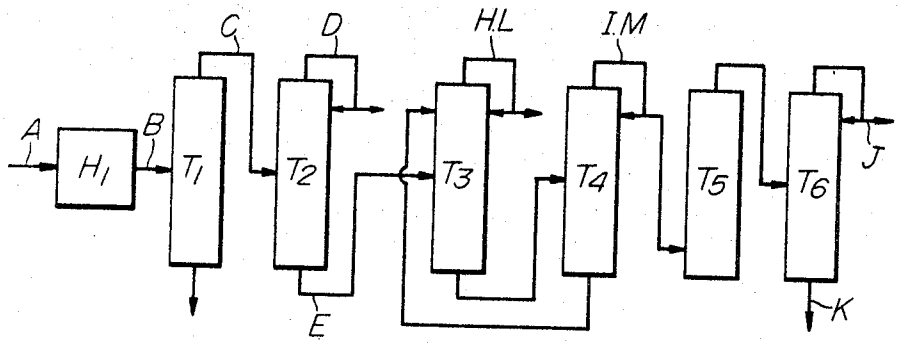
April 1, 1969 MITSUO ASAKA ET AL 3,436,437

PROCESS FOR RECOVERING HIGH PURITY ISOPRENE BY EXTRACTIVE DISTILLATION WITH METHOXYPROPIONITRILE

Filed Nov. 15, 1966



United States Patent Office 3,436,437
Patented Apr. 1, 1969

3,436,437

PROCESS FOR RECOVERING HIGH PURITY ISOPRENE BY EXTRACTIVE DISTILLATION WITH METHOXYPROPIONITRILE

Mitsuo Asaka and Makoto Komatsu, Tokyo, and Susumu Jufiyama, Kodaira-shi, Japan, assignors to Japan Gas-Chemical Company, Inc., Tokyo, Japan, a Japanese corporation

Filed Nov. 15, 1966, Ser. No. 594,484
Claims priority, application Japan, Nov. 17, 1965, 40/70,711; May 2, 1966, 41/27,806
Int. Cl. C07c 7/04
U.S. Cl. 260—681.5 3 Claims

ABSTRACT OF THE DISCLOSURE

A polymerization grade isoprene of high purity is recovered from a C_5 fraction of the by-product oil residue from the thermal cracking of petroleum by heating said C_5 fraction to remove cyclopentadiene contained therein as dimer, removing components boiling lower than acetylenes and isoprene by straight distillation, separating a diolefin fraction and a monoolefin fraction by extractive distillation and further distilling the diolefin fraction to obtain the high purity isoprene.

The present invention relates to an improved process for separating diolefins from hydrocarbon mixtures, particularly C_5 cuts of a cracked residue produced by the thermal cracking of petroleum. The invention also relates to a process for separating diolefins from said C_5 cuts which comprises carrying out an extractive distillation with β-methoxypropionitrile as a selective solvent, and particularly to a process for recovering high purity isoprene from C_5 cuts.

In recent years the thermal cracking of petroleum, and particularly naphtha, has been carried out on a large scale for the purpose of preparing gaseous olefins such as ethylene, propylene and the like. The cracked residue produced by such a thermal cracking contains various C_5 hydrocarbons having different degrees of saturation. The representative composition of the cracked residue and the boiling points of these hydrocarbons are listed in column A of Table I below. As can be seen from Table I, this C_5 cut contains a large amount of isoprene and it is very desirable to recover and utilize the isoprene.

However, problems arise in separating isoprene from hydrocarbon mixtures having such compositions as the presence of a small amount of acetylenic hydrocarbons, particularly lower boiling hydrocarbons than isoprene in the cracked residue produced by the thermal cracking of naphtha, or the presence of components having boiling points close to that of C_5 diolefins in a mixture of C_5 paraffins and C_5 monoolefins. These materials behave similarly to isoprene and render it very difficult to efficiently recover isoprene of high purity.

There has been previously known a process which comprises separating the cracked residue into groups having different degrees of saturation with a selective solvent such as, for example, an ammonium solution of cuprous acetate, Sulfolanes or the like paying attention to a difference in chemical and physicochemical properties based upon a difference in the degree of saturation, and then recovering a pure desired hydrocarbon by rectification. The process comprises carrying out an extractive distillation with a selective solvent based on the combination of a difference in the degree of saturation and a difference in boiling point to raise the concentration of a desired hydrocarbon to a desired value, and then recovering the pure hydrocarbon by rectification.

When C_5 cuts of a cracked residue produced by the thermal cracking of naphtha have been separated according to any previously known process, the recovered isoprene usually contained small amounts of monoolefinic compounds predominantly 2-methyl butene-2, and acetylenic compounds such as butyne-2, isopropylacetylene and isopropenyl-acetylene even though paraffinic hydrocarbons were substantially completely removed from the isoprene.

Several methods have been proposed for recovering isoprene from highly complex C_5 mixtures produced by steam cracking or other high temperature hydrocarbon conversion processes. Two stages of extractive distillation are sometimes applied to remove acetylenic compounds. Alternatively a combination of straight distillation and extractive distillation is carried out to remove acetylenic compounds. These procedures have not been entirely satisfactory because very small amounts of acetylenic compounds have remained in the purified isoprene. In order to purify the product into polymerization grade isoprene, an additional operation for removing impurities is required. This makes the procedures complicated and troublesome and causes a reduction in yield. It is therefore difficult to economically recover polymerization grade isoprene.

It is an object of the present invention to provide a process for recovering isoprene of a polymerization grade of purity which comprises removing acetylenic compounds before extractive distillation and which obviates the above-mentioned defects inherent in previous known processes.

It is another object of the present invention to provide a process for separating diolefins which comprises carrying out an extractive distillation with β-methoxypropionitrile as a selective solvent.

These and other objects will appear more clearly from the detailed specification and claims which follow.

It has now been found that, in case of the C_5 hydrocarbon mixtures as shown in Table I, acetylenes can be completely distilled off by straight distillation after effecting the dimerization of cyclopentadiene, and isoprene of high purity can be recovered.

In order to illustrate the present invention more clearly reference is made to the accompanying drawing which shows a diagrammatic flow plan of the process of the present invention.

In the drawing a feed stock, a C_5 cut, containing a large amount of cyclopentadiene which has a degree of saturation equal to that of isoprene and has chemical and physical properties close to those of isoprene and shows a complicated behavior in distillation process and renders the purification of isoprene difficult, is first treated in heating kettle H_1 at 80° to 120° C. Thus cyclopentadiene is readily dimerized into dicyclopentadiene having a higher boiling point (170° C.) by this heating, and subsequent operations become very easy. The treated C_5 cut is charged to a higher boiling components separating tower T_1 where said dimer and components boiling higher than C_5 are removed as a bottom stream. The overhead stream consisting of components having a boiling point not higher than 55° C. is charged to a lower boiling components separating tower T_2 where components boiling lower than isoprene mainly consisting of isopentane are distilled overhead at about 28° C. at atmospheric pressure. Said feed stock contains about 30 percent of hydrocarbons boiling lower than isoprene. It is possible to distill off acetylenic hydrocarbons at a temperature lower than that anticipated from the boiling points of the pure materials, but it is impossible to distill off substantially all of the boiling lower fractions than isoprene

without loss of isoprene. Acetylene hydrocarbons may be substantially completely distilled off while allowing a part of monoolefinic hydrocarbons to remain in the residue. The amount of overhead stream and the loss of isoprene directly depend on the number of plates of the fractionating tower and a reflux ratio. In the practice of the present invention the loss of isoprene may be up to five percent, preferably up to two percent, of the total content of isoprene and the amount of overhead stream may be up to 30 percent, preferably up to 25 percent, of the total amount of the feed stock. These acetylenic hydrocarbons have been analyzed to include butyne-2, pentyne-1, isopropyl-acetylene and isopropenylacetylene. It is very advantageous to remove these materials at this point since they act as an inhibitor in the polymerization of isoprene. The bottom stream is a C_5 cut having a narrow boiling range and mainly consisting of paraffinic, monoolefinic and diolefinic hydrocarbons.

We have found that β-methoxy-propionitrile can meet all of the above-mentioned conditions. The comparison between this solvent and previously known solvents in the effect on relative volatilities of hydrocarbons and isoprene is shown in the following Table II.

TABLE II.—EFFECT OF SOLVENTS ON RELATIVE VOLATILITIES OF HYDROCARBONS

Solvent	n-Pentane	2-methyl-butene-2
No solvent	0.92	0.88
Acetone	1.80	1.16
Acetonitrile	2.36	1.29
Dimethylformamide	2.44	1.30
N-Methoxypropionitrile	2.37	1.37

The feed stock employed at this stage is one obtained by subjecting a C_5 cut of cracked naphtha residue to a heat treatment to remove cyclopentadiene and has the composition shown in the X column of Table III. The

TABLE I

Components of C_5 cut	Boiling point, °C.	Composition (Percent by weight) Feed stock, A	Inlet of T_1, B	Inlet of T_2, C	Top of T_2, D	Bottom of T_2, E	44th plate of T_2, F	52nd plate of T_2, G	Top of T_3, H	Top of T_4, I	Top of T_5, J	Bottom T_5, K	Top of T_3, L	Top of T_4, M
Paraffinic:														
Isopentane	27.9	13.4	13.4	16.8	65.5	0.7	17.0	9.3	1.2				1.2	
n-Pentane	36.1	22.3	22.3	27.9	0.4	37.8	25.1	29.4	64.0				63.8	
Cyclopentane	49.3	0.6	0.6	0.8		1.0	0.2	0.2	1.7	0.4		0.8	1.8	0.3
Monoolefinic:														
3-methyl-butene-1	20.1	0.6	0.6	0.7	2.6									
Pentene-1	30.0	3.7	3.7	4.7	12.0	2.1	10.0	9.2	3.5	0.1	0.05		3.6	
2-methyl-butene-1	31.2	4.7	4.7	6.0	7.2	5.2	14.3	14.7	8.6	0.1	0.05		8.8	
Transpentene-2	36.4	2.1	2.1	2.6		3.5	1.9	2.1	6.0	0.1	0.05		6.0	
Cis-pentene -2	36.9	1.3	1.3	1.7		2.1	0.9	1.1	3.6	0.1	0.05		3.5	0.1
2-methyl-butene-2	38.6	2.3	2.3	2.9		3.9	1.4	1.5	6.6	0.2	0.1	0.4	6.5	0.3
Cyclopentene	44.2	2.3	2.3	2.9		4.0	0.1	0.9	0.8	8.3		15.5	1.1	7.9
Diolefinic:														
Isoprene	34.1	14.1	14.1	17.7	3.9	21.8	22.7	25.5	4.0	47.3	99.8	15.5	3.7	48.3
Transpiperylene	42.0	4.3	4.3	5.9		7.9	2.2	2.4		19.1	0.03	34.8		18.8
Cis-piperylene	44.1	2.2	2.2	3.1		4.3	1.0	1.1		10.5	0.02	19.1		10.7
Cyclopentadiene	41	10.9	1.9	2.1		2.6	2.0	2.2		6.0		0.4		5.9
Acetylenic:														
Butyne-2	27.2	0.3	0.3	0.4	2.0		0.2							
Isopropyl acetylene	28	1.4	1.4	1.4	6.2		0.8	0.2						
Isopropenyl acetylene	33	0.1	0.1	0.1	0.1									
Other α-Acetylenes					0.1									
Higher boiling fraction than C_5		13.3	22.3	2.3		3.1	0.2	0.2		8.1		13.5		7.7

The C_5 cut thus obtained is then charged to an extractive distillation tower T_3 where diolefinic hydrocarbons are separated by extractive distillation. Selective solvents my be employed at this stage include acetone, acetonitrile, dimethylformamide, dimethylacetoamide, furfural and the like, and the use of β-methoxypropionitrile is particularly preferred. It is possible to selectively separate diolefins from mixtures of hydrocarbons of close boiling range by distilling the mixtures with such a solvent.

When a low boiling solvent is employed as the selective solvent, some of the solvent is contained in the overhead stream from the distillation tower in the form of an azeotropic mixture, and it is then necessary to remove the solvent from the distillate. This method also has disadvantages in that lower temperature cooling water or a pressure operation is required since the temperature at the top of the tower is reduced, and more plates are necessary to strip hydrocarbons from the extract consisting of a mixture of the solvent and the hydrocarbons withdrawn from the tower.

On the other hand, when a high boiling solvent is employed, the above-mentioned disadvantages are obviated but chemical stability of the solvent is desirable since this run is necessarily accompanied by a high temperature operation. Some previously known high boiling solvents may have excellent properties as solvents such as the effect on relative volatilities of various hydrocarbons and diolefines in said solvents, but their chemical stability at higher temperatures is unsatisfactory.

amount of the solvent employed is two parts per one part of hydrocarbons.

TABLE III.—COMPOSITION OF C_5 CUT

	Composition (percent by wt.) X	Y	Z
Isopentane	15.2	23.4	
n-Pentane	23.6	40.0	
Cyclopentane	0.75	0.4	8.11
Pentene-1	4.96	7.21	
Cis-pentene-2	3.66	5.28	0.91
Trans-pentene-2	3.41	4.28	
3-methylbutene-1	0.19		
2-methylbutene-1	7.03	11.1	
2-methylbutene-2	4.05	3.90	3.87
Cyclopentene	2.76		
Isoprene	17.9		55.9
Cis-piperylene	3.43		9.64
Transpiperylene	6.70		19.3
Cyclopentadiene	0.94		2.322

As described above, β-methoxy-propionitrile was found to be comparable as a solvent to previously known solvents and to be particularly superior to previous known solvents for 2-methylbutene-2 which has been heretofore difficult to separate. Further, β-methoxy propionitrile has advantages in that it obviates the above-mentioned defects of low boiling solvents and that it is chemically stable at high temperatures and easily available at low cost.

In an extractive distillation any acetylenic hydrocarbons present in the feed stock tend to be concentrated at the bottom of the tower together with diolefins even

if their boiling points are lower than that of isoprene. However, according to the process of the present invention, acetylenic hydrocarbons are not substantially contained in the diolefins since the acetylenic hydrocarbons has been previously removed in the tower T_2. The amount of the selective solvent added to the distillation tower is preferably one to five times the volume of hydrocarbons recycled as reflux to the plate where the solvent is supplied. The diolefin fraction withdrawn from the bottom of the tower is then passed to a solvent recovery tower T_4 where the solvent is completely removed from the fraction.

The diolefin fraction thus treated is then washed with water at a water wash tower T_5 and is passed to a fractionating tower T_6 where isoprene is separated. The fraction consists of diolefins and a small amount of monoolefins and contains no fraction boiling lower than isoprene. Therefore, isoprene of high purity can be readily obtained from the fraction.

The above operations may be carried out either at atmospheric pressure or at superatmospheric pressure, but for the prevention of the polymerization of isoprene the temperature of any isoprene-rich fraction must not be raised above 90° C.

The following examples are illustrative of the present invention.

Example 1

A C_5 cut having the composition shown in column A of Table I was heated at 110° C. in an autoclave for four hours to obtain a product of the composition shown in column B of Table I. This product was then subjected to a straight distillation to remove low boiling fractions having boiling points up to 55° C. The distillate having the composition shown in column C of Table I was charged to a packed tower (which corresponds to T_2 in the drawing) having an inner diameter of 20 mm., a packing height of 1,500 mm., and a number of theoretical plates of 70, at the 44th plate from the top at a rate of 150 cc./hour. The tower was operated at a reflux ratio of 25. 20 percent by weight of the charged mixture of hydrocarbons was withdrawn from the top of the tower and the remainder was removed from the bottom of the tower. The temperature at the top was 27° C. at atmospheric pressure. The top distillate and the bottom residue had the compositions shown in columns D and E of Table I, respectively. Most of the acetylenic hydrocarbons was removed from the top of the tower by this operation, and substantially no acetylenic hydrocarbons were present at any of the tower lower than the 44th plate from the top. In Table I columns F and G give the compositions at the 44th plate and the 52nd plate, respectively. About 5 percent of isoprene was lost by this operation.

The bottom residue thus obtained was then charged to a packed tower (which corresponds to T_3 in the drawing) having an inner diameter of 20 mm., a packing height of 1,300 mm. and a number of theoretical plates of 60 at the middle of the tower at a rate of 120 cc./hour and acetonitrile containing 2 percent water was fed to the tower at the 12th plate from the top at a rate of 550 cc./hour. The tower was operated at a reflux ratio of 6. 55 percent by weight of the charged C_5 cut was withdrawn from the top of the tower and the remainder was removed from the bottom of the tower. The temperature at the top was 32° C. The bottom stream consisting of a mixture of a fraction mainly comprising diolefins, acetonitrile and water was passed into a solvent recovery tower (which corresponds to T_4 in the drawing) having an inner diameter of 20 mm. and a packing height of 1,000 mm., where the hydrocarbons were separated from acetonitrile. The diolefins thus obtained were then washed with water and distilled in a packed tower (which corresponds to T_6 in the drawing) having an inner diameter of 20 mm., a packing height of 1,500 mm. and a number of theoretical plates of 80. Thus a polymerization grade isoprene having the composition shown in column J of Table I was obtained from the top of the tower.

Example 2

The bottom stream having the composition shown in column E of Table I obtained in Example 1 was charged to a packed tower having a diameter of 20 mm. and a packing height of 1,200 mm. at the middle thereof at a rate of 50 cc./hour and β-methoxy-propionitrile was charged to the tower at a position 100 mm. below the top at a rate of 500 cc./hour. Extractive distillation was carried out at a reflux ratio of 8.5 and a diolefin-free fraction having the composition shown in column L of Table I was obtained from the top of the tower. A fraction consisting of the solvent and the hydrocarbons was withdrawn from the bottom of the tower at a rate of 520 cc./hour and then charged to a stripper having a diameter of 20 mm. and a height of 500 mm. at the middle thereof. Thus a fraction containing mainly diolefins and having the composition shown in column M of Table I was obtained from the top of the tower at a rate of 20 cc./hour.

Example 3

A feed stock having the composition shown in column X of Table III was charged to a packed tower having a diameter of 20 mm. and a height of 1,200 mm. at the middle thereof at a rate of 50 cc./hour and β-methoxy-proprionitrile was charged to the tower at a position of 100 mm. below the top of the tower at a rate of 500 cc./hour. The tower was operated at a reflux ratio of 8.5 (a reflux amount of 280 cc./hour) and a temperature at the top of 35° C. A distillate was withdrawn from the top of the tower at a rate of 33 cc./hour. Thus a diolefin-free fraction having the composition shown in column Y of Table III was obtained.

A fraction consisting of the solvent and the hydrocarbons was withdrawn from the bottom of the tower at a rate of 520 cc./hour and then charged to a stripper having a diameter of 20 mm. and a height of 500 mm. at the middle thereof. Thus a fraction containing mainly diolefins and having the composition shown in column Z of Table III was obtained from the top of the tower at a rate of 20 cc./hour.

Example 4

This example illustrates the result of an experiment carried out at superatmospheric pressure.

A C_5 cut having the composition shown in column A' of Table IV was passed through tube H_1 maintained at 110° C. with a residence time of 5.7 hours where the C_5 cut was heated and dimerized. The oil thus treated was then charged to a distillation tower T_1 having 18 plates at a rate of 10.0 kg./hour. The tower was operated at a reflux ratio of 0.35. The C_5 fraction was withdrawn from the top of the column at a rate of 7.82 kg./hour. The temperature at the top was 60° C. and the pressure was 2.2 atm. (abs.)

The fraction, from which high boiling components had been thus removed, had the composition shown in column C' of Table IV. The fraction was then charged to a rectifying tower T_2 having 130 plates at a rate of 7.82 kg./hour. The tower was operated at a reflux ratio of 18. The fraction boiling lower than C_5 containing mainly isopentane was withdrawn from the top of the tower at a rate of 1.99 kg./hour. The acetylenic hydrocarbons contained in the feed stock were substantially completely collected in this fraction. A substantially acetylene-free fraction having the composition shown in column E of Table IV was obtained from the bottom of the tower. The temperature at the top was 58° C. and the pressure was 2.8 atm. (abs.).

The fraction having the composition shown in column E' of Table IV obtained at the preceding stage was charged to an extractive distillation tower T_3, having 94 plates and operated at a reflux ratio of 5, at the middle

thereof at a rate of 82 kg./hour, and acetonitrile containing 5 percent by weight of water was fed to the tower at the 10th plate from the top at a rate of 39.5 kg./hour. The temperature at the top was 60° C. and the pressure was 2.66 atm. (abs.).

The composition of the C_5 fraction in the distillate withdrawn from the top is shown in column H' of Table IV. A mixture of acetonitrile and a C_5 fraction consisting essentially of diolefins was obtained from the bottom of the column at a rate of 41.0 kg./hour. This mixture was then charged to a solvent recovery tower T_4 having 20 plates and operated at a reflux ratio of 3.0. A diolefin fraction was thus obtained from the top of the tower at a rate of 2.23 kg./hour. The temperature was 60° C. and the pressure was 2.16 atm. (abs.).

The diolefin fraction thus obtained was washed with water in a water-wash tower T_5 to remove the solvent from the fraction. After separating an aqueous layer, the fraction was charged to the isoprene rectification stage. This process was carried out at a reflux ratio of 11 employing a tower T_6 having 106 plates. For a rate of 2.29 kg. of the feed stock per hour, isoprene having a purity not lower than 99.8 percent was obtained from the top of the tower at a rate of 1.05 kg./hour. The composition of the bottom stream is shown in column K' of Table IV. The temperature at the top was 50° C. and the pressure was 1.72 atm. (abs.).

TABLE IV

Components of C_5 cut	Composition (percent by weight)				
	Feed stock, A'	Inlet of T_2, C'	Bottom of T_2, E'	Top of T_3, H'	Bottom of T_6, K'
Lower boiling components than C_4	2.5	3.2	----	----	----
Parafinic:					
Isopentane	13.0	16.6	1.9	3.2	----
n-Pentane	20.5	26.2	35.2	58.2	----
2,3-dimethyl butane	0.1	0.1	0.1	----	0.6
Cyclopentane	0.5	0.6	0.7	----	3.5
3-methyl-pentane	0.4	0.5	0.6	----	3.0
n-Hexane	0.7	0.8	0.9	----	5.3
Monoolefinic:					
3-methyl-butene-1	0.8	1.0	----	----	----
Pentene-1	4.0	5.2	4.0	6.6	----
2-methyl-butene-1	5.3	6.8	7.7	12.7	----
Trans-pentene-2	2.2	2.9	3.8	6.4	----
Cis-pentene-2	1.4	1.8	2.4	3.9	----
2-Methyl-butene-2	2.6	3.0	4.5	7.3	0.1
Cyclopentene	1.8	2.4	3.2	----	15.0
Diolefinic:					
Isoprene	13.6	16.6	21.2	1.7	9.4
Trans-piperylene	4.3	5.5	7.4	----	34.5
Cis-piperylene	2.4	3.0	4.0	----	18.8
Cyclopentadiene	10.8	1.4	1.49	----	8.7
Acetylenic:					
Butyne-2	0.3	0.4	----	----	----
α-Acetylenes	1.3	1.7	----	----	----
Higher boiling components than C_6	11.5	0.2	0.2	----	1.1

What is claimed is:

1. A process for recovering polymerization grade isoprene having a purity of not less than 99.8% from a C_5 hydrocarbon fraction containing C_5 paraffins, C_5 monoolefins, C_5 diolefins containing cyclopentadiene, butene-2 and C_5 acetylenic hydrocarbons and a fraction boiling higher than C_5, which comprises heating the C_5 fraction until the cyclopentadiene contained in said C_5 fraction is reduced to not more than 0.12 mole per mole of isoprene, distilling said C_5 fraction to remove a fraction having a boiling point higher than 55° C., subjecting the resulting overhead fraction to a straight distillation to separate components boiling lower than isoprene and simultaneously distilling off acetylenic hydrocarbons substantially completely while repressing an isoprene loss to not more than 5% of the feed C_5 fraction, subjecting the residual oil to an extractive distillation in the presence of β-methoxypropionitrile to separate a fraction consisting substantially of diolefins and a fraction consisting substantially of monoolefins, and water-washing and rectifying the diolefin to separate isoprene therefrom.

2. A process according to claim **1** wherein said C_5 hydrocarbon fraction is a C_5 fraction obtained by thermal cracking of petroleum, particularly naphtha.

3. A process according to claim **1** wherein the amount of a selective solvent for the extractive distillation charged is one to five times the volume of the hydrocarbons recycled as reflux to the plate where the solvent is charged.

References Cited

UNITED STATES PATENTS

2,361,493	10/1944	Patterson	203—54
2,407,997	9/1946	Patterson	203—54
2,426,705	9/1947	Patterson	202—39.5
2,441,827	5/1948	McKinnis	208—313 X
2,459,403	1/1949	Ahrens	203—54
2,704,778	3/1955	Maisel	260—666
2,768,224	10/1956	Page et al.	260—681.5
2,851,505	9/1958	Henke et al.	260—681.5
3,230,157	1/1966	Hill et al.	203—53
3,242,227	3/1966	Kroeper et al.	260—681.5
3,301,915	1/1967	King et al.	260—681.5
3,317,627	5/1967	King et al.	260—681.5

OTHER REFERENCES

Ferris: "Handbook of Hydrocarbons" 1955: pp. 21–22.

Lynn et al.: "Purification of Isoprene by Fractional Distillation," CEP 57(5) 46–49(1961).

PAUL M. COUGHLAN, JR., *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*

U.S. Cl. X.R.

203—60; 208—313, 330