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PROCESS FOR THE PRODUCTION OF HYDROCARBON-CHLORIDES WITH 4 CARBON ATOMS FROM TRICHLORETHYLENE

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This invention relates to a process for polymerizing trichlorethylene as set forth in the patent 2,161,078 and in the patent application S. N. 283,456 and has for its object to provide an improved process for this purpose.

According to the methods of the forenamed patents the production of hexachlorbutene and pentachlorbutadiene is executed by heating trichlorethylene in an autoclave and in a discontinuous manner. The disadvantages of the discontinuous method of working at operations on a large scale (wholesale trade) are especially great at a process being executed under pressure and at high temperature, because on the one hand the arrangement of large autoclaves demands much material and costs and extensive safety devices and because on the other hand the attendance before all the filling up every time, the heating up to the high reaction temperature, the cooling down, the release and the emptying of the autoclave—is difficult, demands plenty of time and has considerable loss of warmth in consequence.

Now there was found, that the conversion of trichlorethylene into the hydrocarbon-chlorides can be continuously executed whereby a small pressure apparatus easily to be served can be used. Though the polymerisation of the trichlorethylene is a reaction proceeding relatively slowly, the trichlorethylene polymerizes surprisingly also in a satisfactory extent, if it is continuously pressed through a vessel, resistant to pressure and heated to the reaction temperature. A suitable pressure vessel is a tube, through which by a pump or by a pressure bulb the trichlorethylene is pressed through continuously and equally. The velocity with which the trichlorethylene converses in this pressure vessel, and with which it can be passed through correspondingly depends on the temperature and the purity of the trichlorethylene and that of the apparatus. The conversion proceeds under 200° still very slowly, with increasing temperature however the reaction velocity increases very much. About 250° were found as a generally suitable temperature, because at this temperature a sufficient reaction is obtained and the material of the wall of the vessel is unimportantly corroded. But also above this temperature till about 300° can be worked very well. Suitable materials for the inner wall of the vessel resp. for its lining are lead, nickel, silver, enamel. The pressure in the reaction vessel is suitably held on about 20 atu. Sometimes the technical trichlorethylene or the parts of the pressure apparatus, being in contact with it, contain organic or unorganic contaminations, having the effect of splitting off HCl or inhibit the polymerization. If adding small quantities of the substances named in the patent application S. N. 283,456 it is possible to reduce the splitting off of HCl from the polymerization product to a low degree and to make inactive the eatalysts which inhibit the polymerization.

The continuous process can also be executed in this way, that the polymerized trichlorethylene is wholly or partly splitted in pentachlorbutadien and hydrogen chloride, if the trichlorethylene is mixed with a small quantity of iron chloride and is pressed through the pressure tube in this way. At the high reaction temperature a small quantity of ironchloride is sufficient to obtain a nearly quantitative splitting off of HCl. But it is absolutely to avoid that the quantity of ironchloride which has proved as sufficient for the completely splitting off of HCl is exceeded because with increasing content of iron a delay of the trichlorethylene-polymerization enters, which primary proceeds. The quantity of ironchloride which is to add changes in the course of the reaction, because on the one hand a part of the added ironchloride is made inactive by contaminations in the trichlorethylene and in the apparatus and because on the other hand one part of the added ironchloride always remains in the reaction apparatus. The reaction can also be executed in the presence of a catalyst like superoxides.

Example 1

Through a heated, with lead lined tube of 1 m length and 5 cm wideness 3 l trichlorethylene to whom 1 drop of pyridine was added, were led pro hour. The temperature was in the middle of the tube 260°. The pressure was held on about 20 atu. The reaction product was cooled when leaving the tube and led off by a valve of release in a state cooled. The so obtained reaction product contained about 55% of unchanged trichlorethylene and about 45% of high boiling hydrocarbon-chlorides. In the latter constituent were contained about 92% of hexachlorbutene, about 6% of pentachlorbutadien and 2% of compounds, which could not be destilled. The splitting off of HCl corresponded approximately with the present pentachlorbutadien and was about 1,3 mol. pro hour.

Example 2

Through the same tube—according to the method of working described in example 1 3 l of trichlorethylene—to whom 0,02 g of ironchloride pro liter trichlorethylene were added—were

pumped through pro hour. The temperature was 240°, the pressure was also held on about 20 atu. The obtained product contained on average 60% of unchanged trichlorethylene and 40% of high boiling hydrocarbon-chlorides, consisting of about 90% of pentachlorbutadien, of 8% of hexachlorbuten and of 2% of higher molecular compounds. At the same time a quantity of HCl was obtained corresponding with the formed pentachlorbutadien. Continuously working, the quantity of ironchloride was diminished, when the velocity of polymerization decreased, on the other hand more ironchloride was added, when the decomposition of hexachlorbuten sank below 90°.

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