A combination process for the conversion of primary or secondary alkanols to perfluorinated acyl fluorides and/or perfluorinated ketones wherein said alkanols are esterified with acyl fluorides and the resulting partially fluorinated esters passed to an electrochemical fluorination step to produce perfluorinated esters which are thereafter cleaved on contacting with a source of fluoride ion under reacting conditions. Perfluorinated acyl fluoride resulting from said cleavage is recycled to the esterification step and the remaining perfluorinated acyl fluoride and/or perfluorinated ketone is recovered as product. In an alternative embodiment the perfluorinated ester is transesterified with a primary or secondary alkanol to produce a perfluorinated product, and a partially fluorinated ester resulting therefrom is recycled to the electrochemical fluorination step.
RECYCLE OF ACYL FLUORIDE AND ELECTROCHEMICAL FLUORINATION OF ESTERS

BACKGROUND OF THE INVENTION

This invention relates to the production of perfluorinated organic compounds from alkanols. It is broadly known to utilize electrochemical fluorination techniques to produce specific perfluorinated products from selected feeds. Such techniques to produce some given classes of products have not achieved widespread commercial utilization, however, at least in part due to the difficulty of providing an economically feasible system which can utilize inexpensive feed materials.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a process for producing perfluorinated acyl halides and/or perfluorinated ketones utilizing relatively inexpensive starting materials. It is a further object of this invention to continuously produce perfluorinated acyl fluorides for use in producing partially fluorinated esters for subsequent fluorination steps; it is yet a further object of this invention to produce specific perfluorinated ketones employing a mixture of perfluorinated acyl fluorides without the necessity of separating said mixture, and it is yet a further object of this invention to produce hexafluoroacetone; and it is still yet a further object of this invention to generate, in situ, makeup perfluorinated acyl fluoride to compensate for fluoride unavoidably lost, e.g., during the production of perfluorinated ketones from secondary alkanols.

In accordance with this invention, perfluorinated acyl fluoride from the fluoride ion cleavage of a perfluorinated ester is recycled to an esterification step for reaction with primary or secondary alkanols to produce partially fluorinated esters for a subsequent electrochemical fluorination step. In accordance with an alternative embodiment of the invention, partially fluorinated esters from an ester interchange are recycled to an electrochemical fluorination step.

BRIEF DESCRIPTION OF THE DRAWING

The drawing, forming a part hereof, is a schematic representation of an electrochemical fluorination unit in accordance with the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, perfluorinated ketones and/or perfluorinated acyl fluorides are prepared by a multistep process involving the following:

1. Esterification of primary or secondary alkanols with acyl fluorides;
2. Electrochemical fluorination of esters prepared in step (1) to produce perfluorinated esters;
3. Alkali metal fluoride cleavage of the perfluorinated esters prepared in step (2) to produce perfluorinated ketones and/or perfluorinated acyl fluorides; or
3'. Cleavage of the perfluorinated esters by 
HF \( H^+ + F^- \) catalysis; or
3'' Transesterification of the perfluorinated ester with a primary or secondary alkain to produce a perfluorinated product, hydrogen fluoride, and a partially fluorinated ester recyclable to (2); and

The use of esters derived from primary alkanols is herein described as Embodiment I whereas Embodiment II involves the use of esters derived from secondary alkanols. In the practice of the present invention, Embodiment I gives rise predominantly to perfluorinated acyl fluorides whereas Embodiment II gives rise to approximately equimolar quantities of perfluorinated ketone and perfluorinated acyl fluoride. The present invention is a combination process consisting of three basic steps (1–3), and a fourth step (4) which, by recycling a product from step (3) to step (1), provides an unobvious cooperation between the three basic steps and thus provides a simple integrated process for producing the desired products.

In accordance with Embodiment I of a combination esterification-electrochemical fluorination-fluoride ion cleavage process for the production of perfluorinated acyl fluorides, suitable esters to the electrochemical fluorination step are prepared by reacting C1 to C10 primary alkanols such as methanol, ethanol, n-propanol, n-butanol, 3-methylbutanol, n-hexanol, n-decanol and the like with C1 to C10, preferably C3 to C9, acyl fluorides such as acetyl fluoride, carbonyl fluoride, and trifluoroacetyl fluoride. These esters are perfluorinated in the electrochemical fluorination step and then cleaved with an alkali metal fluoride to yield approximately two mols of perfluorinated acyl fluoride per mol of perfluorinated ester. Two different perfluorinated acyl fluorides are produced from perfluorinated esters containing different numbers of carbon atoms in the alkyl and acyl portions. Sufficient perfluorinated acyl fluoride is conveniently recycled to the esterification step to sustain the overall process.

Although it is not intended to limit the scope of the instant invention unduly, the following simplified schematic representations describe some specific examples of Embodiment I of the present invention process:

A. EMBODIMENT I:

Conversion of primary alkanols to perfluoroacyl halides

1. Scheme No. 1: Ester feedstocks containing different numbers of carbon atoms in the alkyl and acyl portions

   \[ \text{Primary Alkanol} + \text{Acyl Fluoride} \rightarrow \text{Primary Ester} \]

   \[ \text{Primary Ester} \rightarrow \text{Perfluoroacyl Fluoride} \]

2. Scheme No. 2: Ester feedstocks containing different numbers of carbon atoms in the alkyl and acyl portions

   \[ \text{Primary Alkanol} + \text{Acyl Fluoride} \rightarrow \text{Primary Ester} \]

   \[ \text{Primary Ester} \rightarrow \text{Perfluoroacyl Fluoride} \]
In theory, sufficient perfluorinated acyl fluoride, i.e., trifluoroacetyl fluoride, should be produced in the cleavage step (3) to sustain the esterification step (1). However, some fluorine values are lost in some by-products such as carbon tetrafluoride and carbonyl fluoride and therefore, additional trifluoroacetyl fluoride for "make-up" must come to the esterification step (1) from some alternate source such as trifluoroacetyl fluoride make-up stream, by purchase, etc. The C₆ perfluorinated acyl fluoride produced in Scheme No. 1 can be hydrolyzed to give the valuable C₆ perfluorinated acid.

It is contemplated that a single perfluorinated acyl fluoride can be prepared in the instant process by employing an ester feedstock containing equal numbers of carbon atoms in the acyl and alkyl portions of the ester as shown in the following schematic representation:

**A. EMBODIMENT I**

b. Scheme No. 2: Ester feedstocks containing the same number of carbon atoms in the acyl and alkyl portions.

(1) Esterification Step

CH₃CH₂CH₂OH + CF₃CF₂CF₂O → CH₃CH₂CH₂O-CCF₂CF₂ + HF
Primary Alkanol (n-Propanol) Perfluorinated Acyl Fluoride (Perfluoro-propaonyl Fluoride)

(2) Electrochemical Fluorination Step

CH₃CH₂CH₂O-CCF₂CF₂ → CF₃CF₂CF₂O-CCF₂CF₂
Primary Ester Feedstock Perfluorinated Ester (Heptafluoro-n-propyl Perfluoro-propionate)

(3) Alkali Metal Fluoride Cleavage of Perfluorinated Ester To Give One Single Perfluorinated Acyl Fluoride

CF₃CF₂CF₂O-CCF₂CF₂ → 2 CF₃CF₂CF₂
Perfluorinated Ester Perfluorinated Acyl Fluoride (Perfluoro-propionate)

Sufficient perfluorinated acyl fluoride, i.e., perfluoro-propoxyfluoride, is produced in the cleavage step (3) to sustain the esterification step (1) and if desirable the balance of the perfluorinated acyl fluoride, e.g., perfluoro-propoxyfluoride, can be hydrolyzed to a valuable perfluorinated carbonylic acid, e.g., perfluoro-propionic acid.

Furthermore, in accordance with Embodiment I, the reaction of carbonyl fluoride with primary alkanols in a 1:1 molar ratio can be utilized to prepare suitable fluoroformate ester feedstocks.

**A. EMBODIMENT I**

c. Scheme No. 3: Fluoroformate esters as fluorination feedstocks

(1) Esterification Step

CH₃CH₃CH₂OH + COF₂ → CH₃CH₂(O-CF₂ + HF
Primary Acyl Partially Fluorinated Alkoxy Fluoride (Carbonyl Fluoroformate) (n-Butyl (n-Butanol) Fluoride)

(2) Electrochemical Fluorination Step

2 CH₃(CH₂)₃OH + COF₂ → 2 CF₃(CH₂)₃O-CF₂ + 2HF
Primary Acyl Carbonate Ester (Di-n-octyl Carbonate)

45 Carbonate Ester Perfluorinated Carbonate (Di-n-octyl carbonate) (n-Octanol) (Di-n-perfluoroctyl Carbonate)

(3) Alkali Metal Fluoride Cleavage of Perfluorinated Ester To Give Two Different Acyl Fluorides

CF₃CF₂CF₂O-CCF₂CF₂ → 2 CF₃CF₂CF₂
Perfluorinated Ester Perfluorinated Acyl Fluoride (Carbonyl Fluoroformate) (n-Octanoyl Carbonate) (Butyl (n-Butanol) Fluoride)

In theory, sufficient acyl fluoride (carbonyl fluoride) should be produced in the cleavage step (3) to sustain the esterification step (1). The loss of any fluorine values to various fluorine containing by-products can be made up with carbonyl fluoride from some other source such as by the electrochemical fluorination of CO₂ by purchase, etc. The C₆ perfluorinated acyl fluoride can be hydrolyzed to give the valuable C₆ perfluorinated carbonylic acid.

In accordance with Embodiment II of the present invention, secondary alkanols containing three to ten carbon atoms such as isopropanol, 2-butanol, 3-
hexanol, 4-methyl-2-pentanol, 2-octanol, 4-decanol and the like are reacted with C<sub>1</sub> to C<sub>10</sub>, preferably C<sub>1</sub> to C<sub>5</sub>, acyl fluorides such as acetyl fluoride, carbonyl fluoride, trifluoroacetyl fluoride and the like to give ester feedstocks for the electrochemical fluorination step resulting after cleavage, in the production of perfluorinated ketones and perfluorinated acyl fluorides. The perfluorinated acyl fluoride products can be selectively separated from the effluent and recycled to prepare additional ester feedstocks to the electrochemical fluorination step by reaction with the appropriate secondary alkane. The perfluorinated ketone compounds can be separated and used as chemical intermediates to prepare fluorine-containing alkane or used in special applications as dielectric agents.

Although not intended to limit the scope of the instant process unduly, the following simplified schematic representation describes an example of Embodiment II of the present invention process:

**B. EMBODIMENT II: Conversion of secondary alkane to perfluoroketones**

(a) Scheme No. 5:

1. **(1) Esterification Step**
   \[
   \begin{align*}
   \text{OH} & \quad \text{O} \\
   \text{CH}_2	ext{CH}_2	ext{CHO} + \text{CF}_2\text{CF} & \quad \rightarrow \quad \text{CH}_3	ext{O} \\
   \text{Secondary} \quad \text{Acyl Fluoride} & \quad \text{Partially Fluorinated} \\
   \text{Alkane} \quad \text{(Trifluoro-} & \quad \text{Ester} \quad \text{(Iso-} \\
   \text{acetyl) Fluoride) } & \quad \text{propyl) Trifluoroacetate)} \\
   \end{align*}
   \]

2. **(2) Electrochemical Fluorination Step**
   \[
   \begin{align*}
   \text{CH}_3	ext{O} & \quad \text{ECF} \\
   & \quad \text{CF}_3	ext{O} \\
   \text{HC} & \quad \text{O} \quad \text{CCF}_3 & \quad \rightarrow \quad \text{F} \quad \text{O} \quad \text{O} \quad \text{CCF}_3 \\
   \text{CH}_3 \quad \text{ECF} & \quad \text{CF}_3 \quad \text{O} \\
   & \quad \text{Cell} \\
   \text{Partially} \quad \text{Perfluorinated Ester} & \quad \text{(Heptaffluoroisopropyl} \\
   \text{Fluorinated} \quad \text{Trifluoroacetate)} & \quad \text{Ester} \\
   \text{(Trifluoroacetate)} & \quad \text{(Heptaffluoroisopropyl} \\
   \text{(Trifluoroacetate)} & \quad \text{Acyl Fluoride} \\
   \text{(Hexaffluoro-} & \quad \text{(Trifluoroacetyl} \\
   \text{isopropyl} & \quad \text{Fluoride} \\
   \text{Trifluoroacetate)} & \quad \text{(Trifluoroacetyl} \\
   \text{(Trifluoroacetate)} & \quad \text{Fluoride)}
   \end{align*}
   \]

3. **(3) Alkali Metal Fluoride Cleavage of Perfluorinated Ester to Give Perfluorinated Acyl Fluoride**
   \[
   \begin{align*}
   \text{CF}_3	ext{O} & \quad \text{O} \quad \text{O} \\
   & \quad \text{CF}_2\text{CF} \\
   \text{F} \quad \text{O} \quad \text{O} \quad \text{CCF}_3 & \quad \rightarrow \quad \text{O} \quad \text{O} \quad \text{F} \quad \text{O} \quad \text{CCF}_3 \\
   \text{CF}_3 \quad \text{MgF}_2 & \quad \text{CF}_2\text{CF} \\
   \text{Perfluorinated} \quad \text{Perfluorinated} & \quad \text{Acyl Fluoride} \\
   \text{Ester} \quad \text{(Heptaffluoro-} & \quad \text{(Trifluoroacetyl} \\
   \text{isopropyl) Ketone} & \quad \text{Fluoride) \\
   \text{Trifluoroacetate)} & \quad \text{Trifluoroacetate)}
   \end{align*}
   \]

The perfluorinated ketone, e.g., hexafluoroacetone, is separated for use as a dielectric or hydrogenated to the valuable alcohol 1,1,1,3,3,3-hexafluoroisopropanol.

The perfluorinated acyl fluoride product, e.g., trifluoroacetyl fluoride, is conveniently recycled to sustain the esterification step (1).

In a manner completely analogous to that shown for Embodiment I schemes No. 3 and No. 4, secondary alkane can also be converted to perfluoroketones in processes wherein carbonyl fluoride is the acyl halide intermediate and wherein the fluorofluoroformate and/or carbonate esters of secondary alkane are the ester intermediates.

In the practice of the present inventive process, fluorine values are generally lost to some extent in the form of carbon tetrafluoride and carbonyl fluoride by-products.

Therefore, in Embodiment II, e.g., insufficient acyl fluoride is produced in the fluoride ion cleavage step (3) to sustain the esterification step (1). The additional acyl fluoride required to sustain the esterification step (1) can be conveniently "made-up" by the use of minor amounts of a primary alkane such as ethanol as shown below:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} + \text{CF}_2\text{CF} & \quad \rightarrow \quad \text{CH}_3\text{O} \quad \text{CCF}_3 + \text{HF} \\
\text{Ethanol} \quad \text{Trifluoroacetyl} & \quad \text{Ethyl Trifluoroacetate} \\
\text{Fluoride} & \quad \text{Trifluoroacetate}
\end{align*}
\]

By inspection of the above representation, it can be seen that each mol of perfluoroethyl trifluoroacetate cleaves to two mols of trifluoroacetyl fluoride. Hence, one mol of trifluoroacetyl fluoride results in the cleavage step (3) for each mol of ethanol used in the esterification step (1). Thus, a suitable trifluoroacetyl fluoride level can be maintained in the manner to sustain the esterification step of the present process. Alternatively, ethyl trifluoroacetate, prepared separately, can be admixed with, e.g., isoamyl trifluoroacetate and fed to the ECF cell. However, it is particularly convenient to provide a feedstream comprising a mixture of a suitable primary alkane such as ethanol and a suitable secondary alkane such as isopropanol to be fed directly to the esterification step of the inventive process such that sufficient trifluoroacetyl fluoride for recycle would be produced in the cleavage step of said process.

As mentioned earlier, carbonyl fluoride can be the acyl fluoride intermediate in the Embodiment II of the process for converting the secondary alkane to fluoroformate or carbonate esters and ultimately to perfluoroketones. However, even if other acyl fluorides, such as trifluoroacetyl fluoride, are present in the system, minor amounts of carbonyl fluoride can be generated in situ as a result of the decomposition of some intermediate and/or product compounds. This byproduct quantity of carbonyl fluoride need not be separated and removed from the process.

For example, in the use of the present invention to produce hexafluoroacetone and trifluoroacetyl fluoride, one can recycle a mixture of by-product carbonyl fluoride along with the trifluoroacetyl fluoride to the esterification step. As shown in the foregoing schemes, mixtures of the resulting trifluoroacetate and fluoroformate esters of isopropanol can be used in Embodiment II to produce a mixture of hexafluoroacetone, trifluoroacetate fluoride and carbonyl fluoride (a by-product not shown in the above simplified equations). This technique eliminates the necessity of making the difficult separation of carbonyl fluoride and trifluoroacetyl fluoride before recycling the acyl fluoride to the esterification step and also minimizes the loss of fluorine values from the process.
This is because the mixture of carbonyl fluoride and trifluoroacetyl fluoride can be reacted with a secondary alkanol to give a corresponding mixture of partially fluorinated esters as follows, e.g., and

\[
\begin{align*}
\text{CF}_2\text{CF}_2\text{O} & \quad \text{OH} \\
\text{CF}_2\text{H} & \quad \text{CH}_2 \\
\text{CF}_2\text{H} & \quad \text{CH}_2
\end{align*}
\]

This mixture of partially fluorinated esters can be recycled to the electrochemical fluorination cell to give perfluorinated esters as follows, e.g.,

\[
\begin{align*}
\text{CF}_2\text{H} & \quad \text{CFOCF} \\
\text{CF}_2\text{H} & \quad \text{CFOCCF}_3
\end{align*}
\]

On fluoride ion cleavage, each of these perfluorinated esters gives the desired perfluorinated ketone, e.g.,

\[
\begin{align*}
\text{CF}_2\text{H} & \quad \text{C}=\text{O} \\
\text{CF}_2\text{H} & \quad \text{COF} + \text{CFCF}_2
\end{align*}
\]

plus a mixture of, e.g.,

\[
\begin{align*}
\text{COF} & \quad \text{CF}_2\text{H} \quad \text{CF}_2\text{H}
\end{align*}
\]

which can be used to start the cycle over again.

In the esterification step of the present process, the alkanol and acyl fluoride are reacted either batchwise or continuously under suitable conditions of temperature, pressure, and contact time as is known in the art to give the desired ester product. Generally, the alkanol and acyl fluoride are used in an approximately 1:1 molar ratio except in reactions involving the use of carbonyl fluoride directed toward the preparation of carbonate esters wherein two mols of alkanol are used per mol of carbonyl fluoride. The use of an acid acceptor such as pyridine is preferred in the formation of the carbonates but the use of an acid acceptor is optional in the preparation of the trifluoroacetates produced by the reaction of alkanol and trifluoroacetyl fluoride. Generally the use of an acid acceptor such as alkali metal carbonate is preferred for use in the preparation of acetates produced by the reaction of alkanol and acetyl fluoride. Fluorofomates and carbonates are prepared by the direct interaction of carbonyl fluoride and alkanol. It is presently preferred to use an acid acceptor in the preparation of the carbonate esters.

The esterification process is normally carried out in the temperature range of -80°C to +20°C and, if desirable, in the absence of any diluent. For example, trifluoroacetyl fluoride in the vapor form can be passed directly into isopropanol at -40°C to 0°C to give high yields of the ester isopropyl trifluoroacetate. This esterification product contains hydrogen fluoride byproduct but is suitable to be passed to the electrochemical fluorination step of the present process. For the preparation of acetates requiring the use of acid acceptors, it may be convenient to employ low boiling perhalogenated solvents such as 1,1,2-trichloro-1,2,2-trifluoroethane to provide a system which can be refluxed under mild temperature conditions to effect the esterification. The product ester from such runs can be isolated and purified by methods well known in the art as extraction, extractive distillation, fractionation, etc.

The fluoroformates prepared by the use of carbonyl fluoride are generally prepared at low temperature conditions such as -20°C to 0°C. The carbonyl fluoride vapor is passed directly into the cold alkanol. The so-formed fluoroformates are readily converted to carbonates by adding an acid acceptor such as pyridine and sufficient alkanol to provide two mols of alkanol per mol of carbonyl fluoride and allowing the temperature to increase to about 25°C. The fluoroformates and carbonates containing hydrogen fluoride are sufficiently pure to be passed to the electrochemical fluorination step of the present process.

The esterification reaction can be carried out over the time period of a few minutes to several hours. The reaction rates to fluoroformates and trifluoroacetates are rapid and for all practical purposes the esterifications are complete after the desired weight of the gaseous acyl fluoride has been absorbed by the alkanol reactant.

The esterification reaction is conveniently carried out at atmospheric pressure or slightly less than atmospheric pressure as it is desirable to manipulate the often very volatile reactants and products at low temperatures.

Since hydrogen fluoride is produced as a by-product in the esterification step it is desirable to carry out this step in apparatus which is inert to HF such as monel, KEL-F fluorocarbon polymer, and the like.

In the electrochemical fluorination step of the present process, the electrochemical fluorination is carried out generally within the broad teaching of U.S. Pat. Nos. 3,511,760, 3,511,762 and 3,711,396. The electrochemical fluorination step can be carried out over a broad range of temperatures and pressures limited only by the freezing point and the vapor pressure of the specific HF-containing electrolyte system such as the KF·2HF electrolyte. It is preferred that the electrochemical fluorination process be carried out at temperatures such that the vapor pressure of the electrolyte is less than about 50 mm Hg. Presently, the preferred temperature range is about 70° to about 120°C.

Current densities are preferably in the range of 100-300 milliamperes per square centimeter of anode geometric surface area but current densities in the range of 50-1000 milliamperes per square centimeter are suitable. In general, current densities will be high enough so that anodes of moderate size can be employed yet low enough so that the anode is not corroded or disintegrated. Voltages in the range of 4 to 20 volts per unit cell can be used.

Feed rates to the electrochemical fluorination cell vary over a broad range, however, in general the upper limit on flow rate will be that beyond which the feedstock begins to escape from the porous carbon anode into the bulk of the electrolyte. The lower limit of the feed rate will be determined by the requirement to supply the minimum amount of feedstock sufficient to prevent evolution of free fluorine. Generally gaseous feed-
stock flow rates within the range of 3 to 600 preferably 12 to 240 ml (STP) per minute per square centimeter of anode cross-sectional area are satisfactory. In terms of anode area, gaseous feed rates in the range of 0.5 to 10 milliliters per minute per square centimeter of anode geometric surface area are suitable.

The feedstock and products obtained therefrom are retained in the cell for a period of time which is usually less than one minute. This is because the feed is introduced into the bottom of the anode and the product is taken out of the top in a continuous operation as opposed to a batch process. Unconverted feed and partially fluorinated materials can be recycled to the cell for the production of more highly fluorinated products. In the present process the perfluorinated ester can be fractionated from the cell effluent and passed to the anode metal fluoride cleavage step (3).

In the anode metal fluoride cleavage step of the present process, the perfluorinated ester, fractionated from the electrochemical fluorination cell effluent, is contacted with a bed of an anode metal fluoride such as sodium fluoride maintained in the temperature range of 80° to 220°C under conditions to give a mixture of perfluorinated ketone and/or perfluorinated acyl fluoride. Partially fluorinated ester intermediates in the electrochemical fluorination cell effluent should be recycled to the electrochemical fluorination cell because such intermediates on contact with sodium fluoride at an elevated temperature are highly fragmented to lower molecular weight materials. Some cleavage of the perfluorinated ester takes place in the electrochemical fluorination cell in the temperature range of about 100°C. Operation of the anode metal fluoride bed at about 100°C effects the cleavage of the perfluorinated ester and the fluoride bed absorbs any HF which may be in the ester feed whereas operation of the anode metal fluoride bed at about 200°C effects the cleavage of the perfluorinated ester but the bed does not absorb the HF at this higher temperature.

In another inventive though less preferred embodiment of the present process, the cleavage and esterification steps can be essentially combined. This can be accomplished by introducing the suitable alkanol, either a primary or secondary alkanol depending upon the ultimate products desired, into the process at a point in which it contacts the perfluorinated ester. Such a convenient point is the electrochemical fluorination cell effluent from which the partially fluorinated products have been removed for recycle to the cell.

The contacting of the alkanol with the perfluorinated ester is carried out under transesterification conditions such that at least a substantial amount of perfluoroketone or perfluoroacyl fluoride is produced. Such products are formed through the rapid decomposition of the corresponding unstable perfluoroalcohols which are formed as intermediates. Other products of this transesterification step are hydrogen fluoride and the ester of the feed alkanol and the corresponding acyl fluoride. The ester is separated and introduced as the primary feed to the cell and the perfluoroketone or perfluoroacyl fluoride is separated from the hydrogen fluoride and removed from the process as product. The hydrogen fluoride is returned to the process for ultimate conversion in the cell. For example the ester interchange and subsequent decomposition can be as follows:

$$
\text{C}_2\text{F}_5\text{O} \rightarrow \text{C}_2\text{F}_5\text{O} \rightarrow \text{C}_2\text{H}_4\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4\text{O} \rightarrow \text{C}_2\text{F}_5\text{O} \rightarrow \text{C}_2\text{H}_4\text{CH}_2\text{OH} + \text{HF}
$$

FIG. 1 shows a simplified schematic representation of the present invention process. The suitable alkanol or mixture of alkanols is introduced as primary feedstock into the process through line 32. Make-up amounts of the suitable fluorides, if used, are introduced through line 34. The alkanol and acyl fluoride pass into esterification zone 95 where they contact recycle acyl fluoride from line 28 and form the fluorinatable ester. Esterification zone 95 can comprise one or more reactors and can include related heating means, hold tanks, separations means, control means, and other apparatus suitable for producing the desired fluorinatable ester stream.

The fluorinatable ester is passed through line 36, and combined with partially fluorinated recycle ester from line 18, and then passed into electrochemical fluorination zone 45 in which it contacts an HF-containing electrolyte under electrolysis conditions suitable for producing a perfluorinated ester. Hydrogen fluoride, another principal feedstock, is introduced into the process through line 12. Electrochemical fluorination zone 45 can comprise one or more cells together with associated electrodes, control apparatus, power supply, etc., suitable for fluorinating the feed ester at maximum conversion consistent with minimum by-product formation.

By-product hydrogen exits the electrochemical fluorination zone (by means not shown) and fluorinated organic effluent passes from the electrochemical fluorination zone 45 to separation zone 55 via line 16. Separation zone 55 can comprise one or more separation means such as fractionators which are sufficient to separate partially fluorinated esters. Such partially fluorinated esters are passed from separation zone 55 through line 18 for recycle to electrochemical fluorination zone 45.

A perfluoroester-containing stream passes from separation zone 55 to cleavage zone 65 which can comprise one or more reactors with associated support apparatus in which the perfluoroester can contact a solid alkali metal fluoride under conditions suitable to substantially cleave the ester into perfluoroketone and/or perfluoroacyl fluoride products. The cleavage products exit the cleavage zone 65 via line 22 and are passed into separation zone 75. Separation zone 75 can comprise one or more conventional separation units such as fractionators, extractors, adsorption units, etc., which are suitable for isolation and recovery of the desired products of the process.

A perfluoroacyl fluoride-containing stream is passed from separation zone 75 via line 26 to separation zone 85 in which by-products are separated and removed from the process through line 30. Recycle acyl fluorides pass from separation zone 85 via line 28 and are introduced into esterification zone 95.

Hydrogen fluoride will generally be carried out of the electrochemical fluorination zone 45 to some degree but can be separated from organic products by conventional means such as adsorption at one or more convenient points (not shown) in the process and recycled back to the fluorination zone.
CALCULATED ILLUSTRATIVE EMBODIMENT

An illustrative method for carrying out one specific embodiment of the process of this invention is described below with reference to FIG. 1. The system discussed is based on Embodiment II, scheme No. 5 which shows the production of hexafluoroacetone with recycle of the trifluoroacetyl fluoride product to the esterification reactor. In the FIGURE the numerals have the following meanings:

10 — Recycle Stream and Fresh Ester Feedstock
12 — Hydrogen Fluoride Inflow
45 — Electrochemical Fluorination (ECF) Zone
16 — Electrochemical Fluorination Cell Effluent
55 — Fractionation Column
18 — Partially Fluorinated Ester Intermediates Recycle to ECF Zone
20 — Perfluorinated Ester, CF₃COF Stream
65 — Alkali Metal Fluoride Cleavage Reactor
22 — Effluent from Alkali Metal Fluoride Cleavage Reactor
75 — Fractionation Column
24 — Perfluorinated Ketone Product
26 — Trifluoroacetyl Fluoride, CF₃COF Stream
85 — Fractionation Column
30 — CF₃COF Stream
28 — Trifluoroacetyl Fluoride Line
95 — Esterification Reactor
32 — Isopropanol Feed Line
34 — "Make-up" Trifluoroacetyl Fluoride Feed Line

5

Returning now to FIG. 1, the invention will be more fully explained with respect to producing hexafluoroacetone. The perfluorinated ester is cleaved to hexafluoroacetone and trifluoroacetyl fluoride. These products along with minor amounts of carbon tetrafluoride and carbonyl fluoride are passed to column 75 to separate hexafluoroacetone product as bottoms through conduit 24. The trifluoroacetyl fluoride, carbon tetrafluoride and carbonyl fluoride are taken overhead through conduit 26 to fractionation column 85. In column 85 the lower boiling carbonyl fluoride and carbon tetrafluoride are passed overhead through line 30 and the trifluoroacetyl fluoride is passed via conduit 28 to the esterification reactor 95 for conversion to additional isopropyl trifluoroacetate feedstock. Optionally, some or all of the carbonyl fluoride present in line 26 can be combined with the trifluoroacetyl fluoride and passed via line 28 into the esterification zone.

In a calculated run assuming a 25% per pass hydrogen replacement in the electrochemical fluorination zone, Table I indicates the approximate compositions of the streams shown in FIG. 1. One mole of heptafluoroisopropyl trifluoroacetate counts as one mole of hexafluoroacetone and one mole of trifluoroacetyl fluoride. The amount of hydrogen fluoride carried from the ECF zone 45 will vary considerably depending on a number of parameters but approximately 1 mol of HF should pass through line 16 per hour. The values in Table I are based on the assumption of a steady state operation at a current level of 536 amperes (10 Faradays/hour) with a current efficiency of 90% for the conversion of C-H to C-F.

The cleavage zone contains beds of granular sodium fluoride maintained at about 150°C. In the esterification zone, the temperature is maintained at about 0°C with a residence time of about 30 minutes.

### TABLE I

**PRODUCTION OF HEXAFLUOROACETONE AND TRIFLUOROACETYL FLUORIDE BY THE ALKALI METAL FLUORIDE CLEAVAGE OF HEPTAFLUOROISOPROPYL TRIFLUOROACETATE**

<table>
<thead>
<tr>
<th>Components</th>
<th>Flow Rate (Moles/ Hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>4.50 (10)</td>
</tr>
<tr>
<td>Isopropyl Trifluoroacetate</td>
<td>0.90 (10)</td>
</tr>
<tr>
<td>Partially Fluorinated</td>
<td>0.257 (10)</td>
</tr>
<tr>
<td>Isopropyl Trifluoroacetates</td>
<td>0.257 (10)</td>
</tr>
<tr>
<td>Trifluoroacetyl Fluoride</td>
<td>0.579 (10)</td>
</tr>
<tr>
<td>Lights (CF₃COF, CF₃CF₂F, CF₃F)</td>
<td>0.193 (10)</td>
</tr>
<tr>
<td>Hexafluoroacetone</td>
<td>0.514 (10)</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.643 (10)</td>
</tr>
</tbody>
</table>

Under these conditions the principal streams of the process will contain the specific components and in the approximate amounts shown in Table I whereas the stream numbers correspond to those of FIG. 1.

While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

What is claimed is:

1. A process for producing perfluorinated acyl fluorides comprising in combination:
   1. contacting a primary alkanol with an acyl fluoride under esterification conditions to produce a partially fluorinated ester;
   2. passing said partially fluorinated ester to an electrochemical fluorination cell to produce a perfluorinated ester;
   3. cleaving said perfluorinated ester to produce said perfluorinated acyl fluorides and acyl fluoride for recycle;
4. recycling a portion of said acyl fluoride from step (3) to step (1) to sustain said esterification; and
5. recovering a portion of said perfluorinated acyl fluoride as product.

2. A process according to claim 1 wherein said alkanol is a C₃ to C₁₀ primary alkanol and said acyl fluoride is a C₁ to C₁₀ acyl fluoride.
3. A process according to claim 1 wherein said alkanol is selected from the group consisting of n-hexanol, n-propanol, n-butanol, and n-octanol and said acyl fluoride is selected from trifluoroacetyl fluoride, perfluoropropanoyl fluoride and carbonyl fluoride.
4. A process according to claim 1 wherein said cleavage is carried out by passing said perfluorinated ester over an alkali metal fluoride catalyst at a temperature within the range of 80°C to 220°C.
5. A method according to claim 1 wherein said cleavage is carried out by contacting said perfluorinated ester with an alkali metal fluoride catalyst.
6. A method according to claim 1 wherein said electrochemical fluorination step is carried out by passing feed into the bottom of an anode and taking the product out of the top in a continuous operation so that the residence time for the feed and products within the cell is less than 1 minute.
7. A process for producing perfluorinated ketones comprising in combination:
   1. contacting a secondary alkanol with an acyl fluoride under esterification conditions to produce a partially fluorinated ester;
   2. passing said partially fluorinated ester to an electrochemical fluorination cell to form a perfluorinated ester;
   3. cleaving said thus formed perfluorinated ester to produce said perfluorinated ketone and perfluorinated acyl fluoride;
   4. recycling said perfluorinated acyl fluoride from said step (3) to said step (1) to sustain esterification; and
   5. recovering said perfluorinated ketone as product.
8. A method according to claim 7 wherein said alkanol is a C₃ to C₁₀ secondary alkanol and said acyl fluoride is a C₁ to C₁₀ acyl fluoride.
9. A method according to claim 7 wherein said alkanol is isopropanol and said acyl fluoride is acetyl fluoride.
10. A method according to claim 7 wherein said cleavage is carried out by passing said perfluorinated ester over an alkali metal fluoride catalyst at a temperature within the range of 80°C to 220°C.
11. A method according to claim 7 wherein said cleavage is carried out by passing said perfluorinated ester over an HF catalyst.
12. A method according to claim 7 wherein make-up acyl fluoride is produced by passing a minor amount of a primary alkanol into the esterification step.
13. A method according to claim 12 wherein said primary alkanol is ethanol, said secondary alkanol is isopropanol and said acyl fluoride is trifluoroacetyl fluoride.
14. A method according to claim 13 wherein said electrochemical fluorination is carried out by passing said partially fluorinated ester to the bottom of an anode and recovering product from top of said anode in a continuous operation, the contact time for feed and products within the cell being less than 1 minute.
15. A method according to claim 7 wherein said electrochemical fluorination is carried out by passing said partially fluorinated ester to the bottom of an anode and recovering product from top of said anode in a continuous operation, the contact time for feed and products within the cell being less than 1 minute.
16. A process for producing perfluorinated products comprising in combination:
   A. passing a partially fluorinated ester to an electrochemical fluorination cell to form a perfluorinated ester;
   B. contacting said perfluorinated ester under transesterification conditions with a primary or secondary alkanol to produce said perfluorinated product, hydrogen fluoride and a partially fluorinated ester; and
   C. recycling said partially fluorinated ester to said step (A).
17. A process according to claim 16 wherein said alkanol is a secondary alkanol and said product is a ketone.
18. A process according to claim 16 wherein said alkanol is isopropanol and ketone is hexafluoroacetone.

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