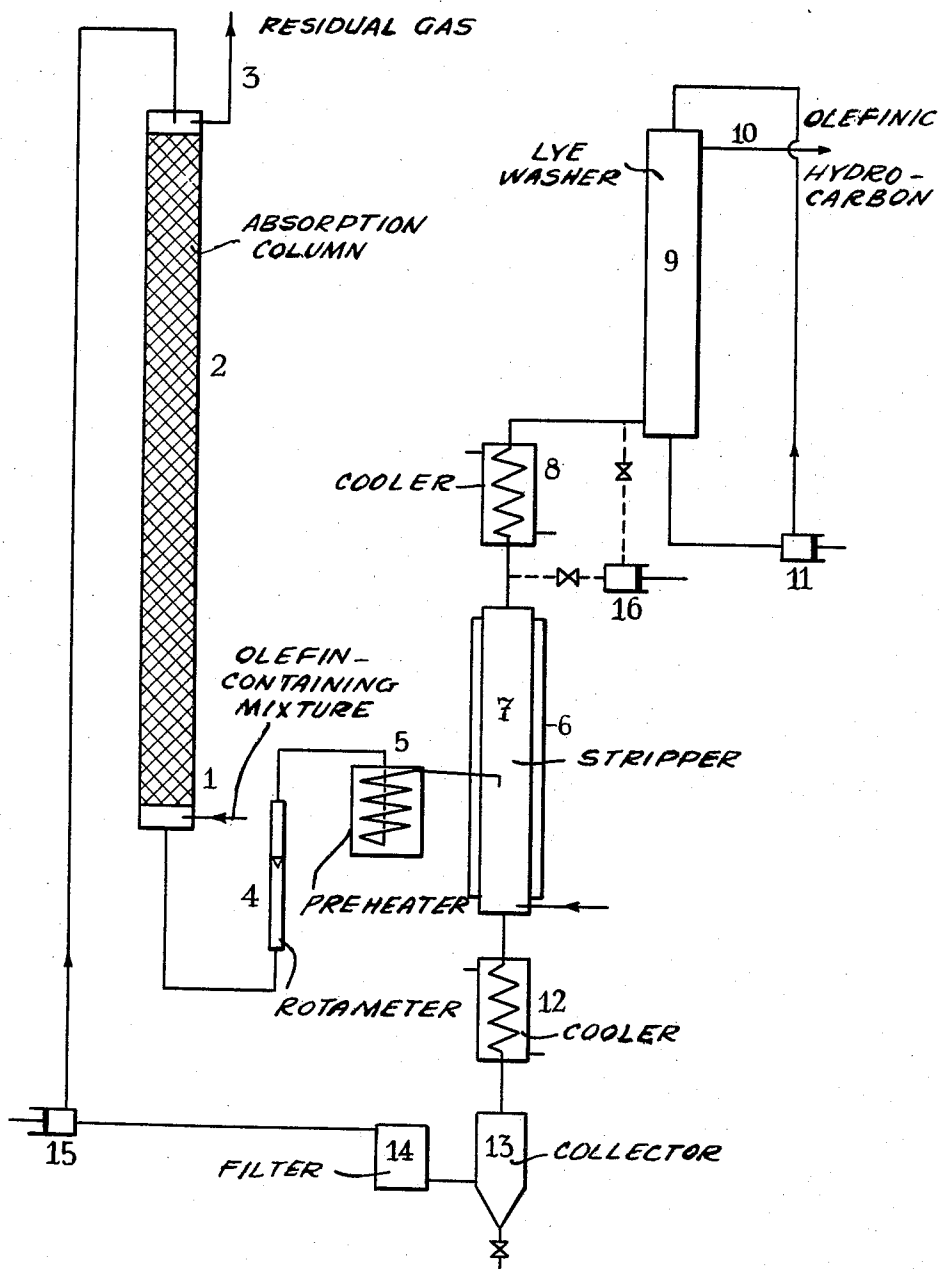


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PROCESS FOR SEPARATING OLEFINIC HYDROCARBONS USING SILVER
FLUOBORATE AND SILVER FLUOSILICATE SOLUTIONS
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PROCESS FOR SEPARATING OLEFINIC HYDROCARBONS USING SILVER FLUOBORATE AND SILVER FLUOSILICATE SOLUTIONS

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The present invention relates to a process for separating olefinic hydrocarbons.

It is already known that olefins and substituted olefins form complex compounds with heavy metal salts by an addition reaction with the metal ions (for example Pt, Ag, Cu(I) or Hg(II) ions). Of these salts the Ag, Cu(I) and Hg(II) salts are of particular technical interest for the separation of olefins or substituted olefins from mixtures with other hydrocarbons or their substitution products.

Contrary to cuprous salts, mercury salts and silver salts are insensitive to atmospheric oxygen; the industrial use of mercury appears, however, dangerous owing to the high toxicity of the latter. The complex mercury olefin compounds further possess such a high stability that the olefin molecules bound therein must again be freed by means of acids or alkali. In contradistinction thereto, the complex silver or cuprous olefin compounds can again be decomposed to metal salts and olefins by simple boiling of their solutions. In view of these facts it appears advantageous, particularly for the preparation of olefins in a pure state, to use complex silver olefin compounds, especially when in view of the improved space/time yield the advantage of a high solubility of the olefin in the silver solution outweighs the disadvantage of the higher cost of the silver.

Numerous processes for separating olefins by means of aqueous solutions of the nitrates, chlorides, acetates or sulfates of the above mentioned three metals (Ag, Cu(I), Hg(II)) are described in literature. In many cases mono- or polyhydric alcohols, amines, hydroxylamines, cyclic amines, cyclic ethers, nitriles etc. are added. The addition of such dissolving intermediaries generally also leads to an improved solubility of the non-olefins and thus impairs the separating effect. The solubility of the olefins is substantially determined by the concentration of the metal ions, an increase in the metal content of the solutions being associated with a strong increase in solubility. The same effect is obtained by pressure increase; it is, however, more convenient to work under atmospheric pressure or slight superatmospheric pressure.

Now we have found that highly concentrated aqueous solutions of silver fluoborate, silver fluosilicate or combinations thereof, have a dissolving power for olefinic hydrocarbons that is superior to that of aqueous silver nitrate solutions. For example, such solutions may contain up to above one kilogram of silver per liter of purely aqueous solution (that is, for example, four times the concentration of a silver nitrate solution saturated at room temperature), and as anion fluoborate or fluosilicate ions or combinations thereof. The dissolving power for olefins of these solutions is about ten times higher than that of the best cuprous salt solutions of which, for example, Hagen-Häuber's cuprous nitrate solution in aqueous ethanolamine dissolves at room temperature about 30-35 liters of ethylene per liter of solution. 1 liter of an indus-

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trial silver fluoborate solution containing, per liter, 800 grams of silver and furthermore an amount of fluosilicate ions, dissolves at room temperature at least about 200 liters of ethylene or about 250 liters of propylene.

5 The olefins can subsequently be quantitatively removed from the solution by boiling.

The present invention provides a process for separating olefinic hydrocarbons from hydrocarbon mixtures containing said olefins, which comprises contacting said hydrocarbon mixtures with an aqueous solution of a compound containing silver and fluorine, i.e. silver fluoborates and/or silver fluosilicates or mixtures thereof.

10 The present process is especially suitable for the separation of fluid olefins from fluid hydrocarbon mixtures, the term "fluid" being understood in both cases to mean gaseous or liquid.

The process of the invention can be carried out in a simple circulation apparatus for the continuous separation of olefins from hydrocarbon gases.

20 An apparatus suitable for use in carrying out the process of this invention is illustrated diagrammatically in the accompanying drawing:

Referring to the drawing, the gas to be used enters the apparatus at 1. In the absorption column 2 it meets the concentrated solution of AgBF_4 and/or silver fluosilicate flowing in countercurrent and is brought into intensive contact with said solution and all the olefin is washed out except for a very small rest so that the gases need not be recycled. The residual gas leaves the column at 3. The solution charged with the olefins proceeds through a flow-measuring device 4 (for example a rotameter) and a preheating coil 5 to stripper 7 provided with a heating jacket 6, in which stripper nearly all the olefin is set free by heating or distillation of the solution.

35 The olefin then travels via cooler 8 to lye washer 9 where any acid vapors possibly entrained are washed out so that a current of neutral olefin gas having a degree of purity of considerably above 99% leaves the washer at 10. The lye is recycled by means of pump 11.

40 The silver fluoborate solution which has been freed from the olefin in the stripper with addition of a small amount of vapor (for promoting the stripping and replacing about the amount of the water that has been evaporated) proceeds to cooler 12 and is then collected in a collector

45 13, freed from impurities in suspension by means of a filter 14 and returned into the absorption column by pump 15. Reservoirs for the silver solution and for the lye as well as further fittings are not shown in the drawing. The above described apparatus enables space/time yields of about 100 liters of olefin gas per liter of absorption space and hour to be obtained. With appropriate constructional modifications and after arrangement of an additional pump 16, the apparatus may of course also be used for the liquid extraction of olefin-containing hydrocarbon mixtures (for example benzines obtained by synthesis or from cracking) and subsequent distillation of the olefin-containing silver solution.

55 The gas to be used in the process of the invention may also contain carbon dioxide, carbon monoxide, oxygen, hydrogen, nitrogen or noble gas. It has further been found that a content of acetylene of at most 1% does not interfere with the process of the invention; it is bound as silver acetylide which remains suspended in the solution in the form of small dark particles together with small amounts of silver and may be continuously removed from said solution by means of the filter 14. Acetylene concentrations of above 1% after some time give rise to the separation of relatively large amounts of silver acetylide which may cause disturbances. It is suitable previously to hydrogenate selectively the acetylene to yield ethylene. Higher initial concentrations of carbon monoxide (above 10% necessitate a high absorption column

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of high separating efficiency and further require a reduced apparatus charge since CO also shows a certain liability to form complex compounds with silver ions. Contrary to cuprous salt solutions, silver solutions of the aforesaid kind show a considerably smaller stability of linkage for CO than for olefins so that in this case, too, separation can be effected when proceeding cautiously. Even in the case of an initial concentration of above 30% of CO, the content of carbon monoxide in the final product can be decreased to about 4%, for example, with a maximum charge even after one throughput.

The other aforesaid gases, added in any desired initial concentration, are in each case separated quantitatively; their concentration in the olefinic product is in most cases below 0.1%.

The following examples serve to illustrate the invention but they are not intended to limit it thereto.

Example 1

A silver fluoborate solution containing, per liter, about 800 grams of silver was recycled at a velocity of about 1.5 liters per hour, while the apparatus was charged with industrial ethylene of the following analysis:

94.1% C_2H_4
0.5% CO_2
1.0% H_2
3.0% C_2H_6
Rest C_2H_2 , O_2 , N_2

A current of very pure ethylene was obtained having a C_2H_4 content of at least 99.9% and having a velocity of about 61–62 liters per hour. There further formed about 2 liters per hour of waste gas of the following composition:

4.1% C_2H_4
3.9% O_2
0.8% CO
17.5% H_2
53.7% C_2H_6
20.0% N_2

(there was no CO_2 present since this had been removed by previous washing with alkali).

The space/time yield amounted to about 100 grams of ethylene per liter of absorption space and hour. 99.8% of the ethylene used was obtained with the aforesaid purity of 99.9%.

Example 2

With the use of an industrial mixture of crude ethane and crude ethylene of the following composition:

46.1% C_2H_4
48.8% C_2H_6
0.5% CO_2
Rest H_2 , N_2 , O_2 , traces of C_2H_2 and CO

At a velocity of about 50 liters per hour and while otherwise proceeding as described in Example 1, a current of pure ethylene of about 22 liters per hour and a current of waste gas of about 28 liters per hour were obtained. Ethylene content of the product:

Pure ethylene: 99.9% C_2H_4
Waste gas: Between 4 and 7% C_2H_4

Space/time yield: about 45 grams of C_2H_4 per liter of absorption space and hour; about 90% of the ethylene contained in the gas charged was obtained in a very pure state.

Example 3

The apparatus was provided with a column 4 meters high and filled with Raschig rings. With the use of a silver fluoborate solution of 600 grams of silver per liter at a circulation velocity of 4 liters per hour, there were obtained per hour, 180 liters of pure ethylene (99.4% C_2H_4 , 0.6% CO) from a gas containing 30% of ethylene, 10% of methane, 50% of hydrogen and 10% of CO . The waste gas still contained 1% of ethylene and 14% of

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CO . By returning part of the pure ethylene into the lower part of the column, the CO content of the ethylene could be reduced to less than 0.3%.

Example 4

In the apparatus provided with a column 4 meters high 600 liters per hour of a mixture of propane and propene in a ratio of 2:1 traveled towards a quantity of 2.5 liters of silver fluoborate solution containing, per liter, about 800 grams of silver. By stripping the silver solution at 120° C. there were obtained, per hour, about 200 liters of propylene having a purity of 99.9%. There were further obtained 400 liters of waste gas containing 1% of propylene and 99% of propane.

Example 5

200 cc. of a silver fluoborate solution containing, per liter, 600 grams of silver were shaken at 20° C. with 150 grams of a mixture of liquid propane and propylene in a ratio of 63:37%. In the silver solution 40 grams of propylene of 99% strength dissolved which could be obtained by expansion and boiling at 100° C. In the supernatant liquefied gas phase remained 110 grams of propane/propylene having a propylene content of 15%.

Example 6

Solubility of olefins in various metal salt solutions: A silver fluoborate solution containing, per liter of solution, 1200 grams of silver absorbs at 1 atmosphere absolute and 20° C. 350 liters of ethylene or 400 liters of propylene, whereas a Hagen-Häuber's cuprous solution absorbs at 20° C. and 1 atmosphere absolute only 25 liters of ethylene or 5 liters of propylene.

A silver fluoborate solution containing, per liter, 600 grams of silver, absorbs at 20° C. and 1 atmosphere absolute: 110 liters of ethylene, 140 liters of propylene, 100 liters of butylene, 155 liters of butadiene or less than 1 liter of carbon monoxide. A silver fluosilicate solution containing, per liter, 600 grams of silver absorbs 50 liters of ethylene.

We claim:

1. A process for separating a fluid olefinic hydrocarbon from a fluid hydrocarbon mixture containing said olefin which comprises bringing said hydrocarbon mixture into contact with an aqueous solution of a member selected from the group consisting of silver fluoborate, silver fluosilicate and a mixture thereof.

2. A process as defined in claim 1 wherein the initial hydrocarbon mixture contains at most about 1% acetylene.

3. A process as defined in claim 1 wherein the initial hydrocarbon mixture contains in addition a permanent gas other than hydrocarbon.

4. A process as defined in claim 3 wherein the permanent gas is carbon dioxide.

5. A process as defined in claim 1 wherein the initial hydrocarbon mixture is brought into contact with a concentrated aqueous solution of a member selected from the group consisting of silver fluoborate, silver fluosilicate and a mixture thereof.

6. A process as defined in claim 1 wherein the aqueous solution brought into contact with the hydrocarbon mixture is subsequently heated for liberation of the olefin absorbed therein.

7. A process as defined in claim 1 wherein water is added to the aqueous solution after the solution is heated for liberation of the olefin absorbed therein, the amount of water added being about equal to the amount of water evaporated in the heating step, and the solution is recycled for further use in the separation process.

8. A process for separating a fluid olefinic hydrocarbon from a fluid hydrocarbon mixture containing said olefin which comprises bringing said hydrocarbon mixture into contact with an aqueous solution essentially containing silver fluoborate and thereafter heating said solution for liberating the olefin absorbed therein.

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9. A process for separating ethylene from a gaseous hydrocarbon mixture containing ethylene which comprises bringing said hydrocarbon mixture into contact with an aqueous solution of a member selected from the group consisting of silver fluoborate, silver fluosilicate and a mixture thereof.

10. A process for separating propylene from a gaseous hydrocarbon mixture containing propylene which comprises bringing said hydrocarbon mixture into contact with

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an aqueous solution of a member selected from the group consisting of silver fluoborate, silver fluosilicate and a mixture thereof.

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