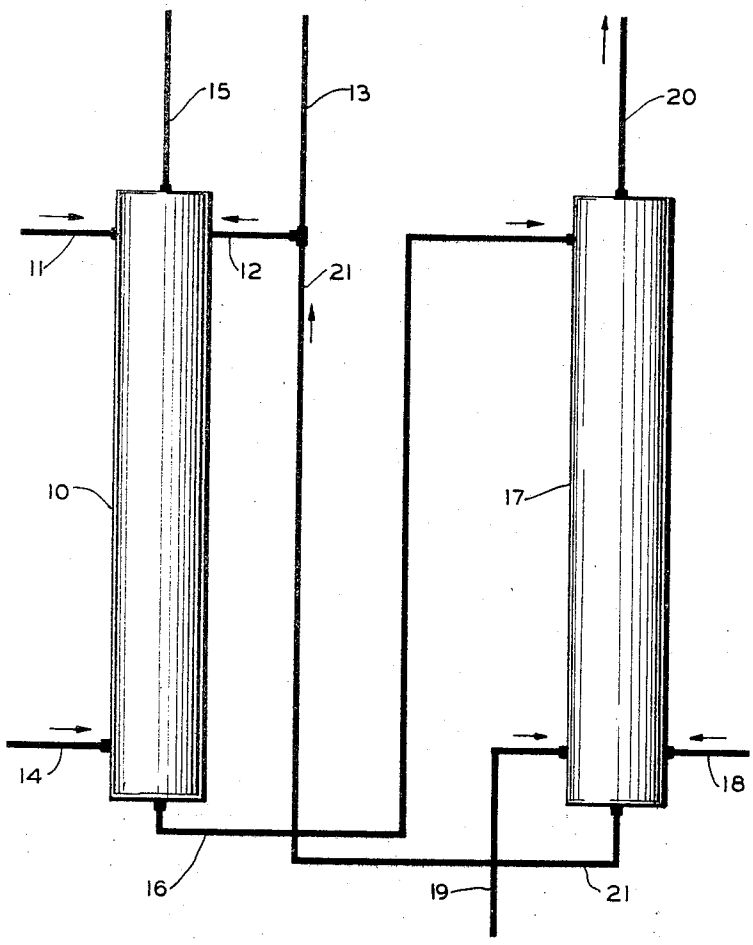
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SEPARATION OF AROMATIC HYDROCARBONS

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SEPARATION OF AROMATIC HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

Mixtures of vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons are separated by contacting the mixture with an aqueous solution of silver fluoroborate and/or silver fluorosilicate to produce an extract fraction and a raffinate fraction. The extract fraction is then contacted with an unsaturated aliphatic hydrocarbon to produce a hydrocarbon fraction substantially richer in the vinyl aromatic hydrocarbon than the initial aromatic hydrocarbon mixture.

The present invention relates to a process for the separation and purification of aromatic hydrocarbons. More particularly, the present invention relates to the process for the separation of vinyl aromatic hydrocarbons, i.e., styrene, from alkyl aromatic hydrocarbons, i.e., xylenes and ethylbenzene.

The term "vinyl aromatic hydrocarbons," as used herein, refers to aromatic hydrocarbons containing a monoethylenically unsaturated aliphatic substituent, e.g., styrene, a-methylstyrene, b-methylstyrene, vinyl toluene. "Alkyl aromatic hydrocarbons," as used herein, refers to those aromatic hydrocarbons having saturated aliphatic substituents, e.g., xylene, ethylbenzene and the like.

One of the most difficult separations problems existing in industry today is that of separating vinyl aromatic hydrocarbons from close boiling alkyl aromatic hydrocarbons. In most instances, separation of such hydrocarbons is difficult at best by distillation. However, to render the problem more difficult, the unsaturated vinyl aromatic hydrocarbons are usually easily polymerized and thus tend to polymerize and foul the equipment used for separation by distillation. Probably the most exemplary and commonly encountered difficulty separable vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons are styrene and o-xylene. These two compounds are very difficult to separate one from another and because of the entirely different uses of the two, either is an undesirable contaminant in the other and thus it is desired to have means for effectively separating the two.

In addition to distillation, it is known that such compounds as mercuric chloride, mercuric acetate, and the like, will complexe with styrene. Such complex formation offers a means of separating styrene from o-xylene. However, additional and improved separations of this type are desired. Further, it is often quite difficult to recover the vinyl aromatic hydrocarbons from the complex. Severe conditions usually necessary for recovering the complexed vinyl aromatic hydrocarbons from the complex often result in substantial polymerization and loss of the vinyl aromatic hydrocarbons.

It is now an object of the present invention to provide a new and improved process for the separation of aromatic hydrocarbons. A further object of the present invention is to provide a new and improved process for the separation of vinyl aromatic hydrocarbons from alkyl aromatic hydrocarbons. An additional object of the present invention is to provide a new and improved process for the separation of vinyl aromatic hydrocarbons from alkyl aromatic hydrocarbons wherein the vinyl aromatic hydrocarbons

can be substantially totally recovered. Yet another object of the present invention is to provide a process for the separation of vinyl aromatic hydrocarbons from alkyl aromatic hydrocarbons which as a benefit thereof provides a means whereby olefins and/or conjugated diolefins may be effectively removed from admixture with non-conjugated diolefins. Another object of the present invention is to provide a new and improved process for the separation of styrene from o-xylene. Additional objects will become apparent from the following description of the invention herein disclosed.

The present invention which fulfills these and other objects, is a process for the separation of vinyl aromatic hydrocarbons from aromatic hydrocarbon mixtures containing vinyl aromatic hydrocarbons in admixture with alkyl aromatic hydrocarbons, which comprises contacting said aromatic hydrocarbon mixture with an aqueous solution of a silver salt selected from the group consisting of silver fluoroborate, silver fluorosilicate and mixtures thereof, separating an extract fraction containing said aqueous solution of a silver salt and the aromatic hydrocarbons absorbed therein, and a raffinate fraction containing aromatic hydrocarbons not absorbed by said aqueous solution of a silver salt, and recovering from said extract fraction an aromatic hydrocarbon fraction substantially richer in vinyl aromatic hydrocarbons than the initial aromatic hydrocarbon mixture.

As a particularly useful mode of operating the process of the present invention, the aromatic hydrocarbon mixture containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons is contacted with the aqueous solution of the silver salt and the resulting mixture of aqueous silver salt solution and aromatic hydrocarbons then contacted with a saturated aliphatic hydrocarbon of 3 to 15 carbon atoms. Contacting of the mixture of aromatic hydrocarbons and aqueous silver salt solution with the saturated aliphatic hydrocarbons greatly facilitates the separation of the non-absorbed aromatic hydrocarbons from the aqueous silver salt solution and aromatic hydrocarbons absorbed therein. The saturated aliphatic hydrocarbons are not absorbed to any extent by the aqueous silver salt solution and act as a selective solvent for the aromatic hydrocarbons not absorbed and held by the aqueous silver salt solution. When the saturated aliphatic hydrocarbons are contacted with the mixture of aromatic hydrocarbons and aqueous silver salt solution in accordance with the process defined herein, extract and raffinate phases readily form, which phases may be easily separated.

The recovery of the vinyl aromatic hydrocarbons from the aqueous silver salt solution extract phase may be accomplished by any available means. The vinyl aromatic hydrocarbons may be distilled from the extract phase. However, it is generally desired to carry out such a distillation under reduced pressure to avoid high temperatures which would likely cause polymerization of the vinyl aromatic hydrocarbons. When distillation is used as the means of recovering the vinyl aromatic hydrocarbons from the aqueous silver salt solution, reduced pressures within the range of 75 to 300 mm. Hg are preferred.

A particularly useful method of recovering the vinyl aromatic hydrocarbons from the aqueous silver salt solution extract phase comprises contacting such extract phase with an unsaturated aliphatic hydrocarbon selected from the group consisting of olefins, conjugated diolefins and mixtures thereof. It has been found that the olefins and/or conjugated diolefin when in excess will displace the vinyl aromatic hydrocarbons from the aqueous silver salt solution and are in turn preferentially absorbed and held therein. The olefins and/or conjugated diolefins may be removed from the aqueous salt solution by distillation under usually significantly less stringent conditions of temperature and pressure than those re-

quired for the removal of vinyl aromatic hydrocarbons. However, quite surprisingly, the olefins and/or conjugated diolefins, as the case may be, may in turn be displaced from the aqueous silver salt solution by contact with an excess of vinyl aromatic hydrocarbons. In view of the ability of the olefins and/or conjugated diolefins to displace the vinyl aromatic hydrocarbons and in turn the vinyl aromatic hydrocarbons to displace the olefins and/or conjugated diolefins from the aqueous silver salt solution, the present invention in a particularly useful embodiment provides a dual process whereby vinyl aromatic hydrocarbons may be separated from alkyl aromatic hydrocarbons and olefins and/or conjugated diolefins such as isoprene, may be separated from non-conjugated diolefins, saturated hydrocarbons, etc., using the same solvent solution and, if desired, the same or substantially the same equipment. Such a dual process comprises (1) contacting a mixture of aromatic hydrocarbons containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons with an aqueous solution of a silver salt selected from the group consisting of silver fluoroborate, silver fluorosilicate and mixtures thereof, (2) separating a first raffinate fraction containing the non-absorbed aromatic hydrocarbons and a first extract fraction containing the aqueous silver salt solution and the aromatic hydrocarbons absorbed therein, (3) contacting said first extract fraction with a mixture of hydrocarbons containing olefins and/or conjugated diolefins and non-conjugated diolefins and/or saturated hydrocarbons and/or other hydrocarbons, the quantity of said mixture of hydrocarbons being such that the olefins and/or conjugated diolefins are in molar excess to said vinyl aromatic hydrocarbons contained in said first extract fraction, thereby displacing the aromatic hydrocarbons absorbed in said first extract fraction and forming a second extract fraction comprising said aqueous silver salt solution and the unsaturated aliphatic hydrocarbons absorbed therein and a second raffinate fraction comprising the hydrocarbons not absorbed by said aqueous silver salt solution and the aromatic hydrocarbons displaced from said first extract fraction, (4) separating said second raffinate fraction and said second extract fraction and (5) recycling at least a part of said second extract fraction to step (1) above as a substitute for at least a part of said aqueous silver salt solution and thereafter continuously repeating the above steps.

To further describe the above disclosed dual process of the present invention which provides for the separation of vinyl aromatic hydrocarbons from alkyl aromatic hydrocarbons and also for the separation of olefins and/or conjugated diolefins from non-conjugated diolefins and other hydrocarbons, reference is made to the accompanying drawing which is a diagrammatic presentation of a particularly useful and practical method of carrying out the dual process of the present invention. With reference to the drawing, an aromatic hydrocarbon mixture containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons is introduced into a liquid-liquid extraction column **10** by means of line **11**. Concurrently with the introduction of the aromatic mixture by line **11**, a solvent solution comprised of an aqueous solution of a silver salt which is either silver fluoroborate, silver fluorosilicate, or combinations thereof, is introduced into column **10** by means of line **12**. The aqueous silver salt solution introduced by line **12** will generally contain in addition to the aqueous silver salt solution, olefins and/or conjugated diolefins which have been absorbed therein as described below. If desired, however, some fresh aqueous silver salt solution may be introduced into line **12** by means of line **13**. Lines **11** and **12** generally will intersect column **10** at a point near but below the top of column **10** and at substantially the same distance from the top of column **10**. It is relatively important in this embodiment, that lines **11** and **12** be so arranged that the compositions introduced thereby will be intimately co-mingled one with another, almost immediately upon introduction into column **10**. Concurrently with the introduction of the aromatic hydrocarbon mixture through line **11** and the solvent solution through line **12**, a saturated aliphatic hydrocarbon of 3 to 15 carbon atoms is introduced into column **10** by means of line **14**. This aliphatic hydrocarbon flows upwardly through column **10** and countercurrently contacts the descending mixture of solvent solution and aromatic hydrocarbon feed. A raffinate phase is continuously taken overhead from column **10** by means of a line **15** through which the raffinate phase is passed to a distillation or other recovery means (not shown) whereby the components of the raffinate are separated. The components of the raffinate in the continuous operation of the process, comprise the aliphatic hydrocrabon, the aromatic hydrocarbons not absorbed by the solvent solution and the unsaturated aliphatic hydrocarbons which were contained in the solvent solution at the time of its introduction into column **10** through line **12**.

An extract phase is continuously removed from column **10** by means of line **16**. This extract phase comprises the aqueous silver salt solution and aromatic hydrocarbon components of the aromatic hydrocarbon mixture which dissolves therein. The extract phase is then introduced into a second liquid-liquid extraction column **17**. In column **17**, the extract phase from column **10** passes downwardly countercurrently contacting an upflowing unsaturated aliphatic hydrocarbon feed mixture comprised of olefins and/or conjugated diolefins and non-conjugated diolefins and/or other hydrocarbons which are introduced into column **17** by means of line **18**, and an up-flowing saturated aliphatic hydrocarbon of 3 to 15 carbon atoms which is introduced into column **17** by means of line **19**. The second raffinate phase is continuously taken overhead from column **17** by means of line **20**. This second raffinate phase is carried by line **20** to distillation or other recovery means (not shown) whereby the components of the second raffinate phase are separated. These components of the second raffinate phase comprise the saturated aliphatic hydrocarbon, the non-absorbed portion of the hydrocarbon feed mixture, and the aromatic hydrocarbons which were contained in the first extract phase at the time of its introduction by means of line **16** into column **17**.

By means of line **21**, an extract phase, referred to as the second extract phase, is removed from column **17** and returned through line **21** to line **12** for re-use in column **10**. This second extract phase is comprised of an aqueous silver salt solvent solution and unsaturated aliphatic hydrocarbons absorbed therein.

Those skilled in the art will readily appreciate that many modications of the above-described dual process of the present invention and the arrangement of equipment therefor, may be made. However, so long as such modifications depend upon the principles and concepts above discussed, such modifications may be practiced without departing from the spirit and scope of the present invention.

To further describe and to specically illustrate the present invention, the following examples are presented. These examples are not to be construed as in any manner limiting the present invention.

EXAMPLE I

One hundred and ninety grams of a mixture consisting of 89.0 grams o-xylene, 99.7 grams styrene and 1.3 grams of other hydrocarbon impurities were agitated with 3500 ml. of a 47% aqueous silver fluoroborate solution (specific gravity 1.5999) at a temperature of −25° C. The resulting solution was then thoroughly agitated with 210 ml. (138.4 grams) of n-hexane. The agitation was stopped and a raffinate and extract phase allowed to form. The extract and raffinate phases were then separated. The raffinate phase contained the n-hexane and the aromatic hydrocarbons which were not absorbed by the aqueous silver fluoroborate solution, while the extract phase contained the aqueous silver fluoroborate solution and the

aromatic hydrocarbons absorbed therein. The aromatic hydrocarbons in the extract and raffinate phases were recovered and analyzed. The following table represents the weight percent composition of the aromatic hydrocarbon feed, the aromatic hydrocarbon raffinate, and the aromatic hydrocarbon extract.

TABLE

Wt. Percent	Feed	Raffinate (Hexane-Free Basis)	Extract
Styrene	52.44	25.5	87.3
o-Xylene	46.86	74.5	12.7
Impurities	0.70	(1)	(1)

[1] Not Calculated.

EXAMPLE II

One hundred and ninety grams of a mixture of 90.2 grams of o-xylene and 99.8 grams of styrene were thoroughly agitated with 3500 ml. of the 47% aqueous silver fluoroborate solution of Example I at a temperature of −25° C. The resulting solution was then agitated with 200 ml. of n-hexane. Agitation was stopped and an extract and raffinate phase allowed to form. The extract and raffinate phases were then separated and the aromatic hydrocarbons contained in each recovered. To recover the aromatic hydrocarbons absorbed by the silver fluoroborate solution, the extract phase was subjected to distillation at a temperature of 51 to 63° C. and a pressure of 95 to 102 mm. absolute. The overhead from this distillation which was the aromatic hydrocarbons contained in the extract phase and the aromatic hydrocarbons recovered from the raffinate phase were subjected to analysis. The weight percent composition of the original aromatic hydrocarbon feed and the aromatic hydrocarbon raffinate and aromatic hydrocarbon extract are presented in the following table.

TABLE

Wt. Percent	Feed	Raffinate	Extract (Benzene Free)
Styrene	52.55	8.0	90.7
o-Xylene	47.45	92.0	9.3

The total recovery of styrene was approximately 67.4% of that available.

EXAMPLE III

Five hundred and fifty grams of a mixture of 259.6 grams o-xylene and 290.4 grams styrene were thoroughly agitated with 10,500 ml. (16,795 grams) of the 47% aqueous silver fluoroborate solution of Example I at a temperature of about 24° C. The resulting solution was then thoroughly agitated with 600 ml. of n-hexane. Agitation of this mixture was stopped and an extract and raffinate phase allowed to form. The extract and raffinate phases were then separated. The extract phase was diluted with 500 ml. of water and then subjected to distillation at a temperature of approximately 54° C. and a pressure of 95 mm. absolute. About 6000 ml. of distillate was obtained as an overhead from this distillation and was extracted with 500 ml. of benzene to insure complete recovery of aromatic hydrocarbons from the distillate. The aromatic hydrocarbons from the distillate and those from the raffinate phase were then subjected to analysis. The following table presents the weight percent composition of the original feed mixture and the aromatic hydrocarbon raffinate and aromatic hydrocarbon extract.

TABLE

Wt. Percent	Feed	Raffinate	Extract
Styrene	52.8	22.5	93.1
o-Xylene	47.2	77.5	6.9

The above represents a raffinate yield of styrene of 71.1 grams (24.5% of that available) and the extract distillate yield was 198.1 grams (68.2% of that available) equivalent to a 92.7% recovery of the available styrene in the original feed.

EXAMPLE IV

A mixture of 90.2 grams o-xylene and 99.8 grams styrene was thoroughly agitated with 3500 ml. (5598 grams) of the 47% aqueous silver fluoroborate solution of Example I at a temperature of approximately 24° C. The resulting mixture was then thoroughly agitated with 200 ml. of hexane. Agitation was stopped and an extract and raffinate phase allowed to form. The extract and raffinate phases were then separated. Following the separation, the extract phase was then contacted with 1360 grams of isoprene which displaced the aromatic hydrocarbons contained in the extract phase and formed a new extract phase containing the aqueous silver fluoroborate solution and isoprene. The displaced aromatic hydrocarbons were then separated from the new extract. Next, the new extract was brought into contact with 1890 grams of styrene which displaced the isoprene from the new extract and resulted in formation of still another extract containing the aqueous silver fluoroborate solution and styrene. The aromatic hydrocarbons from the raffinate phase, the aromatic hydrocarbons displaced from the first extract phase and the isoprene displaced from the second extract phase were subjected to analysis. The weight percent composition of the original aromatic hydrocarbon feed and these various fractions is presented in the following table.

TABLE

	Wt. percent		
	Styrene	o-Xylene	Isoprene
Aromatic Hydrocarbon Feed	52.55	47.45	----------
Aromatic Hydrocarbon Raffinate	23.01	76.99	----------
Aromatic Fraction Displaced by Isoprene	90.51	9.45	----------
Isoprene Fraction Displaced by Styrene			100.00

The above procedure resulted in the recovery of 100% of the available styrene from the original aromatic hydrocarbon feed in the respective purities set forth in the above table.

The aqueous silver salt solutions used in the process of the present invention include the silver salts, silver fluoroborate, and silver fluorosilicate. These silver salts may be used alone or in combination. The preferred silver salt is the silver fluoroborate. Usually, the aqueous silver salt solution will contain the silver salt in a concentration of 30 to 60% by weight of the solution. Preferred, however, are concentrations of 45 to 55% by weight.

In carrying out the process of the present invention, most often about 10 to 70 parts by weight of aqueous silver salt solution by part by weight of vinyl aromatic hydrocarbons in the aromatic hydrocarbon mixture to be separated are employed. Preferably, however, the amount of aqueous silver salt solution used is within the range of 20 to 50 parts by weight by part by weight of vinyl aromatic hydrocarbons. Usually, the greater the concentration of the silver salt in the aqueous silver salt solution, the less the amount of the salt solution required. However, regardless of the concentration of the silver salt within the silver salt solution, so long as it is within the above-defined concentrations, the amount of aqueous silver salt solution used will be within the above ranges.

When olefins and/or conjugated diolefins are employed to displace the vinyl aromatic hydrocarbons from the aqueous silver salt solution or the process of the present invention is operated as a dual process, as above described, it is generally desirable that the amount of olefins and/or conjugated diolefins contacted with the vinyl aromatic hydrocarbon containing aqueous silver salt solution be in weight ratio to the aqueous silver salt solution within the range of from 10:1 to 70:1, preferably within the

range of from 20:1 to 50:1. Within these ranges, however, it is necessary that the amount of olefin and/or conjugated diolefin employed always be greater on a molar basis, than the amount of vinyl aromatic hydrocarbons contained in the aqueous silver salt solution.

The aromatic hydrocarbon mixture containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons which are to be separated in accordance with the present invention is generally contacted with the aqueous silver salt solution at a temperature within the range of —30 to 70° C., preferably —20 to 50° C. Pressure does not appear to be critical in the selective absorption of the vinyl aromatic hydrocarbons by the aqueous silver salt solution. Therefore, the pressure at which the process of the present invention is operated is generally based upon practicality.

The period of contact of the aromatic hydrocarbon mixture to be separated with the aqueous silver salt solution may be very short since absorption of the vinyl aromatic hydrocarbons by the aqueous silver salt solution is generally almost immediate. As a practical matter, the period of contact will vary somewhat depending upon the efficiency of the means employed for contacting the aromatic hydrocarbons with the aqueous silver salt solution. The determination of the optimum periods of contact are well within the ability of those skilled in the art and thus require no discussion herein.

When the process of the present invention is operated as a dual process or conjugated diolefins are used to displace and recover the vinyl aromatic hydrocarbons from the aqueous silver salt solution, the same conditions as to temperatures, pressures and contact time may be used as are used for contact of the aromatic hydrocarbons with the aqueous silver salt solution.

It has been found particularly useful in carrying out the process of the present invention to use saturated aliphatic hydrocarbons of 3 to 15 carbon atoms per molecule to extract the non-absorbed aromatic hydrocarbons from the aqueous silver salt solution. As noted above, the use of the saturated aliphatic hydrocarbons of 3 to 15 carbon atoms greatly facilitates the formation of an extract and raffinate phase and thus considerably simplifies the present separations process. Non-limiting examples of such hydrocarbons are propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, isobutane, isopentanes, isoheptanes, isodecanes, isododecanes, isotridecane, cyclopentane, cyclohexane, methylcyclohexane, cycloheptane, and the like. Most often, the saturated aliphatic hydrocarbons are paraffinic hydrocarbons and may be straight-chain or branched-chain. The most useful saturated aliphatic hydrocarbons are the paraffinic hydrocarbons of 4 to 7 carbon atoms per molecule.

The amount of saturated aliphatic hydrocarbons of 3 to 15 carbon atoms used in the process of the present invention may vary considerably. The actual amount of such aliphatic hydrocarbon used will depend to a large extent on the amount of alkyl aromatic hydrocarbons in the aromatic hydrocarbon mixture and the degree of separation desired, etc. Usually, however, about 0.5 to 10 volumes of saturated aliphatic hydrocarbon will be used per volume of alkyl aromatic hydrocarbon in the aromatic hydrocarbon feed mixture to be separated. Preferably, however, about 1 to 3 volumes of the saturated aliphatic hydrocarbon will be used per volume of alkyl aromatic hydrocarbons in the feed mixture.

In employing the saturated aliphatic hydrocarbons of 3 to 15 carbon atoms to remove the unabsorbed alkyl aromatic hydrocarbons from the silver salt solution, these aliphatic hydrocarbons may be contacted with the mixture of aqueous silver salt solution and aromatic hydrocarbons absorbed therein after the initial contact and agitation of the aromatic hydrocarbon feed with the silver salt solution has ceased or the saturated aliphatic hydrocarbon may be brought into contact with the aqueous silver salt solution concurrently with the aromatic hydrocarbon feed which is to be separated. Further, the saturated aliphatic hydrocarbon may be introduced concurrently with the aromatic hydrocarbon mixture to be separated into countercurrent contact with the aqueous silver salt solution. Instead, however, the saturated aliphatic hydrocarbons may be contacted countercurrently with the aromatic hydrocarbon mixture to be separated and the aqueous silver salt solution.

The aromatic hydrocarbon mixtures which may be separated in accordance with the present invention are those containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons. While the present invention is operable in separating a wide range of such hydrocarbons, it is most practical for the separation of aromatic hydrocarbon mixtures containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons within the C_8 to C_{12} range. The present invention is particularly useful and practical for the separation of styrene from close boiling o-xylene and for the separation of a-methylstyrene and/or vinyl toluene from close boiling alkyl aromatic hydrocarbons.

The olefins and/or conjugated diolefins useful in displacing absorbed vinyl aromatic hydrocarbons from the aqueous solution of a silver salt are preferably those containing 2 to 8 carbon atoms per molecule though those having higher numbers of carbon atoms may be used. These olefins and/or conjugated diolefins may be in relatively pure state or may be in admixture with other hydrocarbons such as paraffins, naphthenes or even alkyl aromatic hydrocarbons. While the olefins and/or conjugater diolefins may be cyclic, straight-chain or branched-chain in structure, it is preferable that they be straight or branched-chain. Usually, the conjugated diolefins are preferred over the olefins. When the present invention is operated with a C_8 to C_{12} aromatic hydrocarbon feed mixture containing vinyl aromatic hydrocarbons, isoprene or other conjugated diolefins of 5 to 7 carbon atoms are particularly useful.

What is claimed is:

1. A process for the separation of vinyl aromatic hydrocarbons from aromatic hydrocarbon mixtures containing vinyl aromatic hydrocarbons in admixture with alkyl aromatic hydrocarbons, which comprises contacting said aromatic hydrocarbon mixture with an aqueous solution of a silver salt selected from the group consisting of silver fluoroborate, silver fluorosilicate and mixtures thereof, separating an extract fraction containing said aqueous solution of a silver salt and the aromatic hydrocarbons dissolved therein, and a raffinate fraction containing aromatic hydrocarbons not absorbed by said aqueous solution of a silver salt, and recovering from said extract fraction an aromatic hydrocarbon fraction substantially richer in vinyl aromatic hydrocarbons than the initial aromatic hydrocarbon mixture, by contacting said extract fraction with an amount of an unsaturated aliphatic hydrocarbon selected from the group consisting of olefins and conjugated diolefins such that said unsaturated aliphatic hydrocarbon is in molar excess to the vinyl aromatic hydrocarbons contained within said extract fraction.

2. The process of claim **1** wherein the silver salt in said aqueous solution of a silver salt comprises approximately 30 to 60 percent by weight of said solution.

3. The process of claim **1** wherein the amount of aqueous silver salt solution contacted with said aromatic hydrocarbon mixture is such as to cause a ratio by weight of aqueous silver salt solution to vinyl aromatic hydrocarbons in said aromatic hydrocarbon mixture within the range of about 10:1 to 70:1.

4. The proces of claim **1** wherein the aromatic hydrocarbon mixture is one containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons within the C_8 to C_{12} range.

5. The process of claim **1** wherein the aromatic hydro-

carbon mixture is contacted with the aqueous silver salt solution at a temperature within the range of —30 to 70° C.

6. The process of claim 1 wherein the mixture resulting from the contacting of the aromatic hydrocarbon mixture with the aqueous solution of the silver salt is contacted with a saturated aliphatic hydrocarbon of 3 to 15 carbon atoms.

7. The process of claim 6 wherein about 0.5 to 10 volumes of said saturated aliphatic hydrocarbon is used per volume of alkyl aromatic hydrocarbon in the aromatic hydrocarbon mixture which is contacted with the aqueous silver salt solution.

8. The process of claim 6 wherein the saturated aliphatic hydrocarbon is a non-cyclic paraffinic hydrocarbon of 4 to 7 carbon atoms per molecule.

9. A process for the separation of vinyl aromatic hydrocarbons from alkyl aromatic hydrocarbons and unsaturated aliphatic hydrocarbons selected from the group consisting of olefins and conjugated diolefins from mixtures of such unsaturated hydrocarbons with other hydrocarbons which comprises (1) contacting a mixture of aromatic hydrocarbons containing vinyl aromatic hydrocarbons and alkyl aromatic hydrocarbons with an aqueous solution of a silver salt selected from the group consisting of silver fluoroborate, silver fluorosilicate and mixtures thereof, (2) separating a first raffinate fraction containing the non-absorbed aromatic hydrocarbons and a first extract fraction containing the aqueous silver salt solution and the aromatic hydrocarbons absorbed therein, (3) contacting said first extract fraction with a mixture of hydrocarbons containing unsaturated aliphatic hydrocarbons selected from the group consisting of olefins and conjugated diolefins, the quantity of said mixture of hydrocarbons being such that said unsaturated aliphatic hydrocarbons are in molar excess to said vinyl aromatic hydrocarbons contained in said first extract fraction, thereby displacing the aromatic hydrocarbons absorbed in said first extract fraction and forming a second extract fraction comprising said aqueous silver salt solution and said unsaturated aliphatic hydrocarbons absorbed therein and a second raffinate fraction comprising the hydrocarbons not absorbed by said aqueous silver salt solution and the aromatic hydrocarbons displaced from said first extract fraction, (4) separating said second raffinate fraction and said second extract fraction and, (5) recycling at least a part of said second extract fraction to step (1) above as a substitute for at least a part of said aqueous silver salt solution and thereafter continuously repeating the above steps.

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