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ELECTROCHEMICAL PROCESS OF MAKING FLUORINE-CONTAINING CARBON COMPOUNDS

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This application is a continuation-in-part of my copending application Ser. No. 677,407 (filed June 17, 1946), since abandoned. The latter was filed as a continuation-in-part of the following prior applications which thereafter were abandoned in its favor: Ser. Nos. 384,729 (filed March 22, 1941), 569,265 (filed December 21, 1944), and 626,434 (filed November 2, 1945).

This invention relates to my discovery of a basically new process of making fluorocarbons and other fluorine-containing carbon compounds. The process is simple in operation, does not involve the use or formation of free fluorine at any stage, and has great versatility in enabling the direct production of many types of product compounds using organic starting compounds which are readily available and relatively inexpensive. It is an electrochemical process and its utility has been demonstrated by extensive pilot plant operations employing a 2000-ampere cell, as well as by many laboratory experiments.

This process was publicly disclosed in the oral presentation on September 15, 1948, at the Portland, Oregon, session of the 114th meeting of the American Chemical Society, of five papers authored by me and my assistants. Abstracts of these papers had been previously published in the advance "Abstracts of Papers" volume issued by the society (pp. 42–0 to 45–0). News items relating thereto and briefly describing the process have been published in the society's magazine Chemical and Engineering News, vol. 26, p. 2428 (Aug. 16, 1948) and pp. 2878–9 (Sept. 27, 1948). These papers were subsequently published in the Journal of the Electrochemical Society, vol. 95, No. 2, pp. 47–67 (Feb. 1949).

Briefly stated, this new and useful electrochemical process involves electrolyzing a liquid hydrogen fluoride (HF) solution containing a fluorinatable organic starting compound, at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions, but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate. A wide variety of organic compounds are soluble in anhydrous liquid hydrogen fluoride and provide adequate electrolytic conductivity. Use can also be made of soluble organic and inorganic conductivity additives to permit of electrolyzing liquid hydrogen fluoride solutions thereof admixed with relatively insoluble organic starting compounds, such as alkanes, which do not provide adequate conductivity. Pure anhydrous liquid hydrogen fluoride, per se, is non-conductive. The electrolyte is free from water in more than a small proportion but need not be anhydrous in a strict sense.

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Excellent results can be obtained with simple single compartment electrolytic cell arrangements. No diaphragm is needed between electrodes. Fluorination can be completed in one step to directly obtain fully fluorinated product compounds which are relatively insoluble and either evolve with the cell gases or settle to the bottom of the cell from which they can be drained, depending upon their boiling points. The process is suitable for continuous as well as batch operation. The cell can be operated at atmospheric pressure. The cell and the cathodes can be made of iron or steel, and the anodes of nickel, and such cells have been satisfactorily operated at 5 to 8 volts, D. C., in producing a wide variety of product compounds.

The reaction mechanism is not fully understood but the electrolyzing process apparently transforms the organic starting compounds at or adjacent to the anode and may be regarded as an anodic process. Hydrogen is evolved at the cathode, being derived from the hydrogen fluoride; and will also evolve in the cell by derivation from other hydrogen-containing compounds which may be present. Fluorine is not evolved, and the reaction mechanism does not involve the formation of molecular (free elemental) fluorine as an intermediate agent.

Product compounds are obtainable (both cyclic and non-cyclic) which have the same number of carbon atoms and same carbon skeletal structure as do the starting compounds, but with partial or total fluorine atom replacement of hydrogen atoms and other atoms and radicals bonded to the carbon skeleton of the molecule. Fluorine addition occurs in the case of unsaturated and aromatic types of starting compounds to produce fully saturated product compounds. Non-cyclic compounds (in addition to cyclic compounds) having the same number of carbon atoms are ob-

tainable from cyclic starting compounds as the result of bond cleavage and fluorine addition. Also, the use of polycarbon cyclic and non-cyclic starting compounds generally results in appreciable yields of product compounds having fewer carbon atoms in the molecule, due to fragmentation of the carbon skeleton and fluorine addition. Compounds having a greater number of carbon atoms than the starting compounds are obtainable as the result of coupling of carbon radicals formed in the solution. The kinds and relative proportions of product compounds obtainable in any given case will depend upon the starting compound and the operating conditions. By proper selection it is possible to obtain excellent yields of desired products, which can be readily separated by fractional distillation from each other and from low-yield by-product compounds. In commercial operations, use can be made of the production of multiple products in building up stocks of many useful compounds from a much more limited number of starting compounds.

In some cases resinous material is formed in the cell but is generally soluble in the electrolyte solution and does not interfere with the operation. Resinous products containing combined fluorine in proportions up to 60% have been obtained. In many cases no solid residual materials are found even after extended use of the cell. In general, there is little or no corrosion of the electrodes.

To briefly indicate at this point the versatility of the process in enabling the production of fluorocarbon derivatives, mention is made (for illustration and not limitation) of the following types designated by generic formulae wherein R represents saturated fluorocarbon radicals (cyclic or non-cyclic) consisting solely of carbon and fluorine atoms: R'OR'' (obtainable from ethers), R'R''R'''N (obtainable from tertiary amines), R'R''NF (obtainable from secondary amines), RNF_2 (obtainable from primary amines), RCOF (obtainable from monocarboxylic acids),

R'COOR''

(obtainable from esters), RCN (obtainable from nitriles) and RSF (obtainable from mercaptans). Fluorocarbon compounds which contain combined chlorine can be obtained from chlorine-containing starting compounds (e. g., chloroacetic acid). Heterocyclic compounds containing one or more oxygen or nitrogen atoms in the ring can be obtained by replacement of the hydrogen atoms by fluorine atoms in starting compounds of corresponding structure.

True fluorocarbons (carbon fluorides containing only carbon and fluorine atoms) can be directly obtained from hydrocarbon starting compounds, and also by electrolyzing solutions of various hydrocarbon derivatives, to obtain substantial yields of fluorocarbons having the same number of carbon atoms as the starting compounds. For example, alkanes, alcohols and monocarboxylic acids can be employed to yield fluorocarbons having the same number of carbon atoms. In addition, fluorocarbons having fewer and more carbon atoms are produced. Fluorocarbons having fewer carbon atoms than the starting compound can also be produced from hetero compounds wherein carbon atoms are linked by non-carbon atoms, as in the case of ethers and secondary and tertiary amines; the hy groups being released to form corfluorocarbons. Fluorocarbons having fewer or more carbon atoms than the parent hydrocarbon groups can also be obtained from such compounds. A feature of the present process is that it provides a simple and economical procedure for making normally liquid fluorocarbons, having five or more carbon atoms in the molecule.

The formation of fluorocarbons is accompanied by the formation of fluorocarbon hydrides and partially fluorinated hydrocarbons, due to incomplete hydrogen replacement in the case of some molecules. The proportions depend upon the conditions. The fluorocarbon monohydrides and dihydrides are of particular value because they have a high degree of thermal stability and chemical inertness and are non-combustible, and yet the hydrogen atoms offer points of attack for the synthesis of fluorocarbon derivatives. Thus these fluorocarbon hydrides can be thermally chlorinated and brominated to yield the corresponding fluorocarbon chlorides and bromides, as disclosed in a paper published in the Journal of the American Chemical Society, vol. 68, pp. 968–969 (June 1946) of which I was a co-author.

Saturated fluorocarbons and fluorocarbon derivatives are obtainable in good yields ranging from the simplest compound, CF_4, which is a low-boiling gas, up to high-boiling compounds having eight or more carbon atoms in the molecule and having boiling points above 100° C.

The fluorocarbon and related compounds obtainable by this process have utility for many purposes. The saturated fluorocarbons, fluorocarbon hydrides, fluorocarbon ethers, and trifluorocarbon amines, for example, have a high degree of thermal stability and chemical inertness, they do not burn, and they have uniquely low refractive indices and dielectric constants as compared with ordinary organic compounds. The liquid compounds (containing five or more carbon atoms) have exceptionally low surface tensions and viscosities, coupled with high densities. These and other compounds can be used for such purposes (depending upon boiling points) as refrigerants, fire extinguishers, inert solvents and diluents, heat exchange fluids, turbine impellents, dielectrics, hydraulic mechanism fluids, and lubricants. The products of this process can also be used as intermediates in the synthesis of other chemical compounds. In particular, the fluorocarbon acid fluorides (RCOF) provide the reactive starting compounds for making a vast number of derivative compounds containing a fluorocarbon radical and having unique properties on that account.

All organic compounds potentially capable of reacting with fluorine can be employed to produce fluorine-containing carbon compound products by the present process. Fluorine is the most chemically active substance. No organic material is completely resistant to fluorine except carbon tetrafluoride (CF_4). Even the polycarbon saturated fluorocarbons can react by carbon-carbon bond cleavage and fluorine addition, the stable end product being CF_4.

As a practical matter in respect to the commercial utilization of the process, the hydrogen-containing organic compounds which contain at least one hydrogen atom bonded to a carbon atom in the molecule are of main interest. These can all be used for making fluorocarbons, and other fluorine-containing carbon compounds which contain at least one fluorine atom bonded to a carbon atom in the molecule. The sub-classes of these organic starting compounds of particu-