

PATENT SPECIFICATION.

532,942

Convention Date (Italy) : Aug. 13, 1938.

Application Date (in United Kingdom) : July 26, 1939. No. 21752/39.

Complete Specification Accepted : Feb. 4, 1941.



COMPLETE SPECIFICATION.

Improvements in or relating to Processes for the Manufacture of Butadiene.

We, ISTITUTO PER LO STUDIO DELLA GOMMA SINTETICA, a Body Corporate organised under the laws of Italy, of Via G. B. Pirelli No. 1, Milan, Italy, and GIULIO NATTA, a Subject of the King of Italy, of Via Mario Pagano 54, Milan, Italy, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is for improvements in or relating to processes for the manufacture of butadiene.

The synthesis of butadiene (C_4H_6) has attained today a remarkable importance owing to its use in the manufacture of synthetic rubber.

The processes heretofore employed for the manufacture of butadiene starting from alcohol and aldehyde offer, however, many inconveniences, owing to the low industrial yield obtainable, the high cost of the raw materials and the difficulty of obtaining butadiene in a very pure state.

Attempts for the manufacture of butadiene from less expensive raw materials, e.g. butylenes (C_4H_8) obtained as by-products from petroleum cracking, have not heretofore given good results on an industrial scale, owing to the difficulties which have been experienced in the separation of unchanged butylenes from the butadiene produced, the yields of butadiene being low, and owing to the poisoning of the catalysts used after a short time of working.

It has now been found to be possible, according to the present invention, to obtain in a continuous process a high yield in butadiene from butylenes and particularly from alpha-butylene, completely avoiding the above-mentioned inconveniences of the known processes.

According to the invention, such a process consists in this that butylene or a gaseous mixture containing butylene is submitted to dehydrogenation in the presence of a dehydrogenating catalyst consisting of a metal of the eighth group of the periodic system, preferably nickel,

[Price 1/-]

and of a diluent gas consisting of carbon dioxide.

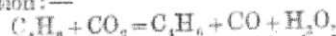
The expression "butylene" as used herein with reference to the process of this invention, connotes chiefly alpha- or Δ . 1-2 . butylene, but also beta- or Δ . 2-3-butylene and/or mixtures of these bodies.

The presence of the carbon dioxide in the mixture promotes the reaction:—



This effect is apparently due to a number of causes. Firstly, the carbon dioxide causes a diminution of the partial pressure of the individual components taking part in the reaction; it is known, of course, that a diminution of pressure favours reactions which take place with an increase of volume. Secondly, the carbon dioxide assists in preventing the formation of free carbon, which, if deposited on the catalyst, would quickly deteriorate it by reacting with it and forming carbon monoxide.

It is evident, however, that the influence of carbon dioxide in the process is much greater than that which could be foreseen on the ground of the foregoing considerations. In fact, on the basis of these considerations, steam should be sufficient to give an effect which is similar to that given by carbon dioxide, but in practice this is not the case. That it is not the case is due, partially at least, to the fact that carbon dioxide takes part in the reaction, either directly with butylene, according to the equation:—



or through its reaction with hydrogen, according to the equation:—



thus promoting the reaction of dehydrogenation of butylene.

While the kinetic mechanism of the reaction is not yet fully explained, the remarkably advantageous action of carbon dioxide can to a certain extent be explained by presuming its activating action on the dehydrogenating catalyst and/or its participation in an intermediate reaction which is kinetically more rapid.

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Should it be desired to economise in the use of more costly metals, good results may be obtained by the use of a porous support for example, alumina, or silica or, preferably, kaolin or bentonite. Thus, excellent results are obtainable with catalysts composed of finely divided nickel on such a support, the nickel having been produced in situ on the support by reduction thereon of a nickel salt such as basic nickel carbonate, nickel oxalate or nickel hydroxide, which has first been precipitated on the support.

The temperature of dehydrogenation in the process may vary within wide limits, but the best results are obtained at temperatures ranging between 500° and 700° C. and preferably between 550° and 600° C. For instance, a mixture consisting of equal volumes of alpha-butylene and carbon dioxide is led at 575° C. through a catalyst layer consisting of bentonite carrying 5% of nickel produced in situ on the bentonite and, after separation of carbon dioxide and of the gases more difficult to condense, yields a mixture containing about equal volumes of butylene and butadiene.

The carbon dioxide, separated by means of a suitable solvent, may be returned to circulation, while the separation of butylene and butadiene may be obtained by condensation; alternatively, the separation of butylene from butadiene may be carried out by a process of selective dissolution in a solvent, following known methods in this respect.

The separated butylene may be returned to circulation and converted into butadiene.

It is possible, by a sufficiently careful control of the operating conditions, to obtain by a single operation such a high yield that it is possible to separate the butylene from the butadiene by polymerisation of the butadiene, for example, with sodium thus directly obtaining synthetic rubber of a good quality.

By thus operating and by returning to circulation the unaltered butylene, it is possible to obtain yields of butadiene which in the aggregate exceed 80% of the butylene used.

The process may be applied not only to the treatment of butylene contained in cracking gases, but also to the treatment of butylene, or mixtures of butylenes, obtained in other ways, for example butylene obtained by dehydration of butylalcohol, also butylene obtained as a by-product in the manufacture of butadiene by processes based on the catalytic

decomposition of a mixture of alcohol and acetic aldehyde on alumina or an equivalent catalyst. Thus, in these last-mentioned processes a quantity of butylene corresponding to 20-30% of the butadiene produced is obtained as a by-product. The recovery of this butylene and its transformation into butadiene by the process according to the invention enables an increase of 20% to be obtained in the total output of butadiene without increasing the consumption of raw materials, alcohol and aldehyde.

It is further possible to use alpha-butylene obtained from normal butyl alcohol by a reaction which may be carried out with practically quantitative yields, that is, by dehydration of the normal butyl alcohol or a catalyst consisting mainly of alumina or kaolin. The butyl alcohol may have been obtained by hydrogenation of aldol.

Besides alpha-butylene, beta-butylene or mixtures of the two may also be used, since during the dehydrogenation of beta-butylene a migration of the pre-existing double bond takes place.

The dehydrogenation reaction of the butylenes is endothermic and the heat of reaction must be supplied from the outside by heating the reaction chamber with hot gases or by indirect or direct heating of the catalyst or of the reacting gases by means of electric resistances. As the reaction is reversible, it is preferable that the reaction gases shall leave the catalyst at the highest temperature of the cycle and be at once cooled down.

It is also possible, in order to avoid the need of addition of heat from the outside, which is expensive owing to the high reaction temperature, to carry out a partial combustion inside the reaction chamber of the hydrogen coming from the dehydrogenation of butylene. For this purpose it is sufficient to mix with the carbon dioxide the small quantity of oxygen or air that is required to develop, by burning, a quantity of heat capable of balancing the heat absorbed by the reaction of dehydrogenation and of bringing the reacting gases to the reaction temperature.

In order to reduce the amount of heat required to bring the gases to the reaction temperature, it is useful to pre-heat the gases which enter in the reaction chamber, by heat exchange with the gases issuing from the reaction chamber. In this case, a small quantity of oxygen or air, substantially less than the lower quantity that will form an explosion mixture with the other gases, is sufficient to maintain stationary the temperature

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of the catalyst without addition of heat from the outside.

In United Kingdom Patent Specification No. 508,764, a process for the preparation of butadiene by dehydrogenation of butane is claimed, which comprises the catalytic dehydrogenation of butylene to butadiene in the presence of carbon dioxide, the butylene having been prepared by the catalytic dehydrogenation of butane, and no claim is made to the process.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that, subject to the foregoing disclaimer, what we claim is:—

1. A process for the manufacture of butadiene by dehydrogenation of butylene, which consists in this that butylene or a gaseous mixture containing butylene is submitted to dehydrogenation in the presence of a dehydrogenating catalyst consisting of a metal of the eighth group of the Periodic System, preferably nickel, and of a diluent gas consisting of carbon dioxide.

2. A process as claimed in Claim 1, wherein the temperature employed in the dehydrogenating operation is between 500° C. and 700° C. and preferably between 550 C. and 600° C.

3. A process as claimed in Claim 2, wherein, in addition to carbon dioxide small quantities of oxygen or air are added to the butylene, in such an amount as to balance the quantity of heat absorbed in the dehydrogenation reaction, by means of a portion of the heat developed in the combustion of a portion of the hydrogen coming from the dehydrogenation of the butylene.

4. A process as claimed in any of the preceding claims, wherein the catalyst is carried on a porous support.

5. A process as claimed in claim 4, wherein the support consists of alumina or silica or a compound thereof such for example as kaolin or bentonite.

6. A process as claimed in any of the preceding claims, wherein the mixture of butadiene, unchanged butylene, carbon dioxide and other gases, which is obtained as the result of the dehydrogenation reaction is fractionated either by condensation or by a process of selective absorption in a solvent in such a way as to recover the carbon dioxide which has not reacted in the process, which carbon dioxide is then returned to the reaction chamber.

7. A process as claimed in any of the preceding claims, wherein the butylene which has not reacted in the process is, after separation from the butadiene, returned to the reaction chamber for retreatment therein.

8. A process as claimed in any of the preceding claims, wherein the butadiene is separated from the unchanged butylene by polymerisation with consequent direct formation of synthetic rubber, the unchanged butylene remaining after this step of the process being preferably returned to the reaction chamber for transformation therein into butadiene.

9. A process as claimed in any of the preceding claims, wherein the butadiene is separated by means of a solvent.

10. A process as claimed in any of the preceding claims, wherein the butylene used is butylene which has been manufactured by dehydration of butyl alcohol which latter has been obtained by hydrogenation of aldol, the hydrogen formed in the dehydrogenation of the butylene being if necessary recovered and employed for the hydrogenation of the aldol.

11. A process for the manufacture of butadiene by dehydrogenation of butylene substantially as hereinbefore described.

Dated this 26th day of July, 1939.

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