210.....	176.5			
220.....	176.5			
230.....	176.5			
240.....	177	(Not determined)	0.968	85

Fractionation was discontinued after 350 parts of distillate had been recovered, and the still residue was then distilled straight, yielding, after separation of the small amount of amine contained therein, 185 parts of an oil of specific gravity of 0.980 at 22° C. and containing 92% indene.

Certain of the agents used in accordance with this invention, while miscible with the indene-containing hydrocarbon oils at distillation temperatures so that azeotropes are formed by these agents with indene and the non-indene oils, are immiscible with the hydrocarbon oils at room temperatures so that they separate therefrom at room temperatures. As examples of agents of this type may be mentioned ethylene glycol, propylene glycol, diethylene glycol mono-methyl ether and mono-ethanol amine. The property of immiscibility of these agents with hydrocarbon oils at room temperatures (about 22° C.) is particularly advantageous, for it permits separation of the agent from the hydrocarbon oils to be effected by mere decantation. The agent thus decanted may be reused in the fractionation of the indene-containing hydrocarbon oil, thus permitting the proper azeotropic ratio of agent to hydrocarbon oil to be maintained in the fractionating column with the use of a minimum amount of agent, obviating the necessity of keeping in storage large quantities of agent for carrying out the fractionation. The following example illustrates this phase of my invention:

Example 12.—16,450 parts of drip oil high-flash naphtha boiling from 176° to 183° C., having a specific gravity of 0.937 at 15.5° C. and an indene content of 54% were mixed with 1,000 parts of propylene glycol and the mixture fractionated in a packed column. The distillate was condensed and permitted to separate into two layers, the lower propylene glycol layer being continuously withdrawn and returned to the bottom of the fractionating column for reuse. The hydrocarbon oil layers separated in the condenser were tested periodically, after removal of the small amounts of propylene glycol remaining in the oils, to determine their specific gravity, from which their indene contents were calculated. The following table showing the volume of each cut tested gives the results of these tests:

Cut No.	Volume of cut tested	Sp. gr. of propylene glycol-free distillate at 15.5° C.	Indene in distillate oil	Parts of propylene glycol removed with oils
			Percent	
1.....	2,575	0.903	23	3
2.....	2,050	0.904	27	4
3.....	1,030	0.904	28	3
4.....	1,200	0.905	29	4
5.....	1,370	0.912	34	4
6.....	1,080	0.928	47	6
7.....	1,100	0.933	51	7
8.....	560	0.947	62	5

Fractionation was discontinued after 10,965 parts of distillate had been recovered and the still residue was then distilled straight, yielding, after separation of the propylene glycol, 3,480 parts of an oil having a specific gravity of 0.982 at 15.5° C. and containing 90% indene. The propylene glycol was recovered practically quantitatively, but was slightly contaminated with hydrocarbon oils. It can be reused for further separation of indene and non-indene oils. Thus, for every 100 parts of crude high-flash naphtha containing 54% indene, the distillation yielded about 67

parts of an oil containing 34% indene and about 21 parts of an oil containing 90% indene.

If it is desired to obtain pure indene from the hydrocarbon oils of high indene content obtained according to the practice of this invention, the hydrocarbon oils may be cooled to from about -10° to about -20° C. and the solid indene thus formed may be separated from the oils.

From the above description it will be evident this invention provides a simple and inexpensive method of obtaining oils of a high indene content from oils of a relatively low indene content.

My copending applications Serial Nos. 335,329 and 335,330, filed on the same date as the present application, are directed to species of the generic invention disclosed and claimed in this application.

In the claims the term "tar base" is intended to include not only tar base fractions recovered from coal tar, which fractions may contain pyridine bases, or aniline, or both, but it is also intended to include substantially pure tar bases, such as aniline.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an organic compound having a radical selected from the group consisting of the hydroxyl, the carboxyl, the amino, and the pyridinic nitrogen radicals and capable of forming azeotropes with indene and the non-indene oils contained in the hydrocarbon oil.

2. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an organic compound containing a hydroxyl group and capable of forming azeotropes with indene and the non-indene oils contained in the hydrocarbon oil.

3. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an organic compound containing a pyridinic nitrogen radical and capable of forming azeotropes with indene and the non-indene oils contained in the hydrocarbon oil.

4. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an organic compound containing an amino group and capable of forming azeotropes with indene and the non-indene oils contained in the hydrocarbon oil.

5. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an amount of tar base sufficient to form an azeotrope with non-indene components of the oil.

6. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an amount of mono-ethanol amine sufficient to form an azeotrope with non-indene components of the oil.

7. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an amount of o-chlorophenol sufficient to form an azeotrope with non-indene components of the oil.

8. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an organic compound having a radical which renders the compound relatively strongly polar as compared with indene and other substances present in the hydrocarbon oil and which makes the compound soluble in water or in aqueous solutions of acids or bases, said compound being miscible with the hydrocarbon oil at distillation temperatures, separable therefrom by gravity or on aqueous extraction, chemically inert with respect to the constituents of the hydrocarbon oil, capable of forming azeotropes with indene and the non-indene oils contained therein, and having a distillation temperature at atmospheric pressure of between about 145° and about 220° C.

9. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an amount of aniline sufficient to form an azeotrope with non-indene components of the oil.

10. A method of producing pure indene from a hydrocarbon oil of relatively low indene content having a boiling range in the neighborhood of indene boiling point, which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an organic compound having a radical which renders the compound relatively strongly polar as compared with indene and other substances present in the hydrocarbon oil and which makes the compound soluble in water or in aqueous solutions of acids or bases, said compound being miscible with the hydrocarbon oil at distillation temperatures, separable therefrom by gravity or on aqueous extraction, chemically inert with respect to the constituents of the hydrocarbon oil, capable of forming azeotropes with indene and the non-indene oils contained therein, and having a distillation temperature at atmospheric pressure of between about 145° and about 220° C., recovering the hydrocarbon oil of high indene content from the still residue, cooling the hydrocarbon oil thus recovered to a temperature of between about -10° and about -20° C., and separating pure indene from the cooled oil.

11. In a method of producing a hydrocarbon oil of high indene content from a hydrocarbon oil of relatively low indene content having a boiling range in the neighborhood of indene boiling point, the step which comprises distilling the hydrocarbon oil of relatively low indene content in the presence of an organic compound having a radical selected from the group consisting of the hydroxyl, the carboxyl, the amino and

the pyridinic nitrogen radicals and capable of forming azeotropes with indene and the non-indene oils contained in the hydrocarbon oil.

12. In a method of producing a hydrocarbon oil of high indene content, the steps which comprise fractionally distilling a crude selected from the group consisting of coal-tar oils, drip oils, carburetted water-gas tar oils, oil-gas tar oils and light oils recovered in coal-gas and water-gas operations to obtain a hydrocarbon mixture of relatively low indene content having a boiling range in the neighborhood of indene boiling point, adding to this hydrocarbon mixture an amount of tar base sufficient to form an azeotrope with non-indene components of the oil, fractionally distilling the mixture, and recovering the hydrocarbon oil of high indene content from the still residue.

13. In a method of producing a hydrocarbon oil of high indene content, the steps which comprise fractionally distilling a crude selected from the group consisting of coal-tar oils, drip oils, carburetted water-gas tar oils, oil-gas tar oils and light oils recovered in coal-gas and water-gas operations to obtain a hydrocarbon mixture of relatively low indene content having a boiling range in the neighborhood of indene boiling point, adding to this hydrocarbon mixture an amount of mono-ethanol amine sufficient to form an azeotrope with non-indene components of the oil, fractionally distilling the mixture, and recovering the hydrocarbon oil of high indene content from the still residue.

14. In a method of producing a hydrocarbon oil of high indene content, the steps which comprise fractionally distilling a crude selected from the group consisting of coal-tar oils, drip oils, carburetted water-gas tar oils, oil-gas tar oils and light oils recovered in coal-gas and water-gas operations to obtain a hydrocarbon mixture of relatively low indene content having a boiling range in the neighborhood of indene boiling point, adding to this hydrocarbon mixture an amount of ortho-chlorophenol sufficient to form an azeotrope with non-indene components of the oil, fractionally distilling the mixture, and recovering the hydrocarbon oil of high indene content from the still residue.

15. In a method of producing a hydrocarbon oil of high indene content, the steps which comprise fractionally distilling a crude selected from the group consisting of coal-tar oils, drip oils, carburetted water-gas tar oils, oil-gas tar oils and light oils recovered in coal-gas and water-gas operations to obtain a hydrocarbon mixture of relatively low indene content having a boiling range in the neighborhood of indene boiling point, adding to this hydrocarbon mixture an amount of aniline sufficient to form an azeotrope with non-indene components of the oil, fractionally distilling the mixture, and recovering the hydrocarbon oil of high indene content from the still residue.

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