Montreal Protocol

Process Agents Task Force

Case Study #14

Photochemical synthesis of perfluoropolyetherpolyperoxide, precursors of Z-perfluoro-polyethers and difunctional derivatives.

May 2001

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CS-14 Photochemical synthesis of perfluoropolyetherpolyperoxide, precursors of Z-perfluoro-polyethers and difunctional derivatives.

1. ODS type: **CFC 12**

Application

Photochemical synthesis of perfluoropolyetherpolyperoxide, precursors of Z-perfluoro-polyethers and difunctional derivatives.

Process description

The process consists in a radical co-polymerisation of C_2F_4 and O_2 according to the following reaction:

$$(n + m)\, C_2F_4 + (\frac{n}{2} + m)\, O_2 \rightarrow (C_2F_4O)_n (C_2F_4OO)_m$$

The polymerisation is initiated by UV or gaseous radical initiator fed in a liquid agent (CFC 12) saturated with C_2F_4 and O_2. The characteristics of the raw material (called raw peroxi-oil) leaving the section are controlled by the process parameters (temperature, pressure, C_2F_4 / O_2 ratio).

During the polymerisation some parallel reactions take place:

$$\frac{1}{2} C_2F_4 + \frac{1}{2} O_2 \rightarrow COF_2$$

$$C_2F_4 + \frac{1}{2} O_2 \rightarrow C_2F_4O$$

$$C_2F_4 + F_2 \rightarrow C_2F_6$$

The off gases produced trough these reactions are sent to a thermal destruction unit.

Process flow diagram is reported in fig. 1 and 2. The plant consist of the following equipment: synthesis reactor, cooling exchanger, off gas scrubber, C_2F_4 drying column, radical initiator gas compressor or, in alternative, UV system, raw oil separation column, CFC 12 purification and evaporator. A C_2F_4 stream coming from the C_2F_4 production unit, dried with H_2SO_4, is metered to the synthesis reactor. The reactor is a continuous stirred tank reactor, cooled by an external cooling circuit, containing the reaction agent at low temperature (-50° to -90°C) at a pressure between atmospheric (UV synthesis) and 5

to 10 bar (radical initiator). The excess oxygen is recycled to the reactor by a compressor; the fresh oxygen make-up is fed into the recycling gaseous stream. The mixture of CFC 12 and raw peroxi-oil, extracted from the reactor, is fed to an evaporator from witch the oil, separated from the CFC 12, is sent to the post-treatment unit. The CFC 12 is fed to a distillation column in order to remove the low boiling by-products (COF_2, C_2F_6 and traces of CFC 12). The purified CFC 12, coming from the bottom, is recycled to the reactor.

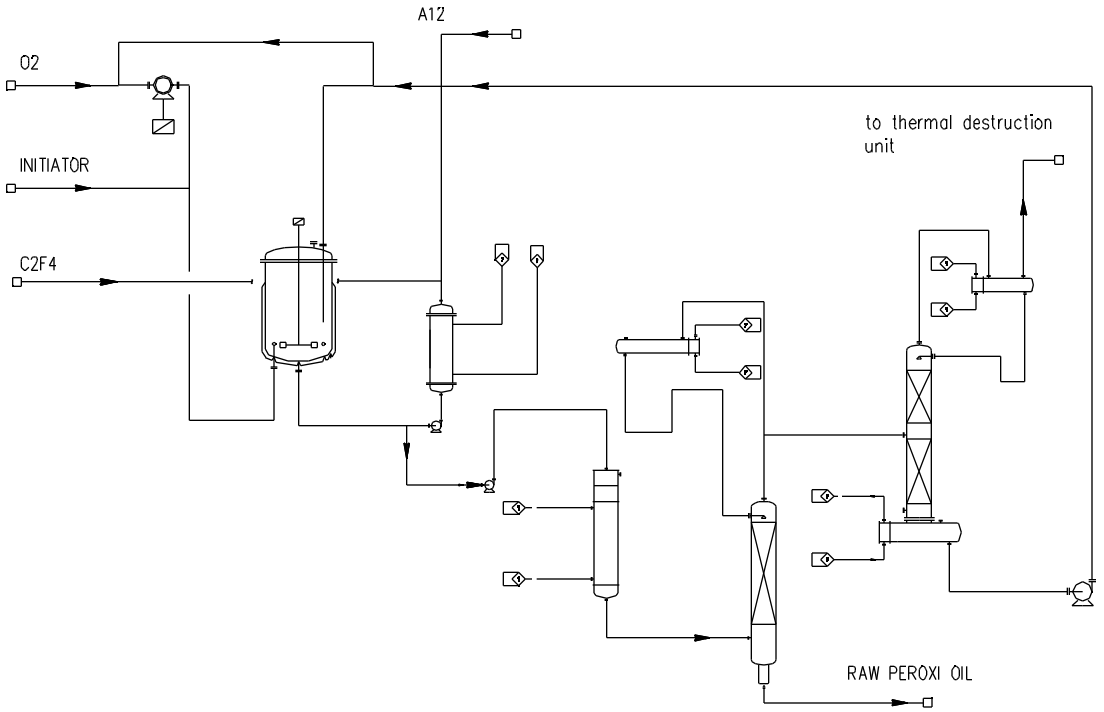

Fig. 1: Synthesis with radical initiator

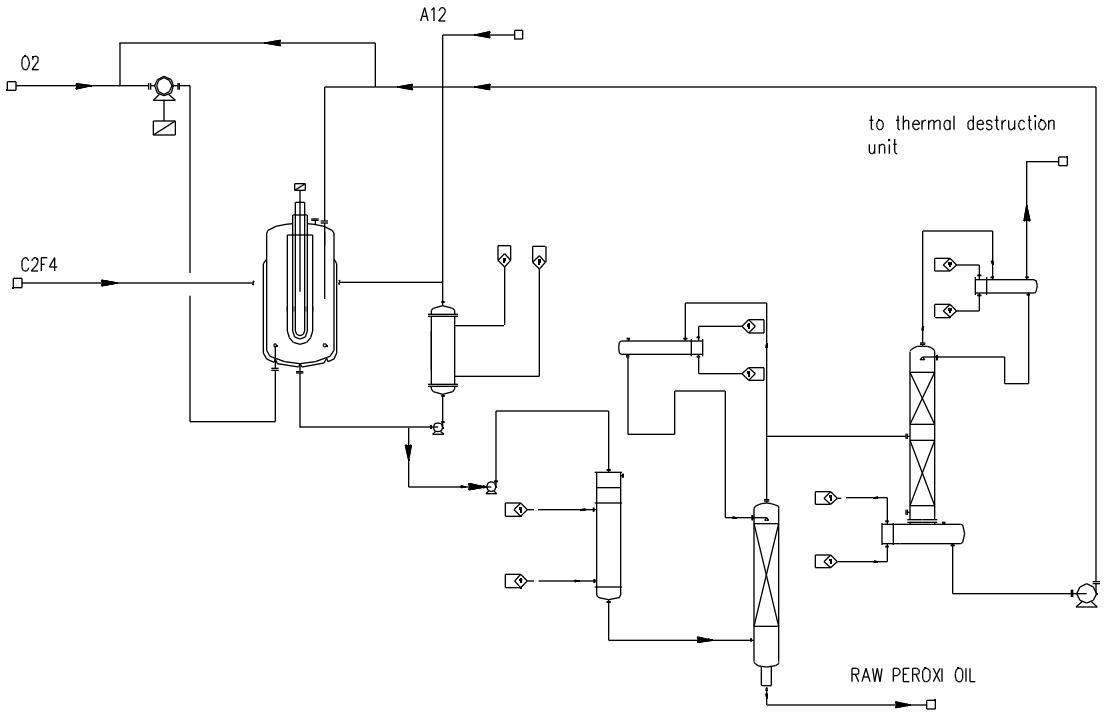

Fig. 2: UV Synthesis

Reason why selected process agent is needed

CFC 12 is liquid at the reaction temperatures (–50°C to –90°C); it dissolves both reactants tetrafluoroethylene and oxygen (whose mixture would otherwise explode); is transparent and inert to UV radiation, apart from a minimal release of radicals that are responsible for initiation and regulation of the molecular weight in case of UV initiated synthesis. Should the breakdown be more than minimal, degradation products would make it impossible to achieve commercial results.

Quantity used

72 t was used in 1997
A consumption of 350 t is expected in year 2000.

Emissions

Emissions are practically zero. CFC 12 is present only in the reactor loop. All unrecycled gaseous emissions are conveyed to a specially designed unit where they react with water at very high temperature and are fully converted to CO_2, HF and HCl. Total (organic and inorganic) fluorine emission allowed from this unit by local authorities amounts to less than one gram per hour (< 1 g/h)