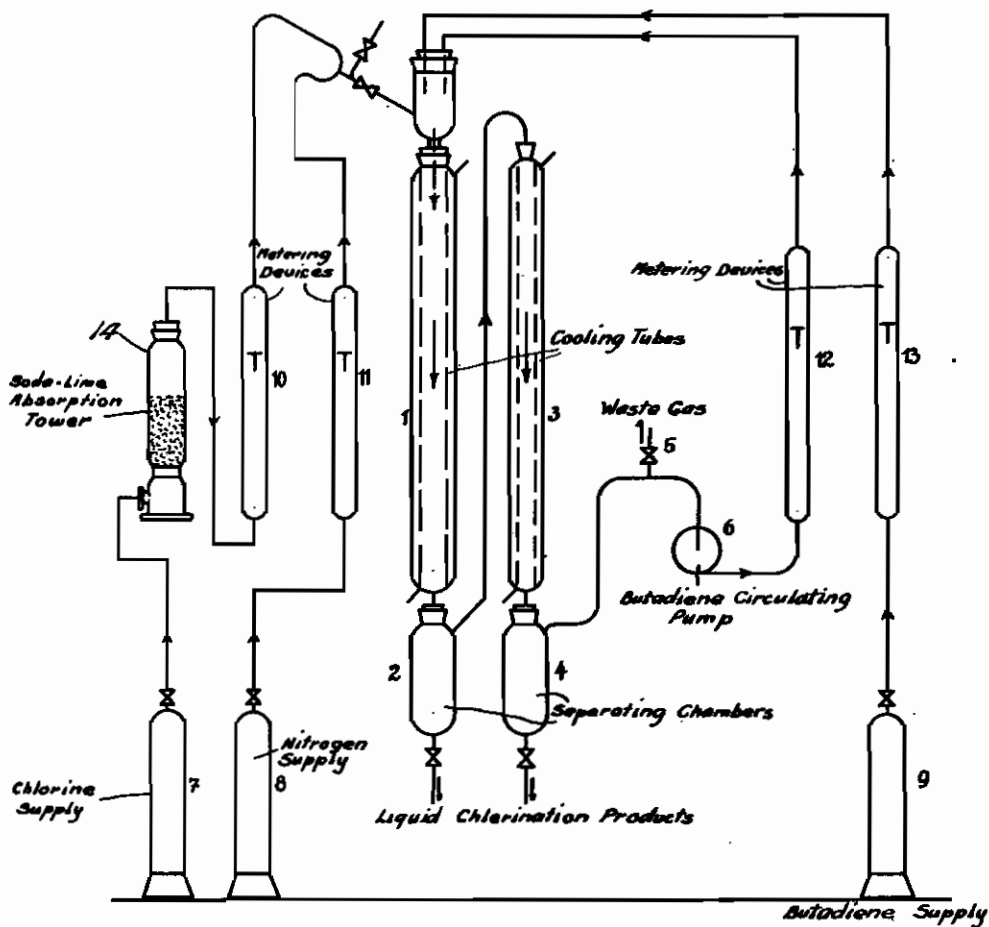


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DICHLOROBUTENES AND A PROCESS
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DICHLOROBUTENES AND A PROCESS OF PREPARING THEM

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The present invention relates to dichlorobutenes and to a process of preparing them.

It is known that dichlorobutene is obtained by adding chlorine in a quantity insufficient for complete chlorination to butadiene in presence of a solvent. It is necessary in this case to use a relatively large quantity of the solvent and to work with a large excess of butadiene in order to prevent further chlorination of the first formed dichlorobutenes into the tetrachlorobutane from becoming the preponderating change. The yield per unit of space and time is, therefore, very moderate and the hydrogen chloride, formed by the substitution-chlorination which always occurs as by-reaction is present in the solution and, by addition, leads in its turn to undesired by-products. Finally, the distillation which is necessary when the reaction has proceeded for a comparatively short time in order to avoid high concentration of the chlorination products renders the process expensive in view of the large amount of solvents which are carried over and unavoidable losses in distillation. It has been proposed to use liquefied butadiene as a solvent, but this necessitates the use of a large excess and the application of very low temperatures, for instance, -75°C ; even then it is not possible to avoid the substitution-chlorination or the subsequent chlorination with formation of tetrachlorobutane.

Now, I have found that the chlorination of butadienes with formation of dichlorobutene may be performed in an economic and technically simple way by causing gaseous butadiene to react with gaseous chloride in the absence of a solvent but in the presence of a substance which is gaseous during the reaction and insensitive towards chloride and butadiene, such as, for instance, nitrogen and the noble gases, halogenated hydrocarbons, carbon dioxide and the like. In this manner the costs for working up the product are considerably diminished in view of the omission of the large quantity of solvent. Furthermore, the dichlorobutene first formed by the circulation of the gas is quickly removed from the reaction zone and thus from further chlorination; the direct chlorination to a higher stage is avoided since the chlorine is much diluted by the gas; a good yield of dichlorobutene is thus obtained.

As diagrammatically illustrated in the accompanying drawing, the reaction may, for instance, be performed in a cooling device which may be charged partially or entirely with filling material, an inlet tube for the chlorine extending into this reaction chamber which tube may have the form

of a nozzle. Butadiene is circulated by means of a pump and caused to react with chlorine diluted with gas; the product of reaction is removed and a quantity of waste gas corresponding with the gas used for diluting the chlorine is continuously withdrawn. The circulating gas becomes mixed with a small proportion of hydrogen chloride which may readily be removed from the gas. The exit gas is freed from small quantities of butadiene and HCl and after cooling or washing may be used further for diluting chlorine so that the working is continuous and economic.

The volume of the inert diluent suitably is equivalent to the volume of the chlorine; there may, however, also be applied considerably larger amounts, for instance, fifty times the volume. The upper limit of the amount to be applied merely depends upon economical considerations.

The proportion of the chlorine used is preferably at most 1 mol per mol of the butadiene; advantageously, there are used not less than 0.75 mol of chlorine per 1 mol of the butadiene.

The reaction may be performed at temperatures of about -20°C to about $+20^{\circ}\text{C}$. The higher the temperatures applied are, the larger are the amounts of the gaseous diluent to be added.

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

1. Referring to the accompanying diagram, an inlet tube for introducing chlorine having a diameter of 1 cm extends about 15 cm into the cooling zone at the upper end of a cooling tube 1 of 135 cm length and a diameter of 3 cm surrounded by a cooling jacket. To a depth of about 10 cm the lower cooling zone is charged with filter rings. A separating chamber 2 for the liquid is connected with a second cooler 3 provided also with a separating chamber 4 for the liquid and with a cock 5 for the waste gas. A pump 6 causes the butadiene to circulate in the apparatus. From the container 7 chlorine is discharged, from 8 nitrogen and from 9 butadiene. 10, 11, 12 and 13 are devices for measuring the speed of the gases.

The temperature in the cooler is maintained at about -5 to $+10^{\circ}\text{C}$ by means of a cooling liquor in its jacket so that butadiene at a speed of circulation of even 2000 liters per hour does not liquify. A mixture of 9.5 liters of chlorine and 100 liters of nitrogen is introduced per hour through the chlorine-inlet tube and at the same time 10 liters of butadiene per hour are introduced at the upper end of the first cooling tube. The liquid chlorination product obtained collects in the two separating chambers; the quantity of

gas introduced is such that a pressure of 5 cm of mercury above atmospheric pressure is maintained in the apparatus. The exit gas contains traces of hydrogen chloride and small quantities of butadiene; it is freed therefrom and may then be used again for diluting the chlorine. After 4½ hours 250 grams of liquid product will have been collected which, when fractionated, yields besides small quantities of butadiene

	Per cent
1:2-dichlorobutene-3, boiling at 42°C-44°C under a pressure of 40 mm-----	34.3
1:4-dichlorobutene-2, boiling at 61°C-63°C under a pressure of 2 mm-----	39.7
Chlorination products of higher boiling point, mainly tetrachlorobutene-----	23.1

2. The operation is the same as in example 1, except for the fact that the chlorine is not diluted with nitrogen but with gaseous difluorodichloromethane at a rate of 50 liters per hour. After 5 hours 280 grams of liquid will have been collected which contain:

	Per cent
1:2-dichlorobutene-3 -----	28.5
1:4-dichlorobutene-2 -----	36.6
Chlorination products of higher boiling point -----	29.7

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