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INDUSTRIAL PRODUCTION AND APPLICATION OF PERFLUOROALKYL-CONTAINING COMPOUNDS

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Compounds containing perfluoroalkyl group are industrially very useful products because of their extremely low surface tension and/or chemical and thermal resistance.

Asahi Glass Co. produces several thousand tons per year of commercial products comprising perfluoroalkyl of perfluoroalkylene-containing compounds. Those are shown in the Table.

Perfluoroalkyl and perfluoroalkylene containing compounds industrially produced and their applications

No. Compound	application
1. $C_nF_{2n+1}C_2H_4CH = CH_2$	Key monomer for oil and water repellent agent
2. $C_nF_{2n+1}COOH$, $-COONH_4$	Surfactant, emulsifier
3. $C_nF_{2n+1}CH = CH_2$	monomer used as a modifier of fluoropolymer
4. $CF_2 = CFO(CF_2CFO)_m(CF_2)_nCOOH$ (with CF_3 branch)	functional monomer for ion exchange membrane polymer used in chlor-alkali production
5. $CONCH_2(C_2F_4)_2CH_2NCO$	fluorinated polyurethane

Two synthetic methods for perfluoroalkyl group are industrially used, electrofluorination of corresponding hydrocarbon molecule and telomerization of perfluoroolefine.

The latter method has an advantage over the former in the fact that the optional chain length can be obtained, and that versatile compounds can be derived from the telomers of different chain length.

Therefore we adopted the telomerization method consistently for producing perfluoroalkyl groups and perfluorinated carbon chain contained in all the commercial products, and elaborated this process to make it an industrially feasible one, and established a continuous telomer production process, which has been operated now in the scale of 600 ton telomers per year, producing 75 Kg telomer per hour.

Starting with perfluoroalkylethyl iodide, which is simply made by ethylene adduct to perfluoroalkyl iodide with AIBN catalyst, two commercially important compounds are synthesized, perfluoroalkylethyl acrylate (A) and perfluorocarboxylic acid by our proprietary processes.

The synthetic process of A is based on a finding of a new reaction producing fluoroalcohol by use of dimethylformamide. Fluoroalcohol is reacted with acrylic acid to form ester. The reactions are summarized as follows.

$$RfC_2H_4I + HCON(CH_3)_2 + 2H_2O \xrightarrow[120\sim140\ ^\circ C]{} RfC_2H_4OH + (CH_3)_2NH\cdot HI + HCOOH$$

$$RfC_2H_4OH + CH_2{=}CHCOOH \xrightarrow[90\sim110\ ^\circ C]{} RfC_2H_4OC(O)CH{=}CH_2 + H_2O$$

Water is necessary in this reaction. However, if excessive amount of water exists, dehydrogen iodide reaction tends to dominate and perfluoroalkyl-ethylene increases. Yield of more than 90% of fluoroalcohol is obtained with continuous addition of water, using highly excessive amount of DMF, more than ten times as much as Rf ethyl iodide. DMF and iodine are recovered after fluoroalcohol is separated from aqueous solution containing DMF and dimethyl amine hydrogen iodide. Thus we established a complete pollution free process without any useless by-products.

Our process of manufacturing perfluoroalkyl carboxylic acid consists of the oxidation of perfluoroalkylethylene, Rf CH_2=CH. This is oxidized by ozone to form ozonide Rf  CH , this ozonide along with the by-product of aldehyde are further oxidised by peracetic acid to carboxylic acid. Applications of various derivatives of these compounds were explained.