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PYROLYSIS PROCESS FOR PREPARING HEXAFLUOROPROPENE FROM TETRAFLUOROETHYLENE POLYMER

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1 Claim. (Cl. 260—653)

This invention relates to a pyrolysis process and more particularly to a process for the manufacture of hexafluoropropene from polytetrafluoroethylene in improved yields.

It was known heretofore that the pyrolysis of polytetrafluoroethylene at temperatures above 600° C. and at pressures up to 150 mm. of mercury yields various fluoroparaffins and fluoroolefins (U. S. 2,406,153). In general, this prior art work was aimed at recovering maximum amounts of monomeric tetrafluoroethylene from polytetrafluoroethylene scrap. For the preparation of other fluorocarbons, including perfluorocyclobutane, etc., pyrolysis of monomeric tetrafluoroethylene was heretofore carried out at higher pressures, e. g. 1 to 200 atmospheres, the reaction time being from a few minutes to several days (U. S. 2,404,374).

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 655°±5° gives a 42% yield of hexafluoropropene at a contact time of 10 to 15 seconds, the yield of hexafluoropropene dropping to 4% when the temperature was raised to 750°±5°. Very recently it has been reported that at 800°, at atmospheric pressure, the yield of hexafluoropropene from tetrafluoroethylene is only 2.1% (J. C. S. 1953, page 2083). Thus, in these previously known procedures, the yields of hexafluoropropene were relatively small. In no instance was hexafluoropropene obtainable as the main product of the pyrolysis of polytetrafluoroethylene, and in the pyrolysis of monomeric tetrafluoroethylene the maximum yield heretofore realized was 42%.

Hexafluoropropene has been, however, a highly valuable and useful intermediate in the manufacture of high quality tetrafluoroethylene-hexafluoropropene interpolymers (U. S. 2,598,283), and there has accordingly existed, for several years, a need for efficient methods for manufacturing this material.

An object of this invention is to provide an improved process for obtaining relatively high yields of hexafluoropropene, especialy yields in excess of 45 to 50% by weight, by pyrolysis of polytetrafluoroethylene. Another object of this invention is to provide a process for obtaining improved yields of highly useful pyrolysis products, especially hexafluoropropene and mixtures of hexafluoropropene with the tetrafluoroethylene, while producing minimum qualities of less useful fluorinated compounds boiling higher than hexafluoropropene. Other objects will appear in the description of the invention given below.

It has been discovered, according to this invention that when the exposure time of the pyrolysis mixture is limited so that it does not exceed 5 seconds, the temperature being 750° C. to 960° C., said exposure time being however not less than 0.3 second if the temperature exceeds 815° C., the pressure not exceeding 100 mm. of mercury, the main product of the pyrolysis of polytetrafluoroethylene is hexafluoropropene. The "exposure time," as that expression is

used herein, is an approximate index of residence time or space velocity and is defined in a manner which simplifies the organization of the experimental data. More specifically, "exposure time" is defined as the time in the reaction zone calculated on the assumption that the entire zone within which pyrolysis occurs, which in the experiments reported herein is the reactor volume heated by the heating means (furnace), is at the average reactor temperature, and on the further assumption that the gaseous reaction mixture is a perfect gas and has an average molecular weight determined by exit gas analysis, usually by infrared, or mass spectra (the average is generally 124±22). This definition of the index greatly simplifies calculations and does not detract too seriously from its practical value. By the use of these simplifications the temperature and feed rate data can be organized in a form which provides a basis for comparison between various runs using differing sizes of heated reaction zone, and differing temperature profiles across and along the said zone.

The pyrolysis of polytetrafluoroethylene under the aforesaid conditions can be performed in a reaction tube made of or lined with iron, alloy steel, or other material substantially inert to the reaction products and which will withstand the temperatures employed. The reaction tube may be heated by means of electric coils or other conventional heating means. The products of decomposition of the polytetrafluoroethylene can be cooled in a heat exchanger with water as the coolant, although other cooling means may be employed. It is sometimes advisable to conduct the pyrolysis gases through a filter cloth or other filtering means to remove any solid material which may be in the gas stream issuing from the exit end of the reaction tube, in order to facilitate handling the gaseous reaction products.

The expression "maximum pyrolysis temperature" as employed herein should be understood to mean the maximum gas temperature developed inside the reaction tube. When the process of this invention is performed in a continuous manner, the temperature inside the reaction tube near the entrance end through which the polytetrafluoroethylene is fed continuously is generally lower than at the center or exit end of the tube, as it takes some time for the polytetrafluoroethylene to be raised from below its minimum decomposition temperature up to the maximum temperature reached within the reaction tube. In fact, the temperature range may spread over as much as one hundred or more degrees centigrade from the entrance end to the exit end. In order to note the temperature of the reaction mixture during a run, and to estimate the average temperature for purposes of calculating "exposure time," it is frequently helpful to insert three or more thermocouples into the tube wall (preferably shielded from the heat source), one at the entrance end, one approximately in the middle of the tube, and another at the exit end of the tube. In general, the maximum temperature within the reaction tube is developed within the last two-thirds thereof. The average temperature can be determined with sufficient accuracy from the profile of the temperature/distance curve, along the reactor. The reactor temperatures, as measured by means of the aforesaid thermocouples inserted through the tube wall, correspond approximately with the actual temperatures in the gas stream flowing through the tube in close proximity to such thermocouples.

The minimum "exposure time" necessary to maintain optimum yields of hexafluoropropene is to some extent also dependent upon the reaction pressure, but as noted in detail below, minor variations in pressure produce only minor changes in the quantity of hexafluoropropene produced. However, at about 790° to 900° C., at a reactor pressure of about 3 to 7 mm. Hg absolute an "exposure time" in excess of about 0.05 second is highly desirable;

at 20 mm. Hg absolute reactor pressure an "exposure time" in excess of about 0.4 second is helpful, while at 50 mm. about 0.5 second "exposure time" is the minimum for highest yields. Regardless of the pressure, within the range herein disclosed, prolonged "exposure time" (above a few seconds) causes the pyrolysis to yield fluorocarbons higher boiling than hexafluoropropene as main products. Thus there is an interdependency between the temperature, pressure, and "exposure time," required for optimum results. Under the preferred conditions herein disclosed about 3% of the polymer passes through the pyrolysis zone without undergoing any substantial change.

The following examples, in which proportions are given by weight unless otherwise indicated, illustrate specific embodiments of this invention.

Example 1.—The reaction tube used for this pyrolysis was a standard iron pipe having an inside diameter of 2½ inches, a length of 42 inches and a wall thickness of approximately 3/16 of an inch. The pipe was heated by placing an electrical tube furnace 36 inches long around the iron pipe. Three thermocouples were inserted through the wall of the reaction pipe by means of thermocouple wells, one near the entrance end of the tube, one in the center and a third near the exit end of the tube. The reaction pipe was evacuated to remove air and any other gases before feeding commenced. Polytetrafluoroethylene subdivided to pass through a ⅛ inch screen was fed continuously by means of a ram extruder into the entrance end of the pipe at a feed rate of 1 lb. per hour. A vacuum pump was connected with the reaction pipe and the pressure inside the tube was maintained at 20 mm. of mercury throughout the period of the reaction. A maximum pyrolysis temperature of 860° C. was achieved in the reaction mixture at the center of the pipe. The thermocouples at the feed exit ends of the pipe read 593° C. and 816° C. respectively. The reaction was continued for one hour, during which the product gases were cooled in a water-cooled heat exchanger, then filtered to remove any solid material from the gas stream. At the feed rate of 1 lb. per hour the exposure time was calculated to be 0.9 second. Before stopping the reaction, a sample of the product gases was analyzed in a mass spectrometer and it was found to have the following composition:

	Approximate weight per cent
C_3F_6, hexafluoropropene	58
C_2F_4	37
C_4F_8	2
High boilers	1

Example 2.—Pyrolysis of polytetrafluoroethylene was carried out in the same pipe as described in Example 1 but under a variety of reaction conditions as noted below. The composition of the product gases was again determined by analysis in a mass spectrometer, the yields (expressed in weight percent based on the weight of polytetrafluoroethylene fed into the reaction tube) being as follows:

Reaction Temp. (° C.)	Reaction Pressure (mm. Hg abs.)	Feed Rate (lb./hr.)	Exposure Time (Sec.)	Yield in Weight Percent			
				C_2F_4	C_3F_6	Higher Boilers	Polymer Dust
650	5.1	3	0.08	81	14	2	3
650	12.5	3	0.15	84	11	2	3
705	2.5	3	0.05	84	11	2	3
705	89	3	1.4	48	31	18	3
790	65	0.7	4.0	33	61	3	3
830	50	2	1.1	32	57	8	3
860	61	1	2.9	16	68	13	3

Example 3.—In an apparatus of the kind described in Example 1 a series of experiments was performed under comparable conditions at relatively short pyrolysis times for the purpose of establishing the criticality of various limitations. These experiments showed that at temperatures above about 815°, an "exposure time" of less than 0.3 second fails to give hexafluoropropene as the main product. These results are set forth in Table 1.

TABLE I

Effect of pyrolysis conditions on yield of low molecular weight fluorocarbons from polytetrafluoroethylene

Maximum Pyrolysis Temperature, ° C.	Individual Temperature Readings, ° C.			Pressure, mm. Hg	Exposure Time, sec.	Tetrafluoroethylene	Hexafluoropropene	Perfluorocyclobutane	Hexafluoroethane	Tetrafluoromethane
	In	Center	Exit							
810	690	805	810	2.5	0.067	50	[1] 48	2	----------	----------
815 to 850	710	815	515	5.1	0.014	85	13	1	----------	----------
	705	850	805	10.2	0.093	88	8	1.6	2.1	----------
	595	815	780	17.8	0.098	72	18	1	----------	----------
	615	815	730	17.8	0.21	71	21	2	----------	----------
855 to 950	690	865	850	5.1	0.035	88	11	1	----------	----------
	615	855	900	5.1	0.042	88	11	0.2	----------	----------
	695	870	820	20.3	0.19	80	18	0.6	0.9	----------
	720	860	695	20.3	0.24	64	29	2.6	----------	----------
910 to 960	705	870	925	2.5	0.021	91	9	0.2	----------	----------
	630	900	955	5.1	0.025	88	11	0.3	----------	----------
	750	955	915	2.5	0.32	22	[2] 42	----------	25	3.2
	705	910	975	2.5	0.021	95	4	0.1	0.4	----------
965 to 1,100	790	955	1,040	2.5	0.021	90	10	0	0.7	----------
	920	1,010	1,095	2.5	0.021	66	10	----------	9	12

[1] Yield, 56 weight percent.
[2] Yield, 51 weight percent.

Each of the products obtained as described in the foregoing examples could be separated from the condensate by distilling, preferably under pressure, e. g. at a positive pressure of about 150 lbs. per sq. in. The hexafluoroethane is recoverable with the tetrafluoroethylene fraction and the mixture can be used in a tetrafluoroethylene cracking unit (as make-up to be added to recycle) in processes for converting monomeric tetrafluoroethylene to hexafluoropropene (cf. copending application of David A. Nelson, Serial No. 427,973, filed May 6, 1954). The data contained in these examples can best be interpreted upon comparison with the results obtained in prior art processes (cf. U. S. 2,406,153 and 2,404,374). From the analyses presented in the examples, and particularly in Table 1, it is evident that best yield of hexafluoropropene is obtained at maximum pyrolysis temperatures in the 750° to 960° C. range; that at constant "exposure time" variations in pressure cause small variations in hexafluoropropene content of the product (although pressure must be low, e. g. below 100 mm., to avoid formation of products other than tetrafluoroethylene and hexafluoropropene, both of which are valuable); that the hexafluoropropene content of the product is sensitive to "exposure time," this sensitivity being, however, not so pronounced at the higher temperatures; and that the selection of con-

ditions for obtaining hexafluoropropene as the main product must take into account some rather unexpected phenomena, viz (1) at "exposure times" below 0.3 sec. yields of hexafluoropropene are invariably bad when the temperature is above about 815° C.; (2) at temperatures below 750° C. the yield is rather poor, although less poor when the exposure time was comparatively long (ca. 31% at 705° C., 1.4 sec.; 42% at 10 to 15 sec.); (3) at temperatures in the 750°–960° C., at which yields are extremely poor at exposure times as high as 10 seconds, yields are comparatively good (in fact, optimum) at contact times of 0.9 sec., 1.4 sec., and 4.0 sec. The best conditions for obtaining optimum yields are: exposure times of not exceeding 5 seconds at 750°–960° C., and not less than 0.3 second if the temperature exceeds 815° C.

Hexafluoropropene, obtained as above described, may be copolymerized by known techniques with other monomers such as tetrafluoroethylene, ethylene, vinyl fluoride, vinyl chloride, methyl methacrylate, and the like to yield products which are particularly useful for molding and extruding into fibers, films and other shapes, including articles which are of value in the electrical insulation field.

I claim:

A process for preparing hexafluoropropene which comprises continuously feeding polytetrafluoroethylene into a reaction zone heated to a maximum pyrolysis temperature within the range of 750° C. to 960° C., continuing the heating in the said zone for an exposure time not in excess of 5 seconds, the said time being however not less than 0.3 second if the temperature exceeds 815°, the pressure being not in excess of 100 mm. of Hg, and withdrawing from the said zone the resulting gaseous pyrolysis mixture containing hexafluoropropene.

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