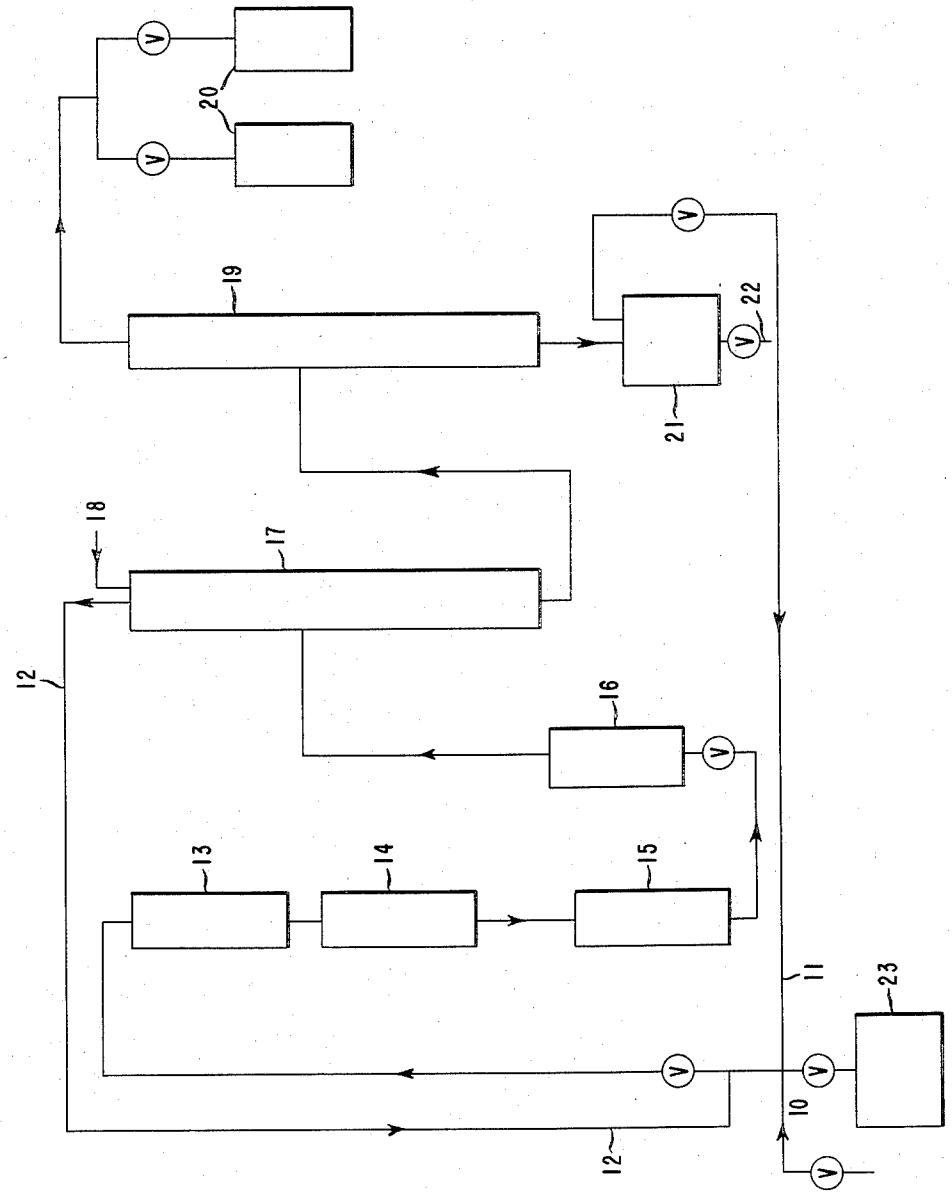
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PYROLYSIS OF FLUOROCARBONS TO HEXAFLUOROPROPYLENE

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INVENTORS
GEORGE P. LARSON
EDWARD H. TEN EYCK

BY Allan R. Plumley
ATTORNEY

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PYROLYSIS OF FLUOROCARBONS TO HEXAFLUOROPROPYLENE

Edward H. Ten Eyck, Parkersburg, W. Va., and George P. Larson, Elizabeth, N.J., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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The present invention relates to the pyrolysis of fluorocarbons to form high amounts of hexafluoropropylene and particularly to a process where tetrafluoroethylene is essentially completely converted to hexafluoropropylene.

It has been reported (Slesser and Schram, "Preparation Properties and Technology of Fluorine and Organic Fluoro Compounds," National Nuclear Energy Series VII–I, 1951, page 593) that the pyrolysis of monomeric tetrafluoroethylene at 665±5° gives a 42% yield of hexafluoropropylene at a contact time of 10 to 15 seconds, the yield of hexafluoropropylene dropping to 4% when the temperature was raised to 750±5°. Recently it has been reported that at 800° C., at atmospheric pressure, the yield of hexafluoropropylene from tetrafluoroethylene is only 2.1% (J.C.S. 1953, 2083). Thus in these previously known procedures the yields of hexafluoropropylene were relatively small. It was believed that the cause of the low yields of hexafluoropropylene was the preferential formation of higher molecular weight fluorocarbons which were sufficiently stable to resist further reaction. Very recently a pyrolysis process was discovered (U.S. Patent 2,758,138 issued to D. A. Nelson, August 7, 1956) which gave rise to high yields of hexafluoropropylene from tetrafluoroethylene under conditions such that the formation of the higher molecular weight fluorocarbons was essentially avoided. This process was carried out at very low pressures with limited flow rates. Although this process gave rise to hexafluoropropylene yields of 75% on the basis of the tetrafluoroethylene fed it still caused a substantial loss of tetrafluoroethylene and was difficult to operate in that it required very low pressures.

It is one of the objectives of the present invention to provide a process for the preparation of hexafluoropropylene from tetrafluoroethylene wherein an essentially 100% yield to hexafluoropropylene is obtained. It is another object of the present invention to provide a process which can be operated at atmospheric pressure. A further object of the present invention is the pyrolysis of higher molecular weight gaseous fluorocarbons to tetrafluoroethylene and hexafluoropropylene. Other objects will become apparent hereinafter.

The objects of the present invention are accomplished by a process which comprises continuously feeding a mixture of tetrafluoroethylene and higher boiling fluorocarbons into a reaction zone at a temperature of 700° to 900° C., separating the hexafluoropropylene formed, recycling the remaining fluorocarbon compounds and continuously adding a quantity of tetrafluoroethylene, which is equal to the quantity of tetrafluoroethylene converted to hexafluoropropylene, to the recycling fluorocarbon

mixture without substantially altering the amount of the higher boiling fluorocarbons. In particular embodiments the process of the present invention comprises introducing continuously into a reaction zone maintained at a temperature of 700 to 900° C. for a contact time of at least 0.05 sec. at a pressure of at least 0.2 p.s.i. (absolute) a mixture of tetrafluoroethylene and fluorocarbons of the class consisting of C_nF_{2n+2}, $C_{3+n}F_{2(n+3)}$, and $C_{3+n}F_{2(n+2)}$, wherein n is a whole number from 1 to 10, the molar ratio of said fluorocarbons to tetrafluoroethylene being at least 0.050, cooling the reaction mixture, continuously separating the hexafluoropropylene and recycling the remaining reaction products, and adding a quantity of tetrafluoroethylene which corresponds to the quantity of tetrafluoroethylene converted to hexafluoropropylene. Under these conditions it was found that all the tetrafluoroethylene reacting was converted to hexafluoropropylene so that an essentially 100% yield of hexafluoropropylene was obtained.

The process of the present invention is based on the discovery that the formation of hexafluoropropylene is not limited to the following reaction:

$$C_2F_4 \rightarrow 2{=}CF_2$$
$$2C_2F_4 + 2{=}CF_2 \rightarrow 2C_3F_6$$

but that higher fluoroolefins and fluorocarbons are capable of supplying difluoromethylene radicals which can form hexafluoropropylene or tetrafluoroethylene under the conditions of the present invention. This is rather surprising since it was heretofore believed that the higher boiling fluorocarbons would continue to build up without leading to the formation of additional tetrafluoroethylene or hexafluoropropylene and that, consequently, these higher fluorocarbons had to be removed from a continuous process. Thus the prior art processes never achieved an essentially 100% yield of hexafluoropropylene from tetrafluoroethylene reacted.

The composition of the fluorocarbon mixture employed in the present invention is not critical, except that the fluorocarbons which are employed should be gaseous at the temperature at which the reaction occurs. Since the formation of hexafluoropropylene occurs through the formation of difluoromethylene radicals rather than through the formation of fluorine radicals, it is generally preferred to employ a fluorocarbon mixture which has a fluorine to carbon ratio of close to two and not exceeding three. Thus fluoroolefins having more than three carbon atoms per molecule and saturated fluorocarbons having more than two carbon atoms are generally preferred. A suitable higher fluorocarbon mixture may be obtained by passing tetrafluoroethylene through the reaction zone at the conditions outlined above, removing the hexafluoropropylene obtained, and recycling the remaining fluorocarbons. The fluorocarbons thus obtained comprise some saturated fluorocarbons having from 2 to 6 carbon atoms and besides tetrafluoroethylene and hexafluoropropylene, higher fluoroolefins having from 4 to 10 carbon atoms. Any other source of higher fluorocarbons, such as obtained from the pyrolysis of polytetrafluoroethylene is, of course, equally suitable. As stated hereinabove, the ratio of the higher fluorocarbons to the tetrafluoroethylene fed should be at least 0.05. A preferred range of ratios is from 0.075 to 1.0.

The process of the present invention is carried out at a temperature of 700 to 900° C. At temperatures above

900° C. the decomposition of the fluorocarbons includes not only the formation of difluoromethylene radicals but also the formation of fluorine radicals, the latter of which primarily form tetrafluoromethane which is not a desirable product in the present invention. At temperatures below 700° C. the decomposition is too slow and insufficient amounts of the tetrafluoroethylene are converted to hexafluoropropylene within reasonable contact times.

The pressure may be varied from below atmospheric pressure to above atmospheric pressure, however, atmospheric pressures are generally preferred since such pressures allow high feed rates. At low pressures, the amount of starting material fed is significantly lower for the same size of equipment since a minimum contact time must be maintained, and it is furthermore more difficult to maintain a uniform heat transfer to the reactants fed. An additional disadvantage is the higher cost and maintenance of low pressure equipment. Pressures greatly above atmospheric pressure are generally avoided for the sake of safety, since the reaction is exothermic in nature and may lead to serious explosions should excessive overheating take place; the danger of overheating increases with increasing pressure. A suitable pressure range is from 0.2 p.s.i. to 65 p.s.i. (absolute).

In order to obtain a complete conversion of tetrafluoroethylene reacting to hexafluoropropylene at the temperatures employed in the process of the present invention, a minimum contact time of at least 0.05 sec. is necessary. Longer contact times such as up to 2 sec. may be employed if desired.

A further significant factor that must be considered in carrying out the process of the present invention is the heat transfer of the gas in the reaction zone. Since the reaction employed in the process of the present invention is exothermic in nature insufficient heat transfer will cause local overheating and carbonization of the reaction products and thus detract from the conversion of the tetrafluoroethylene to hexafluoropropylene and cause plugging of the reaction unit which necessitates costly repair and idleness of the equipment. Overheating which occurs more frequently at higher pressures may be prevented by controlling the flow of the gas through the reaction unit. Flow of a gas through a pipe may generally be characterized by its Reynolds number although laminar flow, generally having Reynolds numbers below 2100, may suitably be employed at low pressures where overheating is less likely to occur, it is generally preferred to employ a turbulent flow having Reynolds numbers above 2500 to avoid overheating. When operating at atmospheric pressures, it is necessary to employ a gas flow having Reynolds numbers above 2500. Although the gas may be more evenly heated in a pipe containing an inert filler, such are not preferred since it was found that filled tubes cause a significant pressure drop which is preferably avoided.

One method of operating the process of the present invention is further illustrated by the attached drawing schematically showing the process of the present invention. Tetrafluoroethylene is admitted to the process stream **10** and admixed with recycled fluorocarbons either boiling above hexafluoropropylene **11** or below hexafluoropropylene **12** in the desired proportion. The mixture is then introduced into the furnace **13** where the tetrafluoroethylene is converted to hexafluoropropylene. The pyrolysis is carried out in reaction tubes made of or lined with alloy steel, or other material substantially inert to the reaction products and which will withstand the temperatures employed. The reaction products are then passed into the cooler **14** where the gases are water cooled and then through an acid absorber **15** to remove impurities, particularly hydrogen fluoride which may have formed during the pyrolysis. The gaseous products are refrigerated and compressed in the compressor **16** and passed to the distillation column **17** where those fluorocarbons boiling below hexafluoropropylene particularly unreacted tetrafluoroethylene are distilled off and recycled **12**. To prevent polymerization of the perfluoroolefins in the reaction products, a polymerization stabilizer **18** is added at the top of the column. The hexafluoropropylene, higher boiling fluorocarbons and stabilizer are passed to a second column **19** where the hexafluoropropylene is distilled off and condensed in the refrigerated storage containers **20**. The remaining fluorocarbons are passed into the flash tank **21** where the stabilizer is separated which may then be recycled to the primary column **17**. The higher fluorocarbons separated from the stabilizer are recycled and admixed with tetrafluoroethylene make-up. If it is desirable, the pyrolysis feed may be premixed in the storage tank **23**.

The invention is further illustrated by the following examples which were obtained by employing a reaction unit substantially as illustrated in the attached drawing.

Examples I to VII.—Into a down-flow reactor comprising a 3′ furnace containing a 15′ long, ½″ diameter stainless steel pipe arranged in loops, heated to the temperature indicated in column 3 of the table below was charged at a pressure indicated in column 4 of the table, a reaction mixture comprising tetrafluoroethylene and higher boiling fluorocarbons at the rates indicated in columns 2 and 8 of the table. The contact time of the gaseous reaction mixture in the reactor was 0.5 sec. The reaction mixture was passed from the reactor through a cooling section comprising a water cooled 3′ section ½″ diameter pipe into an acid absorber bed of soda lime, 12 inch in diameter and 18″ deep, to remove any hydrofluoric acid formed during the reaction. The reaction mixture was then passed into a compressor where the line pressure was increased to 125 p.s.i. and from there into a distillation column comprising a 20′ long, 2″ diameter column filled with stainless steel sieve packing maintained at a temperature of −20° C. at the top of the column and +10° C. at the bottom of the column by cooling with a brine solution. "Terpene B," a commercially available terpene polymerization inhibitor consisting of a mixture of dipentene and terpinolene was introduced at the top of the column at the rate of 1.25 cc. per hour. Substantially pure tetrafluoroethylene was obtained at the top of the column and was combined with makeup tetrafluoroethylene and then recycled to the pyrolysis furnace. The higher boiling fluorocarbons were removed from the bottom of the still passed through a pressure reduction valve into a second distillation column of identical construction as the first maintained at a pressure of 75 p.s.i.g. and a temperature of +20° C. at the top of the column and +40° C. at the bottom of the column. Hexafluoropropylene was taken off at the top of the column and the higher boiling fluorocarbons were taken from the bottom of the column and combined with the tetrafluoroethylene and recycled to the pyrolysis furnace. The table below shows the Reynolds flow number in the furnace, the conversion of tetrafluoroethylene (TFE) to hexafluoropropylene (HFP), the yield of hexafluoropropylene on the basis of the tetrafluoroethylene reacted and the quantity of higher fluorocarbons recycled. The higher fluorocarbons recycled were analyzed to be mixtures of compounds having the following compositions; C_3F_8, C_4F_8, C_4F_6, C_5F_8, C_5F_{10}, C_6F_7, C_6F_9, C_6F_{10}, C_7F_7, C_7F_8, C_7F_{11}, C_8F_9, C_8F_{10}. The analysis of the higher boiling fluorocarbons was carried out by mass spectroscopy and gas chromatography.

In the table below Example 1 demonstrates the results obtained in the absence of any higher boiling fluorocarbons. Examples 3 and 4 demonstrate the ability of higher fluorocarbons to form hexafluoropropylene. Examples 2, 5, 6 and 7 demonstrate substantially 100% yield of hexafluoropropylene obtained on the basis of the tetrafluoroethylene converted and thus on the basis of the additional tetrafluoroethylene fed.

Example No.	TFE Feed, p.p.h.	Reaction Temp., °C.	Furnace Pressure in H_2O, Gage	Reynolds No.	Conversion to HFP, Mole Percent	Percent HFP Yield from TFE	High Boiling Fluorocarbons Recycled, p.p.h.
1	7.0	750	8.9	3100	15.3	89.5	0
2	4.0	770	9.0	3100	33.3	98	1.75
3	0	780	1.5	2800	3.1	----------	8.5
4	0	820	3.0	2800	8.2	----------	8.5
5	9.0	790	7.3	3600	19.5	100	3.3
6	10.0	800	6.6	4000	18.3	100	3.3
7	11.9	810	6.6	4200	17.0	100	2.6

Hexafluoropropylene obtained by the process of the present invention is highly useful as a monomer in the preparation of fluorinated polymers and particularly in the preparation of copolymers with such comonomers as tetrafluoroethylene, vinyl fluoride, vinyl chloride, methyl methacrylate and the like. The polymers thus obtained are useful for molding and extruding into fibers, films and other shapes, including the manufacture of articles which are of value in electrical insulation.

By the process of the present invention tetrafluoroethylene and other high boiling fluorocarbons can be quantitatively converted to hexafluoropropylene and thus the present invention provides a highly economic method for preparing hexafluoropropylene. The process is further advantageous in that it can be operated at atmospheric pressure.

We claim:

1. A process for preparing hexafluoropropylene which comprises continuously feeding into a reaction zone maintained at a temperature of 700 to 900° C. and at a pressure of 0.2 p.s.i. to 65 p.s.i. for a contact time of at least 0.05 sec. a mixture of tetrafluoroethylene and higher boiling fluorocarbons of the class consisting of a mixture of C_nF_{2n+2}, $C_{n+3}F_{2(n+3)}$ and $C_{n+3}F_{2(n+2)}$ wherein n is a number from 1 to 10, the molar ratio of said higher boiling fluorocarbons to said tetrafluoroethylene being at least 0.05, cooling said reaction products, separating hexafluoropropylene therefrom, recycling the remaining fluorocarbons and continuously adding tetrafluoroethylene to said recycling fluorocarbons in the quantity of tetrafluoroethylene converted to hexafluoropropylene without substantially altering the amount of said higher boiling fluorocarbons.

2. A process for preparing hexafluoropropylene from tetrafluoroethylene which comprises continuously feeding into a reaction zone maintained at a temperature of 700° C. to 900° C. and at a pressure of 0.2 p.s.i. to 65 p.s.i. for a contact time of at least 0.05 second under flow conditions exceeding a Reynolds number of 2500, a mixture of tetrafluoroethylene and higher boiling fluorocarbons of the class consisting of a mixture of C_nF_{2n+2}, $C_{n+3}F_{2(n+3)}$ and $C_{n+3}F_{2(n+2)}$ wherein n is a number from 1 to 10, the molar ratio of said higher boiling fluorocarbons to said tetrafluoroethylene being at least 0.05, cooling said reaction products, separating hexafluoropropylene therefrom, recycling the remaining fluorocarbons and continuously adding tetrafluoroethylene to said recycling fluorocarbons in the quantity of tetrafluoroethylene converted to hexafluoropropylene without substantially altering the amount of said higher boiling fluorocarbons.

3. A process for preparing hexafluoropropylene which comprises continuously feeding into a reaction zone maintained at a temperature of 700 to 900° C. and at atmospheric pressure for a contact time of at least 0.05 sec. under flow conditions exceeding a Reynolds number of 2500, a mixture of tetrafluoroethylene and higher boiling fluorocarbons of the class consisting of a mixture of C_nF_{2n+2}, $C_{n+3}F_{2(n+3)}$ and $C_{n+3}F_{2(n+2)}$ wherein n is a whole number from 1 to 10, the molar ratio of said higher boiling fluorocarbons to said tetrafluoroethylene being at least 0.05, cooling said reaction products, separating hexafluoropropylene and recycling the remaining fluorocarbons and continuously adding tetrafluoroethylene to said recycling fluorocarbons in the quantity of tetrafluoroethylene converted to hexafluoropropylene without substantially altering the amount of said higher boiling fluorocarbons.

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