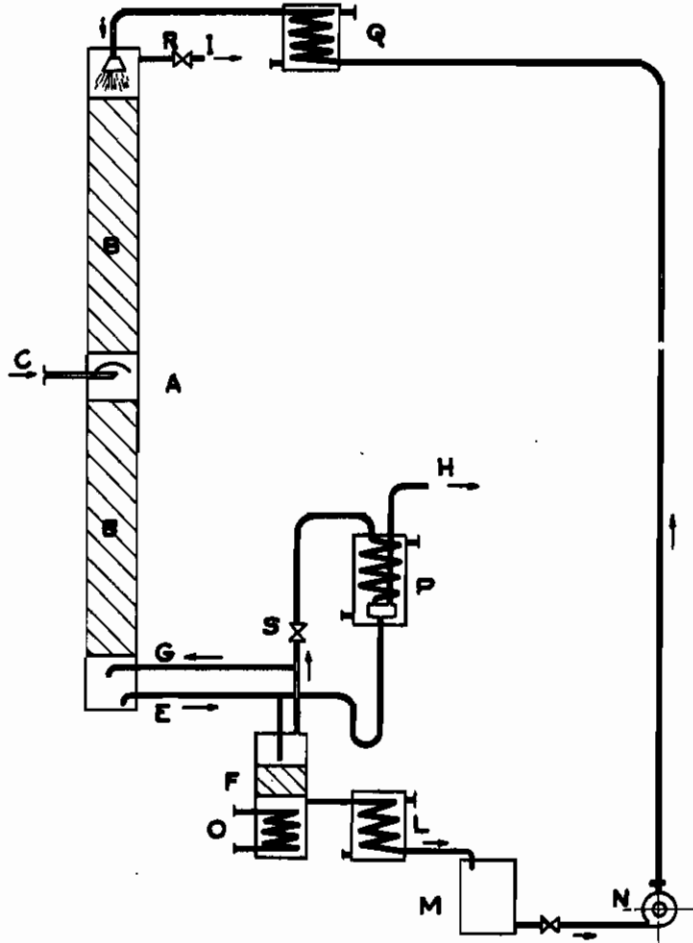


PUBLISHED
MAY 18, 1943.
BY A. F. C.

G. NATTA
PROCESS FOR SEPARATING THE COMPONENTS OF A
MIXING, HAVING VERY NEAR BOILING POINTS
Filed Aug. 11, 1939

Serial No.
289,710



Inventor
GIULIO NATTA.

By

Attorney

ALIEN PROPERTY CUSTODIAN

PROCESS FOR SEPARATING THE COMPONENTS OF A MIXING, HAVING VERY NEAR BOILING POINTS

Giulio Natta, Milano, Italy; vested in the Alien Property Custodian

Application filed August 11, 1939

The methods of distillation and rectification allow the easy separation of the components of a liquid mixing, provided there exists a certain difference between the boiling points of the individual components. Sometimes however cases occur some of which are of remarkable practical interest, wherein the difference between the boiling points is so small that the separation by fractional distillation is very difficult, expensive or even practically impossible to be carried out in industrial apparatus. In such cases one has to recourse to other physical processes e. g. the fractional freezing, or the use of solvents in order to obtain the separation or the diminution in the concentration of one or more of the components.

In some cases, though seldom, also the physical properties of the two components which are to be separated, are nearly all very similar with one another and there follows, consequently, a remarkable practical difficulty in order to effect the separation. Examples of the aforesaid kind are given, for instance, by mixings of paraffins and olefines having the same number of carbon atoms, or by mixings of olefines with diolefines having the same number of carbon atoms. Similarities between the physical properties in the above mentioned cases increase with the increase in the number of carbon atoms and while for instance the separation of ethane from ethylene by rectification is still possible, said separation results more difficult between propane and propylene, butane and butylene, and still more between butylenes and butadienes. In fact between butadiene and alpha butylene have practically the same boiling point, i. e. -5° C.

It has been proposed in some cases, to effect the separation by means of solvents e. g. the dissolution in furfural or in other solvents for obtaining the separation of butadiene from alpha butylene. By this method however, as butylene is also soluble in said solvents, it is not possible to obtain a complete separation but merely an enrichment in butadiene in the dissolved portion of the gas and a corresponding impoverishment in the undissolved portion. Only by repeating the operation of dissolution and extraction it could be possible to obtain a small highly concentrated portion of one of the mixing components.

The process herein proposed allows one to obtain the complete separation of the two mixing components by means of a single operation, carried out in a continuous way, which yields, even

in a continuous way, the two components in the pure state or at least highly concentrated.

The present invention consists in the use of a column filled with Raschig rings, or formed by certain number or plates; in this latter case the column is built up like the usual rectification column.

The mixing of gases or vapours to be separated is introduced in said column at an height which varies according to the composition of the mixing, while at the top of the column is introduced, also in a continuous way if so desired, a solvent in which one of the components of the mixing is more soluble than the other.

The solvent descending in the column gradually becomes richer with one of the components and, when at the bottom of the column, is heated in order to evolve the gases therein dissolved. A portion of said gases, which may even be in a volume substantially greater than the quantity introduced in the column during the same time, ascends in the column in counter current and gradually becomes richer in the other less soluble component.

The above disclosed process is differentiated from the known rectification processes by the fact that the liquid phase is formed by a solution in a comparatively slightly volatile solvent, and further that while in the rectification columns the reflux, required in order to obtain a good working of the column itself, is obtained by condensing vapours and enters at the top of the column, in the present case, the reflux is formed by gases obtained by degasification of the solvent and enters at the bottom of the column.

For instance when a column filled with Raschig rings is used and a mixing containing 30% of butadiene and 70% of butylene, is introduced therein at $\frac{2}{3}$ of its height whilst at the top there is introduced cold aniline in the proportion of one litre for every 15-30 litres of gases, and subsequently, the aniline is degasified by heating at a temperature slightly lower than that of the boiling point and 30% is extracted from the volume of the gas after cooling at the bottom and 70% at the top of the column, it will be observed that the two gases so obtained, respectively consist of butadiene and butylene, the purer the higher is the height of the column and greater the ratio between the volume of solvent and the volume of the gaseous mixing to be treated.

By the use of columns several metres high, it is possible to obtain a practically complete separation.

For the separation of butylene from butadiene other liquids instead of aniline, may be used as a solvent e. g. benzene or better its derivatives which are less volatile, or fufurool, pyridine and generally aromatic or hydroaromatic substances preferably containing a couple of conjugated double bonds, or other substances in which butadiene is more soluble than butylene.

The use of slightly volatile solvents, even if they dissolve the components of the mixing less easily than other volatile solvents, offers the advantages of reducing the losses of solvent, as a consequence of the fact that the gases issuing at the bottom and the top of the column are saturated with the solvent at the temperature at which they are cooled. By using, e. g. in the case of separation of butylene, butadiene, aniline as a solvent and strongly cooling the separated gases, the losses of solvent are practically negligible.

In order to improve the thermal balance of the process, the solvent, which is collected at the bottom of the column and is to be gasified by the hot solvent issuing from the degasifying chamber, may be pre-heated. Said chamber may be a part of the column itself being located at its base or may be kept separate from it.

One of the ways of carrying out the process object of this invention is schematically illustrated in the annexed drawing, and consists in the use of a column (A) filled with Raschig rings (B, B).

Into said column there is introduced, e. g. through the passage C, with a continuous flow, the mixing of gases or vapours to be separated; the passage C being located at an height which varies according to the composition of the mixing, while at the top of the column there is introduced, also continuously, a solvent in which one of the two components is more soluble than the other. The solvent descending the column gradually enriches itself with said more soluble component and when at the bottom E it is heated in F, e. g. by a steam heated coil O in order to evolve the dissolved gases. A portion of said gases, which may even be in a volume remarkably greater than the quantity introduced in the column during the same time, is led again in G and ascends therein in counterflow with the solvent, gradually becoming richer, towards the top, with the less soluble component. Of the two components the less soluble collects at the top and is drawn out in I through the regulator R, while the more soluble component is

drawn out through F by means of the regulating valve S and is cooled in P in order to eliminate the solvent vapours. The degasified solvent is cooled in L and through the tank M and the pump N comes back into cycle entering at the top of the column, eventually after further strong cooling in the refrigerator Q.

The apparatus and procedure disclosed are merely by way of example and other processes may be included within the same general principle. E. g. the column may be formed by a certain number of plates like the usual rectification column. Or the degasifying device may be included in the column itself.

The process disclosed may be used not only for separating butylene from butadiene, but also for extracting them from complex gaseous mixing in which they are contained in small amounts e. g. from residual gases resulting as by-products in the butadiene manufacture. In a similar case both butylene and butadiene are extracted from the less soluble gases accompanying them (ethylene, hydrogen, carbon dioxide, nitrogen etc.) by absorption in a solvent in a washing column which may be filled with Raschig rings.

The solution thus obtained may be degasified and the gases obtained by subjected to a fractional absorption in a second column in order to obtain pure butadiene at the bottom of this latter while at the top butylene, eventually in the impure state owing to small quantities of less soluble components, is obtained. The process may be simplified by introducing in the middle of the fractionating column, instead of the gases extracted from the solvent, the solution itself, extracting thereafter the degasified and cooled solvent at the bottom of the fractionating column while only a small portion is led again at the top of the column and the remaining portion is led to the absorption column.

The above very simple process for the separation of gases or vapours by fractional absorption and reflux of the more soluble component is useful in several applications and in many cases it may advantageously replace certain more expensive chemical processes of separation and purification.

In order to reduce the dimension of the fractionating columns and the required amount of solvent it may be advantageous to operate the apparatus at a pressure higher than the atmospheric pressure, e. g. up to 10 atmospheres.

GIULIO NATTA.