

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 June 2001 (07.06.2001)

PCT

(10) International Publication Number
WO 01/40174 A1

(51) International Patent Classification⁷: C07C 311/48,
C08F 214/22, C07C 303/38

Katharina [DE/US]; 2100 F. Haven Road, Wilmington,
DE 19809 (US).

(21) International Application Number: PCT/US00/32672

(74) Agent: SIEGELL, Barbara, C.; E.I. du Pont de Nemours
and Company, Legal Patent Records Center, 1007 Market
Street, Wilmington, DE 19898 (US).

(22) International Filing Date: 1 December 2000 (01.12.2000)

(25) Filing Language:

English

(81) Designated States (national): AU, CA, CN, JP, KR, SG,
US.

(26) Publication Language:

English

(84) Designated States (regional): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(30) Priority Data:
60/168,539 2 December 1999 (02.12.1999) US

Published:

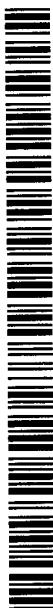
— With international search report.

(71) Applicant (for all designated States except US): E.I. DU
PONT DE NEMOURS AND COMPANY [US/US]; 1007
Market Street, Wilmington, DE 19898 (US).

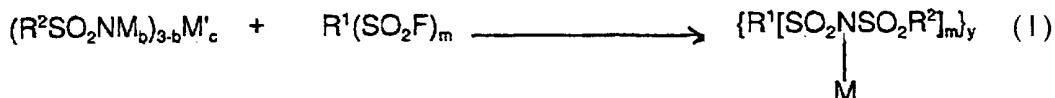
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(72) Inventor; and

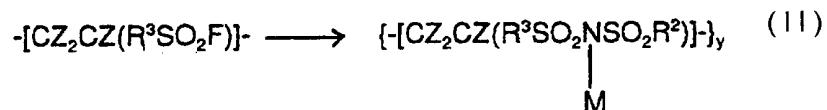
(75) Inventor/Applicant (for US only): BLAU, Hanne, Anna,



(54) Title: METHOD FOR PREPARING IMIDES FROM SULFONYL FLUORIDES



M



M

(57) Abstract: This invention discloses a method for preparing imides (I) and (II) from compounds having a sulfonyl fluoride functional group. The imides so prepared are useful in a variety of catalytic and electrochemical applications. (I) or polymer comprising the unit (II)

TITLE

METHOD FOR PREPARING IMIDES FROM SULFONYL FLUORIDES

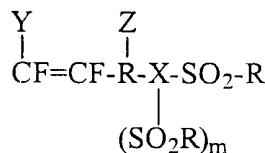
FIELD OF THE INVENTION

This invention is directed to a method for preparing imides from 5 compounds having a sulfonyl fluoride functional group. The imides so prepared are useful in a variety of catalytic and electrochemical applications.

BACKGROUND OF THE INVENTION

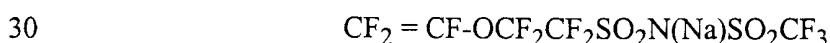
Compounds having a sulfonyl fluoride functional group are well known in the art. In particular, vinyl ethers and olefins having a fluorosulfonyl fluoride 10 group have been found to be particularly useful as monomers for copolymerization with tetrafluoroethylene, ethylene, vinylidene fluoride and other olefinic and fluoroolefinc monomers to form polymers which, upon hydrolysis are converted to highly useful ionomers. One area of important use for ionomers so formed is in the area of lithium batteries. See for example Connolly et al, U.S. 15 Patent No. 3,282,875 and commonly assigned Serial Numbers 09/023,244 and Serial No. 09/061,132.

It is also known to prepare imides from compounds having sulfonyl fluoride functionality particularly fluorinated organic sulfonyl imides are known in the art. For example, DesMartea, U.S. Patent No. 5,463,005, discloses 20 substituted perfluoro-olefins of the formula



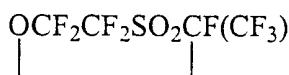
where X = CH or N, Z = H, K, Na, or Group I or II metal, R = one or more 25 fluorocarbon groups including fluorocarbon ethers and/or sulfonyl groups and/or perfluoro non-oxy acid groups, Y = perfluoroalkyl or F, and m = 0 or 1.

Xue, Ph.D. thesis, Clemson University, 1996, discloses the formation of the monomer



by reaction of $\text{CF}_2 = \text{CF}-\text{OCF}_2\text{CF}_2\text{SO}_2\text{Cl}$ with $\text{CF}_3\text{SO}_2\text{NHNa}$ in the presence of Na_2CO_3 in acetonitrile. However, Xue's method is not applicable to the sulfonyl fluoride species without first protecting the double bond.

Further disclosed by Xue, op.cit, is $\text{CF}_3\text{SO}_2\text{NNa}_2$ made by combining $\text{CF}_3\text{SO}_2\text{NHNa}$ and NaH in THF and reacting for four hours at room temperature. The inventors hereof have determined that Xue's method of preparation provides a conversion of less than 10% from $\text{CF}_3\text{SO}_2\text{NHNa}$ to $\text{CF}_3\text{SO}_2\text{NNa}_2$. No method 5 of separation is provided, nor is any method provided for preparing the $\text{CF}_3\text{SO}_2\text{NNa}_2$ at higher yield. Thus no means is provided for producing $\text{CF}_3\text{SO}_2\text{NNa}_2$ in a highly purified state. Xue suggests that $\text{CF}_3\text{SO}_2\text{NNa}_2$ can be reacted with a cyclic sulfone of the formula



10

to produce the vinyl ether monomer, $\text{CF}_2 = \text{CF-OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$. Also disclosed by Xue is a reaction between $\text{CF}_2 = \text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$ and $\text{CF}_3\text{SO}_2\text{NHNa}$ to produce an unusable complex mixture of products. Xue makes 15 no suggestion that $\text{CF}_3\text{SO}_2\text{NNa}_2$ is effective at converting sulfonyl fluoride containing compounds to imides.

Meußdoerffer et al., Chemiker Zeitung, 96. Jahrgang (1972) No. 10, 582-583 discloses a method for synthesizing RSO_2NH_2 wherein R is perfluoroalkyl.

20 Feiring et al., WO 9945048(A1), provides a method for imidizing fluorinated vinyl ether monomers containing a sulfonyl fluoride group by first protecting the double bond and then converting the sulfonyl fluoride into an imide.

Armand et al, EPO 0 850 920 A2, discloses a method for imidizing 25 sulfonyl fluoride and chloride species containing aromatic rings.

SUMMARY OF THE INVENTION

The present invention provides for a process comprising: Contacting, in a liquid dispersion or solution, a composition comprising a sulfonyl amide salt represented by the formula:

30 $(\text{R}^2\text{SO}_2\text{NM}_b)_{3-b}\text{M}'_c$ (III)

wherein R^2 is aryl, fluoro-aryl, or XCF_2 — where X is H, halogen, fluorinated or non-fluorinated linear or cyclic alkyl radicals having 1-10 carbons, optionally substituted by one or more ether oxygens, M' is an alkaline earth metal, $b = 1$ or 2, $c = 0$ or 1, M is an alkaline earth when b is 1 or an alkali metal when b is 2 and $c = 0$, and M 35

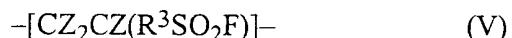
is alkali metal when $b = 1$ and $c = 1$, with the proviso that c is not equal to 1 when $b = 2$

with

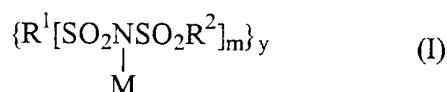
5 a non-polymeric sulfonyl fluoride composition represented by the formula $R^1(SO_2F)_m$ (IV)

10 wherein $m = 1$ or 2, where, when $m = 1$, R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbyl radical, except perfluoroolefin, having 1-12 carbons optionally substituted by one or more ether oxygens, or tertiary amino; or, when $m = 2$, R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbenyl radical having 1-12 carbons optionally substituted by one or more ether oxygens;

15 or with a polymeric sulfonyl fluoride composition comprising monomer units represented by the formula

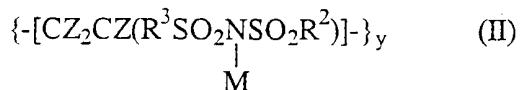


20 wherein R^3 is a diradical selected from the group consisting of fluorinated or non-fluorinated alkenyl, including oxyalkenyl or fluoroxyalkenyl, and each Z is independently hydrogen or halogen, and the Z s need not be the same; and, causing them to react to form a non-polymeric imide composition represented by the formula



30 wherein $y = 1$ or 2, M is an alkali when y is 1 or an alkaline earth metal when y is 2, $m = 1$ or 2, where, when $m = 1$, R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbyl radical, except perfluoroolefin, having 1-12 carbons optionally substituted by one or more ether oxygens, or tertiary amino; or, where $m = 2$, R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbenyl radical having 1-12 carbons optionally substituted by one or more ether oxygens, with the proviso that when $y = 2$ and $m = 2$, M may represent a combination of alkali and alkaline earth metals;

or, in the alternative, a polymeric imide composition comprising monomer units represented by the formula



5

wherein $y = 1$ or 2 ; R^3 is a diradical selected from the group consisting of fluorinated or non-fluorinated alkenyl, including oxyalkenyl or fluoroxyalkenyl, each Z is independently hydrogen or halogen, wherein the Z 's need not be the same; R^2 is aryl, fluoro-aryl, or XCF_2 where X is H, halogen, fluorinated or non-fluorinated linear or cyclic alkyl radicals having 1-10 carbons, optionally substituted by one or more ether oxygens; M is an alkali when y is 1 or an alkaline earth metal when y is 2.

10 As used herein, the term "reacting" is intended to mean allowing or to allow at least two components in a reaction mixture to react to form at least one product. "Reacting" may optionally include stirring and/or heating or cooling.

BRIEF DESCRIPTION OF DRAWING

15 Figure 1 is a representation of the apparatus employed for determining the volume of hydrogen gas evolved from the reactions described in the specific 20 embodiments herein.

DETAILED DESCRIPTION

25 The process of the present invention represents a simple method of providing a very wide range of imides which can be readily and variously ion exchanged to provide superacid catalysts, electrolytes, and ionomers useful for electrochemical applications.

In the practice of the invention it is not necessary to first protect the double bond of an olefinic or vinyl ether prior to imidization. The imidization will proceed without attacking the double bond.

30 Equally useful is the imidization of a polymer comprising monomer units of vinylidene fluoride and monomer units comprising a pendant group having sulfonyl fluoride functionality, particularly a perfluorovinyl ether perfluoroalkoxysulfonyl fluoride, such as described in Doyle et al., WO 9941292(A1). The methods of the art for converting sulfonyl fluorides to imides are not applicable to the copolymers of WO 9941292(A1) and others 35 embodiments containing vinylidene fluoride monomer units because of the base instability of the vinylidene fluoride moiety. Application of the methods of the art

result in extensive and unacceptable degradation of the polymer backbone in vinylidene fluoride containing polymers. The method of the present invention provides for conversion of sulfonyl fluoride to imide in vinylidene fluoride containing polymers without degradation of the polymer backbone.

5 In the present invention, the term "hydrocarbyl" is employed to mean a monoradical consisting of carbon and hydrogen. Included in the term "hydrocarbyl" are alkyl, cycloalkyl, aryl, aryl alkyl and the like. Similarly, the term "hydrocarbenyl" is employed to mean a diradical consisting of carbon and hydrogen. Both hydrocarbyl and hydrocarbenyl radicals, as employed herein, 10 may contain one or more unsaturated carbon-carbon bonds, one or more ether oxygens, and may be partially or fully fluorinated. Essentially any hydrocarbyl or hydrocarbenyl radical is suitable for the practice of the invention except that radicals containing perfluorolefin functionality are not suitable for the practice of the invention. Perfluorovinyl ether functionality however is preferred. Thus, the 15 functional group $\text{CF}_2=\text{CF}-\text{CF}_2-$ is not suitable but the functional group $\text{CF}_2=\text{CF}-\text{O}-$ is not only suitable but is also preferred.

In one aspect of the present invention, dimetal sulfonyl amide salts having the formula $(\text{R}^2\text{SO}_2\text{NM}_b)_{3-b}\text{M}'_c$ (III) are found to be highly effective agents for preparing imides from a wide variety of compounds having a sulfonyl fluoride 20 functionality, both from polymeric and non-polymeric species. In the dimetal sulfonyl amide salts suitable for the process of the invention, R^2 is aryl, fluoro-aryl, or XCF_2- where X is H, halogen, fluorinated or non-fluorinated linear or cyclic alkyl radicals having 1-10 carbons, optionally substituted by one or more ether oxygens, M' is an alkaline earth metal, $b = 1$ or 2 , $c = 0$ or 1 , M is an alkaline 25 earth when b is 1 or an alkali metal when b is 2 and $c = 0$, and M is alkali metal when $b = 1$ and $c = 1$, with the proviso that c is unequal to 1 when $b = 2$.

Preferably, R^2 is fluoroalkyl having 1-4 carbons; most preferably R^2 is CF_3- . Preferably, M is an alkali metal, most preferably sodium, and $b = 2$.

In one embodiment, a non-polymeric sulfonyl fluoride composition 30 represented by the formula $\text{R}^1(\text{SO}_2\text{F})_m$ in liquid dispersion or solution is contacted with the dimetal sulfonyl amide salt (III) to form a reaction mixture. $m = 1$ or 2 , where, when $m = 1$, R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbyl radical having 1-12 carbons optionally substituted by one or more ether oxygens, except perfluorolefin, or tertiary amino; or, when $m = 2$, 35 R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbenyl radical having 1-12 carbons optionally substituted by one or more ether oxygens, preferably $m = 1$. More preferably $m = 1$, R^1 is a perfluorovinyl ether represented by the formula



wherein R^4 is F or perfluoroalkyl having 1-4 carbons, $z = 0$ or 1, and $n = 0$ -3.

5 Most preferably $m = 1$ and R^4 is trifluoromethyl, $z = 1$, and $n = 0$ or 1.

In one embodiment, the process of the invention may be conducted in the absence of an inert liquid diluent when a sufficient excess of a liquid $\text{R}^1(\text{SO}_2\text{F})_m$ is provided to ensure good mixing. However, in the absence of an inert diluent, the reaction may proceed inhomogeneously, and is potentially subject to sudden 10 decomposition. Therefore, it is preferred to conduct the process of the invention in an inert liquid diluent. Numerous aprotic organic liquids are suitable for use as an inert liquid diluent for the process of the invention; the requirements are not strict beyond liquidity and inertness. It is preferred to use a solvent that dissolves the monomer but not the NaF by-product so that it can easily be filtered off. 15 Preferred liquids are ethers, including THF, nitriles, DMSO, amides, and sulfolanes. Ethers are more preferred, with THF most preferred.

The reaction may be conducted at any temperature between the freezing and boiling point of the inert liquid diluent. Room temperature has been found to be satisfactory in the preferred embodiment of the invention. Temperatures from 20 room temperature to 80°C are suitable, with room temperature to 60°C more preferred.

The reaction mixture is preferably stirred or otherwise agitated according to means commonly employed in the art.

In a first preferred embodiment of the process of the invention, the product 25 of the process is most preferably as represented by the formula



where $n = 0$ or 1. It is a particularly surprising aspect of the present invention that 30 the conversion of the $-\text{SO}_2\text{F}$ group may be effected without the necessity of protecting the double bond. The product so-formed, (VIII), may advantageously be employed as a comonomer with fluorinated olefins, non-fluorinated olefins, fluorinated vinyl ethers, non-fluorinated vinyl ethers, and combinations thereof. Preferred comonomers include ethylene, tetrafluoroethylene, hexafluoro-35 propylene, perfluoroalkyl vinyl ether, vinylidene fluoride, and vinyl fluoride. Copolymerizing the monomer (VIII) with a variety of co-monomers may be effected for example according to the teachings of DesMarteau, *op.cit.* or of Feiring et al., *op.cit.* or, more broadly, may be effected according the methods of

Connolly et al., *op.cit.* The ionomers so formed are useful in a wide variety of electrochemical applications.

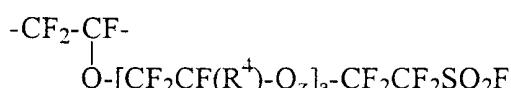
One area of particular utility is in lithium batteries. For this purpose, the product monomer, (VIII), may be ion exchanged to the lithium form by contacting 5 the monomer (VIII) with a dilute solution of LiCl in THF. The polymerizations indicated above may then be effected. In the alternative, the polymerizations may first be effected, followed by ion exchange with LiCl in THF. In an alternative embodiment, the preferred sodium imide of the invention can be treated with aqueous acid to form the acid followed by treatment with aqueous lithium salt to 10 form the lithium ion composition.

In a further embodiment a sulfonyl fluoride polymer composition is contacted with the dimetal sulfonyl amide salt (III) in liquid dispersion or solution to form a reaction mixture. The polymer comprises monomer units represented by the formula

15



wherein R³ is a diradical selected from the group consisting of fluorinated or non-fluorinated alkenyl, including oxyalkenyl or fluorooxyalkenyl, and each Z is 20 independently hydrogen or halogen, and need not be the same. Preferably, R³ is oxyalkenyl. In a second preferred embodiment (V) is represented by the formula



(IX)

25 wherein R⁴ is F or perfluoroalkyl having 1-4 carbons, z = 0 or 1, and a = 0-3. Most preferably R⁴ is trifluoromethyl, z = 1, and a = 0 or 1.

The polymer comprising the monomer units (IX) may comprise up to 50 mol % of said monomer units (IX). Comonomer units incorporated therewith may be derived from numerous olefinically unsaturated species as identified in the 30 art including, ethylene, vinylidene fluoride (VF₂), vinyl fluoride, and combinations thereof to form terpolymers. Additional termonomers include tetrafluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ethers, and such other ethylenically unsaturated species as are known in the art.

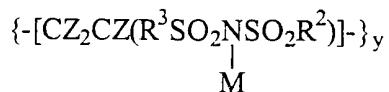
Particularly preferred for the practice of the invention is a copolymer comprising up to 50 mol %, most preferably up to 20 mol %, of comonomer units (IX) and comonomer units derived from VF₂, most preferably at least 50 mol % of monomer units derived from VF₂. It is a surprising aspect of the present invention that the copolymer of (IX) with at least 50 mol % of units derived from VF₂ can be successfully reacted according to the process of the invention to form the corresponding imide. Because of the well-known base instability of VF₂-containing polymers, the methods of the art for forming imides from sulfonyl fluorides are not operable with polymers having any more than trace amounts of monomer units derived from VF₂ because the imidizing agents of the art attack the polymer backbone causing extensive degradation.

There is no particular limitation on the molecular weight of polymers suitable for the practice of the invention. Oligomeric polymers may themselves be liquids at or near room temperature and therefore are well-suited as the liquid dispersing medium of the process. However, it is generally preferred to employ an inert diluent, preferably a solvent for the polymer. As the molecular weight of the polymer increases, solubility and solution viscosity become increasingly difficult problems, making homogeneous reaction difficult. The preferred copolymer of VF₂ and comonomer (IX) is particularly well-suited to the practice of the present invention because of the relatively higher solubility of VF₂-containing polymers in non-fluorinated solvents than other fluoropolymers.

Numerous aprotic organic liquids are suitable for use as solvents for the sulfonyl fluoride polymer composition in the process of the invention. As stated, solubility of the polymer reactant is a limiting factor. Preferred solvents are ethers, including THF, nitriles, DMSO, amides, and sulfolanes. Ethers are more preferred, with THF most preferred. Because of the limitations on solubility associated with high molecular weight, lower molecular weight polymers are preferred.

Suitable and preferred reaction temperatures are as in the case of the non-polymeric reactant hereinabove described.

For the purposes herein, the polymer produced in the process of the invention is represented by the formula



wherein $y = 1$ or 2 ; R^3 is a diradical selected from the group consisting of fluorinated or non-fluorinated alkenyl, including oxyalkenyl or fluorooxyalkenyl, each Z is independently hydrogen or halogen, wherein the Z s need not be the same; R^2 is aryl, fluoro-aryl, or XCF_2^- where X is H, halogen, fluorinated or non-
5 fluorinated linear or cyclic alkyl radicals having 1-10 carbons, optionally substituted by one or more ether oxygens; M is an alkali when $y = 1$ or an alkaline earth metal when $y = 2$. When $y = 2$, M is an alkaline earth metal. Setting $y = 2$ is meant to designate that the alkaline earth metal, M in (II), which has a valence of 2, is bonded to two different polymer chains each of the indicated composition,
10 thus serving as a metallic cross-link. It is also possible, depending upon chain configuration, for the alkaline earth metal M to be bonded to two segments of the same polymer chain.

The process of the present invention is preferably practiced with a purified form of the dimetal sulfonyl amide salt (III). Xue, *op.cit.*, teaches only a process
15 which provides very small amounts of highly contaminated (III). The inventors of the present invention have determined by ordinary methods of chemical analysis that Xue's process produced $CF_3SO_2NNa_2$ with conversion of less than 10%, most of the remainder of his reaction product being unconverted starting material. No method is provided in the art for preparing (III) in pure form.

20 In the process of the invention, the dimetal sulfonyl amide salt starting material $(R^2SO_2NM_b)_{3-b}M'_c$, (III), should first itself be produced at high yield. In (III), R^2 is aryl, fluoro-aryl, or XCF_2^- where X is H, halogen, fluorinated or non-fluorinated linear or cyclic alkyl radicals having 1-10 carbons, optionally substituted by one or more ether oxygens, M' is an alkaline earth metal, $b = 1$ or 2 ,
25 $c = 0$ or 1 , M is an alkaline earth when $b = 1$ or an alkali metal when $b = 2$ and $c = 0$, and M is alkali metal when $b = 1$ and $c = 1$, with the proviso that c is not equal to 1 when $b = 2$.

Preferably, M is an alkali metal and $c = 0$, $b = 2$, and R^2 is a perfluoroalkyl radical. Most preferably M is sodium and R^2 is a trifluoromethyl radical.

30 The inventor hereof has found that surprisingly the dimetal sulfonyl amide salt (III) can be made at much higher purities than in Xue's process, purity of greater than 50%, preferably greater than 90%, most preferably greater than 95%, by contacting a sulfonyl amide or monometal sulfonyl amide salt thereof having the formula $(R^2SO_2NH)_{3-a}M''$, (VII), with at least one alkali or alkaline earth
35 metal hydride and an aprotic liquid to form a reaction mixture which is permitted to react to any desired degree of conversion up to 100%, which is preferred. In the sulfonyl amide or monometal salt thereof (VII), $a = 1$ or 2 , M'' is alkaline earth metal when $a = 1$, M'' is alkali metal or hydrogen when $a = 2$, and R^2 is aryl,

fluoro-aryl, or XCF_2^- where X is H, halogen, or a fluorinated or non-fluorinated linear or cyclic alkyl radical having 1-10 carbons, optionally substituted by one or more ether oxygens. In the hydride may be a mixture of more than one alkali or alkaline earth hydrides, or a mixture of alkali and alkaline earth hydrides. If 5 preferred, the reaction may proceed in stages with different hydrides being fed to the reaction at different times.

Preferably R^2 is perfluoroalkyl, most preferably trifluoromethyl, and M'' is sodium. $CF_3SO_2NH_2$ is the preferred starting material for preparing the $CF_3SO_2NNa_2$ preferred for the process of the present invention. The preferred 10 aprotic liquid is acetonitrile. Preferably the reaction to produce the $CF_3SO_2NNa_2$ is continued until one or the other starting material is completely consumed and reaction stops. More preferably the stoichiometry is adjusted so that only trace amounts of either starting material remain when reaction is complete. Most preferably, the hydride is added at slightly below stoichiometric quantity.

15 The sulfonyl amide and monometal salt thereof (VII) are soluble in the aprotic solvents employed in the process of preparing the dimetal sulfonyl amide salt (III), but the dimetal sulfonyl amide salt (III) itself is not. The solubility difference is exploited herein to separate the reaction product from the reaction mixture and obtain a composition comprising sulfonyl amide salts at least 20 50 mol %, preferably at least 90 mol %, most preferably at least 95 mol %, of which salts are represented by the formula $(R^2SO_2NM_b)_{3-b}M_c'$, (III), as hereinabove defined. Any convenient method known in the art for separating solids from liquids may be employed, including filtration, centrifugation and, distillation.

25 While it is preferred to permit the synthesis of (III) to run to completion, this may not always be practical depending upon the aprotic solvent chosen. In neat acetonitrile, 100% conversion is achieved in ca. 4 hours at room temperature. However, in neat THF, six days of reaction are required for 100% conversion. In the latter case, it may be desired to separate the reaction product before the 30 reactants have fully reacted. The method of separation based upon the heretofore unknown solubility difference hereinabove described provides a practical method for isolating the dimetal sulfonyl amide salt (III) at high purity when conversion has been low.

It has been found in the practice of the present invention that residual 35 hydride left over from the synthesis of the dimetal sulfonyl amide salt (III) is not highly deleterious to the efficacy of the process of the present invention. While not critical, the $CF_3SO_2NNa_2$ preferred for the process of the present invention is substantially free of contamination by NaH. This is achieved by employing

slightly less than the stoichiometric amount of NaH in its preparation, thereby insuring that when the reaction achieves full conversion, the NaH will be exhausted. Any excess of the soluble intermediate $\text{CF}_3\text{SO}_2\text{NHNa}$ is easily separated by washing/filtration cycles, preferably using fresh aliquots of solvent.

5 In preparing the dimetal sulfonyl amide salt,(III) it has been found that the components of the reaction mixture may be combined in any order, but that it is preferred to first mix the sulfonyl amide or a monometal salt thereof (II), with the aprotic liquid to form a solution, following with addition of the hydride after the solution has formed. First mixing the hydride with the aprotic solvent has resulted
10 in poor reaction or slower than expected conversion.

A suitable temperature for preparing the dimetal sulfonyl amide salt (III) will lie between the melting point and the boiling point of the aprotic liquid selected. It has been found to be satisfactory for the practice of the invention to conduct the process of the invention at room temperature. However, somewhat
15 higher temperatures result in faster reaction. In the most preferred embodiment of the invention, acetonitrile is employed as the solvent at a temperature between 0°C and 80°C, preferably between room temperature and 80°C, most preferably between room temperature and 60°C.

20 Aprotic solvents suitable for preparing the dimetal sulfonyl amide salt (III) should be substantially free of water. Water causes the reaction to go in the wrong direction, for example to form $\text{CF}_3\text{SO}_2\text{NHNa}$ and NaOH, and provides a route for making a sulfonate instead of an imide. In a preferred embodiment, it has been found satisfactory to employ acetonitrile having water content less than or equal to ca 500 ppm, with water content less than or equal to ca. 50 ppm more preferred. Acetonitrile is quite hygroscopic, and care should be taken in handling
25 to avoid water contamination from the atmosphere.

The preferred aprotic solvent for the preparation of the dimetal sulfonyl amide salt (III) comprises acetonitrile. Acetonitrile has been found to accelerate the conversion by a considerable amount over other aprotic solvents. In neat
30 acetonitrile, essentially quantitative conversion is achieved in ca. 4 hours. In the presence of as little as 5% acetonitrile in the THF taught by Xue,*op.cit.*, essentially quantitative conversion is achieved in ca. 25 h. These results contrast starkly with the six days required under the conditions taught by Xue.

It is found that solvent selection has a tremendous effect on the rate of
35 conversion, though most aprotic solvents will lead to high conversion over sufficient time. Acetonitrile is highly preferred. Other aliphatic and aromatic nitriles, while suitable, do not appear to be particularly better than the THF employed by Xue but may be employed as substitutes for THF. Suitable nitriles

include higher alkyl nitriles, dinitriles such as adiponitrile, benzonitrile, and the like. Other suitable solvents include ethers, DMF, DMSO, DMAC, and amides. Combinations of suitable solvents are also suitable.

Any of the methods hereinabove, alone or in combination, provide a
5 highly purified form of the sulfonyl amide salt (III) in dramatic distinction over the practice of Xue. The highly purified form of $(R^2SO_2NM_b)_{3-b}M'$, (III), greater than 95% purity, which is readily achieved using the methods herein described, is then suitable for use in the process of the present invention producing pure imides, (I) or (II), at high yields, the purity thereof depending directly upon the purity of
10 (III). Any of the methods of preparation herein described are capable of providing (III) in purities of greater than 95%.

The atmosphere to which the dimetal sulfonyl amide salt (III) is exposed should be substantially free of water as well. Water vapor concentrations of about 25 ppm have been found to be highly suitable. Higher levels of water vapor
15 concentration can be tolerated, but it should be understood that the higher the water vapor concentration of the atmosphere, the greater the contamination during subsequent reaction. As a general rule, the less water, the better, in whatever form.

The term "inert atmosphere" as used herein refers to an anhydrous
20 atmosphere having a water vapor concentration of less than ca. 50 ppm. It is not meant to imply a non-oxidative atmosphere. Thus, the reactions herein may be accomplished in desiccated air as well as in dry nitrogen or other non-chemically active gases. Dry nitrogen, however, is preferred.

In a preferred method of preparation of the dimetal sulfonyl amide salt
25 (III), $CF_3SO_2NH_2$ is dissolved at a concentration in the range of 5-10% by weight in acetonitrile in an inert atmosphere such as nitrogen. At higher concentrations good mixing may become more difficult to maintain as the insoluble $CF_3SO_2NNa_2$ product begins to form, creating a dispersion. Therefore at concentrations higher than about 10% by weight, other forms of agitation may be
30 preferred over simple stirring, such as ultrasonic agitation, or microfluidization such as may be achieved using a MicroFluidizer™ available from Microfluidics, Inc., Newton, MA.

While maintaining the inert atmosphere, NaH is added with agitation continued until the reaction is complete in about 4 hours. Hydrogen gas evolution
35 rate, determined by any convenient method known in the art, has been found to be an effective indicator of reaction. The cessation of hydrogen gas flow signals completion of the reaction.

The amount of NaH added depends upon the particular requirements and intentions of the practitioner hereof. Adding a slight excess over the stoichiometric amount of NaH ensures complete conversion of the $\text{CF}_3\text{SO}_2\text{NH}_2$ or $\text{CF}_3\text{SO}_2\text{NHNa}$ to $\text{CF}_3\text{SO}_2\text{NNa}_2$. However, this leaves $\text{CF}_3\text{SO}_2\text{NNa}_2$ so 5 prepared still contaminated with insoluble NaH from which it is difficult to separate. However, it has been found that residual NaH is largely inert in the process of the invention and to the products thereof. On the other hand, if the goal is to achieve the cleanest possible $\text{CF}_3\text{SO}_2\text{NNa}_2$ then a slight deficit of NaH below the stoichiometric amount may be employed to ensure that the NaH will be 10 fully consumed. Employing a deficit of NaH will result in less than complete conversion of the $\text{CF}_3\text{SO}_2\text{NH}_2$ or $\text{CF}_3\text{SO}_2\text{NHNa}$ to $\text{CF}_3\text{SO}_2\text{NNa}_2$. The soluble residual intermediary $\text{CF}_3\text{SO}_2\text{NHNa}$ is easily washed away from the insoluble $\text{CF}_3\text{SO}_2\text{NNa}_2$.

The dimetal sulfonyl amide salt (III) may be dried under vacuum at 15 elevated temperature but the user must be aware of the possibility of spontaneous and violent decomposition of the material. It is highly recommended to never handle this material in a totally dry state. It is highly recommended to keep the material wet at all times. It seems that the smaller composition $\text{CF}_3\text{SO}_2\text{NNa}_2$ is less stable than the compositions of higher molecular weight like $\text{C}_4\text{F}_9\text{SO}_2\text{NNa}_2$. 20 A suitable temperature depends upon the specific composition thereof. The preferred $\text{CF}_3\text{SO}_2\text{NNa}_2$ should be dried at a temperature preferably not higher than 80°C, most preferably not higher than 65°C. Certain of the compositions of the invention, including the preferred $\text{CF}_3\text{SO}_2\text{NNa}_2$, have been observed to undergo certain decomposition aggressively when heated to the decomposition 25 threshold but it has also been observed at one occasion that the preferred $\text{CF}_3\text{SO}_2\text{NNa}_2$ undergoes spontaneous decomposition at room temperature. The compound is moisture sensitive and should be handled under anhydrous conditions. It is believed that the product is somewhat unstable, and potentially may be subject to explosive decomposition.

30 EXAMPLES
EXAMPLE 1

$\text{CF}_3\text{SO}_2\text{NH}_2$ was purchased from Tokyo Chemical Industry, Portland, Oregon, (TCI) and dried and purified by two cycles of sublimation under a vacuum of about 10^{-3} Torr, employing a water cooled ($\sim 20^\circ\text{C}$) cold-finger, and an 35 oil bath at 80°C. Anhydrous acetonitrile was purchased from EM Science Gibbstown, NJ, slurried with P_2O_5 and distilled to ensure dryness, and stored over molecular sieves inside a dry box until ready to be used. Sodium hydride (95%) was purchased from Aldrich Chemical.

Inside a model HE-63-P dry-box (Vacuum Atmosphere Company, Hawthorne, CA) having a dry nitrogen atmosphere, a round bottom flask was charged with 30.003 g of the sublimed $\text{CF}_3\text{SO}_2\text{NH}_2$ and 750 ml of the dried acetonitrile. 9.003 g of the sodium hydride was slowly added over a period of 5 min while the reaction mixture was stirred with a magnetic stir bar. The temperature of the reaction mixture increased from 21.6°C to 50.5°C during the addition process. The mixture was stirred at room temperature for 20 h. After about 4-5 hours the reaction medium had taken on an opaque "creamy" appearance, and no further bubbling, indicative of the evolution of hydrogen, was 10 observed.

The reacted mixture was filtered through a glass-filter (medium porosity) inside the dry-box. The white solid was washed three times with 100 ml of the anhydrous acetonitrile, transferred from the filter to a Schlenk flask and dried under vacuum (10^{-2} Torr) at room temperature for 5 h, still in the dry box. 15 Approximately 10% of the filtrate was lost in transferring from the filter to the Schlenk flask. The Schlenk flask was sealed, removed from the dry-box, and subject to further evacuation under oil pump vacuum (10^{-3} Torr) for 15 h at room temperature. The Schlenk flask was then immersed in an oil bath set at 50°C and held for four hours at which time the bath was heated to 65°C and the Schlenk 20 flask was held therein for an additional 20 h while still subject to evacuation under oil pump vacuum (10^{-3} Torr). Afterwards, the $\text{CF}_3\text{SO}_2\text{NNa}_2$ was only handled inside the dry-box.

30.0 grams of product were isolated. The product decomposed at 110°C while generating large amounts of a gas.

25 It has been observed at one occasion that the preferred $\text{CF}_3\text{SO}_2\text{NNa}_2$ undergoes spontaneous decomposition at room temperature and it is therefore recommended to not dry this material but instead keep it as a suspension at all times.

EXAMPLE 2

30 Inside the dry box of Example 1, a flask was charged with 5.142 g $\text{C}_4\text{F}_9\text{SO}_2\text{NH}_2$ made from $\text{C}_4\text{F}_9\text{SO}_2\text{F}$ and NH_3 according to the method of Meußdoerffer et al, *op.cit.*, and 100 ml of anhydrous acetonitrile prepared as in Example 1. 0.784 g NaH (Aldrich) was slowly added over a period of 5 min. The mixture was stirred at room temperature for 24 h without observation. Insoluble 35 $\text{C}_4\text{F}_9\text{SO}_2\text{NNa}_2$ had precipitated at the bottom of the flask. The reaction mixture was filtered through a glass filter (fine porosity) and the white residue was washed three times with 50 ml of anhydrous acetonitrile. The residue was collected from the filter and placed in a Schlenk-flask. Afterwards, the material was brought

outside the dry-box and dried under oil pump vacuum (10^{-3} Torr) for 24 h at an oil bath temperature of 65°C. $\text{C}_4\text{F}_9\text{SO}_2\text{NNa}_2$ was only handled inside the dry-box. 4.37 g of product were isolated.

It has been observed at one occasion that the preferred $\text{CF}_3\text{SO}_2\text{NNa}_2$ undergoes spontaneous decomposition at room temperature and it is therefore recommended to not dry this material but instead keep it as a suspension at all times.

EXAMPLE 3

Employing the reagents and equipment of Example 1, inside the dry-box 3.123 g of the sublimed $\text{CF}_3\text{SO}_2\text{NH}_2$ was dissolved in 100 ml of the anhydrous acetonitrile in a round-bottom flask. 1.127 g of the sodium hydride was slowly added to form a first reaction mixture. Addition of NaH took place over a period of 10 min while the first reaction mixture was stirred with a magnetic stirring bar at room temperature. After 3 h, no fluorine could be detected by ^{19}F NMR in the solution indicating complete conversion of $\text{CF}_3\text{SO}_2\text{NH}_2$ to $\text{CF}_3\text{SO}_2\text{NNa}_2$, thereby forming a mixture of $\text{CF}_3\text{SO}_2\text{NNa}_2$ and acetonitrile, with some residual NaH.

$\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (PSEPVE) prepared according to the method of Connolly et al., U.S. Patent No. 3,282,875, was slurried with P_2O_5 and distilled. 10.002 g of the thus- treated PSEPVE was added to the mixture of $\text{CF}_3\text{SO}_2\text{NNa}_2$ and acetonitrile prepared as hereinabove to form a second reaction mixture. The second reaction mixture was stirred at room temperature. After 10 min, the mixture turned clear, indicative of complete reaction of the $\text{CF}_3\text{SO}_2\text{NNa}_2$, and then slightly cloudy, indicative of the precipitation of the NaF by-product. After 30 minutes fluorine NMR confirmed a substantial concentration of the imidized form of PSEPVE. The reacted mixture was centrifuged and then filtered through a glass filter (medium porosity). The residue was washed with 100 ml of anhydrous acetonitrile. All volatiles were removed under vacuum of 10^{-3} Torr at room temperature and the slightly beige residue was heated to 110°C for 16 h at 10^{-3} Torr. Yield was 9.494 g.

^{19}F NMR in CD_3CN confirmed the structure

$\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$.

^{19}F NMR in $\text{CD}_3\text{CN}/\text{Freon-11}$

$(\text{CF}_2\text{A,A}'=\text{CF}\text{B}\text{OCF}_2\text{C}\text{CF}\text{D}(\text{CF}_3\text{E})\text{OCF}_2\text{F}\text{CF}_2\text{G}\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3\text{H})$: -112.6,

-120.9 ppm (A, 1F, A', 1F), -135.7 ppm (B, 1F), -78.0 ppm (CF_2 , C, 2F),

-144.2 ppm (F, D, 1F), -79.1 ppm (CF_3 , E, 3F), -83.7 ppm (CF_2 , F, 2F), -116.0 ppm (CF_2 , G, 2F), -78.9 ppm (CF_3 , H, 3F).

MS: Negative electron spray; 574.14, M-Na.

EXAMPLE 4

Inside the dry-box of Example 1, a round bottom flask was charged with 5.027 g of the $C_4F_9SO_2NH_2$ made from $C_4F_9SO_2F$ and NH_3 according to the method of Meußdoerffer et al, *op.cit.*, and 100 ml of anhydrous acetonitrile

5 prepared as in Example 1. 0.890 g of sodium hydride (Aldrich) was slowly added to form a first reaction mixture. Addition of NaH took place over a period of 10 min while the reaction mixture was stirred at room temperature with a magnetic stir bar. After 22 h of stirring, no fluorine could be detected by ^{19}F NMR in the solution indicating complete conversion, thereby forming a

10 mixture of $C_4F_9SO_2NNa_2$ in acetonitrile, contaminated by some residual NaH.

7.797 g of the PSEPVE of Example 3 was added to the mixture of $C_4F_9SO_2NNa_2$ and acetonitrile prepared hereinabove to form a second reaction mixture. The second reaction mixture was stirred at room temperature. After 10 min, the mixture turned clear, indicative of complete reaction of the

15 $CF_3SO_2NNa_2$, and then slightly cloudy, indicating the precipitation of the NaF by-product. NMR of the reaction mixture taken after 30 min confirmed the substantial presence of the imidized form of PSEPVE. The reaction mixture was centrifuged and then filtered through a glass filter (medium porosity). The residue was washed with 100 ml of anhydrous acetonitrile. All volatiles were removed

20 under vacuum and the slightly beige residue was heated to 110°C for 16 h at 10^{-3} Torr. Yield was 8.358 g.

^{19}F NMR in CD_3CN confirmed the structure

$CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)SO_2(CF_2)_3CF_3$

^{19}F NMR in CD_3CN /Freon-11

25 $(CF_2^{A,A'}=CF^{B}OCF_2^{C}CF^{D}(CF_3^{E})OCF_2^{F}CF_2^{G}SO_2N(Na)SO_2CF_2^{H}CF_2^{I}CF_2^{J}CF_3^{K})$: -112.6, -120.7 ppm (A, 1F, A', 1F), -135.6 ppm (B, 1F), -78.0 ppm (CF₂, C, 2F), -144.1 ppm (CF, D, 1F), -79.1 ppm (CF₃, E, 3F), -83.7 ppm (CF₂, F, 2F), -115.9 ppm (CF₂, G, 2F), -112.6 ppm (CF₂, H, 2F), -120.6 ppm (CF₂, I, 2F), -125.8 ppm (CF₂, J, 2F), -79.1 ppm (CF₃, K, 3F).

30 MS: Negative electron spray; 723.98, M-Na.

EXAMPLE 5

Benzonitrile (Aldrich) was dried by mixing with P_2O_5 and then distilling. Employing reagents and equipment of Example 1, inside the dry-box 3.008 g of the sublimed $CF_3SO_2NH_2$ was dissolved in 90 ml of the dried benzonitrile in a

35 round-bottom flask. To form a first reaction mixture, 1.018 g of the sodium hydride was slowly added while the reaction mixture was stirred with a magnetic stirring bar at room temperature. The reaction mixture changed its appearance after 10 min. A white precipitate was formed causing a thickening of the slurry.

Shortly after, the reaction mixture changed its color to yellow. After 60 min, the reaction mixture was red. After 6 h, fluorine could still be detected by ^{19}F NMR in the solution. After a total of 24 h at room temperature, 8.511 g of PSEPVE of Example 3 was added, thereby forming a second reactions mixture. The second 5 reaction mixture was stirred at room temperature. The color changed from red to yellow. ^{19}F NMR in CD_3CN after 2 h confirmed the formation of the structure $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$.

EXAMPLE 6

In this Example, an apparatus was employed for determining the volume 10 of hydrogen gas evolved by the reaction as a function of time. The apparatus is depicted in Figure 1. One neck of a three necked round bottom flask, 1, holding a magnetic stirring bar, 2, was fitted with a solid reactant addition device SRAD, 3, having a 75° angle to be employed for feeding a solid to the flask. A second neck was fitted with a thermocouple probe, 4, and a third neck was fitted with a 15 stopcock, 5. The stopcock, 5, was connected via a 4 cm piece of Tygon® tubing, 6, to an Aldrich Safe-purge (TM) valve, 7, containing mineral oil. The Safe-purge valve, 7, was connected via a rubber hose, 8, to a water-filled 250 ml graduated cylinder, 9, that is deployed upside-down in a water-filled 600 ml beaker, 10. In operation liquid reactants were charged to the flask through any of the necks, 20 SRAD, 3, was charged with the desired amount of solid reactant and reaffixed to the flask, 1, in the downward-pointing position shown in the figure. The beaker, 10, was filled to about 50% of capacity with water while the graduated cylinder, 9, was filled completely with water. The stopcock, 5, was opened, and the adaptor, 3, was inverted thus delivering the solid reactant to the reactants in the flask and 25 thereby initiating the reaction. As hydrogen was evolved from the reaction it displaces the water from the graduated cylinder providing a volumetric means for determining the rate and total amount of hydrogen evolution.

Employing the methods and material of Example 1, inside the dry-box, 0.546 g of the sublimed $\text{CF}_3\text{SO}_2\text{NH}_2$ was dissolved in 100 ml of the anhydrous 30 acetonitrile in the three neck round bottom flask of Figure 1. 0.213 g of the sodium hydride was carefully placed in the SRAD. The flask was carefully brought outside the dry box and connected to the remainder of the apparatus of Figure 1. After all connections had been established, the stopcock to the reaction flask was opened. The reaction mixture was stirred at room temperature and the 35 SRAD was inverted thereby feeding the NaH to the solution in the flask. Immediately, a reaction could be observed. 80 ml of gas were collected over a period of 5 min. The temperature of the reaction mixture increased from 23°C to 26°C . Over the next 120 min, the formation of gas slowed down and 74 ml of gas

were collected in the graduated cylinder. During this period, the appearance of the reaction mixture changed. The fine residue in the reaction mixture changed to a thicker precipitate that settled easily to the bottom of the flask when the stirring was stopped. The reaction mixture was stirred for another hour at room 5 temperature, 10 ml of additional gas were collected during this period. The flask was brought into the dry box and a sample of the solution was submitted for NMR. No fluorine could be detected, indicating the complete conversion of $\text{CF}_3\text{SO}_2\text{NHNa}$ into insoluble $\text{CF}_3\text{SO}_2\text{NNa}_2$.

EXAMPLE 7

10 Excess $\text{CF}_3\text{SO}_2\text{NH}_2$ and NaOH were reacted in water to prepare $\text{CF}_3\text{SO}_2\text{NNaH}$. Water and excess $\text{CF}_3\text{SO}_2\text{NH}_2$ were removed under vacuum (10^{-3} Torr) at 70°C ; the residue was dried for 16 h at 10^{-3} Torr at 110°C . Following the procedures of Example 1, inside the dry box, a 250 ml two neck round bottom flask with a magnetic stirring bar was charged with 1.034 g of the 15 $\text{CF}_3\text{SO}_2\text{NNaH}$. The material was dissolved in 100 ml of anhydrous acetonitrile of Example 1. The procedures of Example 10 were followed but the three necked flask was replaced by the two-necked flask and the thermocouple was omitted. The reaction mixture was stirred at room temperature and the SRAD was inverted thereby feeding the NaH to the solution in the flask. No immediate reaction could 20 be observed. Over the first 150 min, only a total of 10 ml of an evolving gas could be collected. After 150 min, the formation of gas started. Over the next 105 min, additional 135 ml of gas were collected in the graduated cylinder. During this period, the appearance of the reaction mixture changed. The fine residue in the reaction mixture changed to a thicker precipitation that settled easily 25 at the bottom of the flask when the stirring was stopped. The reaction mixture was stirred for another 14 h at room temperature. 10 ml of additional gas were collected during this period. The flask was brought into the dry box and a sample of the solution was submitted for NMR. No fluorine could be detected, indicating the complete conversion of $\text{CF}_3\text{SO}_2\text{NHNa}$ into insoluble $\text{CF}_3\text{SO}_2\text{NNa}_2$.

30 EXAMPLE 8

Following the procedure of Example 10, inside the dry-box, a 250 ml three neck round bottom flask was charged with 75 ml of anhydrous acetonitrile prepared as in Example 1. 0.189 g NaH was placed in the SRAD. 0.879 g of the $\text{CF}_3\text{SO}_2\text{NHNa}$ of Example 10 was dissolved in 25 ml acetonitrile prepared as in 35 Example 1 and placed in an addition funnel which substituted for the thermocouple of Example 10. After the required connections were made, the reaction mixture was stirred at room temperature and the NaH was immediately added to the solvent. 6 ml of gas were collected over a period of 3 h. The

CF₃SO₂NHNa solution was added and the reaction mixture was continued to be stirred at room temperature. 1 h 45 min after the addition of the CF₃SO₂NHNa, an additional 4 ml of gas had been collected. The reaction mixture turned slightly yellow. 4 h after the addition of the CF₃SO₂NHNa, the reaction seemed to start.

5 6 h and 40 min after the addition of the mono-sodium solution, a total of 80 ml of gas since the addition had been collected. The reaction mixture was stirred for another 14 h 30 min. A total of 116 ml gas had been collected. 103 ml are the expected amount. The flask was brought into the dry-box and an NMR sample was collected from the solution. Only a trace of a fluorine signal at -80.6 ppm

10 could be detected, indicating the conversion of CF₃SO₂NHNa into insoluble CF₃SO₂NNa₂.

2.120 g PSEPVE was added to the now bright yellow solution, containing a yellowish solid. The reaction mixture turned orange and after 15 min stirring at room temperature, the reaction mixture turned clear. A fine precipitate formed.

15 An NMR sample was collected after 1 h showing the formation of the product CF₂=CFOCF₂CF(CF₃)OCF₂CF₂SO₂N(Na)SO₂CF₃ and excess PSEPVE.

COMPARATIVE EXAMPLE 1

Inside the dry-box of Example 1, a flask was charged with 0.93 g of CF₃SO₂NHNa from Example 11, 0.135 g NaH (Aldrich) and 20 ml of anhydrous THF (Aldrich; distilled off Na metal). The reaction mixture was stirred for 4 h at room temperature and was then filtered through a glass filter (fine porosity). The filtrate was collected in a flask and brought outside the dry-box. All solvents were removed under vacuum (10⁻³ Torr) and the residue was heated to 65°C for 24 h at 10⁻³ Torr. 0.862 g (5.04 mmol) of CF₃SO₂NHNa were recovered, corresponding to 92.6% of the starting material. The dried material was brought into the dry-box and 50 ml of anhydrous acetonitrile were added because it is suspected that CF₃SO₂NNa₂ is slightly soluble in THF. The majority of the material was dissolved in the acetonitrile and only a slight trace of a solid could be observed in the solution. It was not attempted to separate this residue. It should be safe to assume that less than 10% of the CF₃SO₂NHNa have been converted to CF₃SO₂NNa₂ after 4 h in THF at room temperature.

EXAMPLE 9

Following the procedures of Example 11, inside the dry-box, the round bottom flask was charged with 0.866 g of the CF₃SO₂NHNa of Example 11. The material was dissolved in 100 ml of anhydrous THF (Aldrich; distilled from Na metal; stored over molecular sieves inside the dry-box). 0.171 g of NaH was placed in the SRAD. After the required connections were made according to Example 10, the reaction mixture was stirred at room temperature and the NaH

was added to the solution. No obvious reaction could be observed. A total of 113.3 ml of collected hydrogen would represent complete conversion under normalized conditions. The gas collected as a function of time is shown in Table 1.

5

TABLE 1

Elapsed time (after addition of NaH)	Gas Collected (ml)	estimated % conversion
0 h 45 min	4	3.5
2 h 30 min	10	8.8
5 h 45 min	10	8.8
21 h 45 min	18	15.9
26 h 15 min	25	22.1
32 h 45 min	28	24.7
47 h	38	33.6
49 h 15 min	43	38.0
53 h 30 min	47	41.6
84 h 45 min	53	46.9
86 h 45 min	55	48.6
97 h 15 min	65	57.5
118 h	78	69.0
122 h 15 min	85	75.2
139 h 45 min	110	97.3
142 h	114	100.5

The reaction was completed after six days at room temperature. The reaction flask was brought inside the dry-box.

2.511 g PSEPVE was added to the colorless reaction mixture that 10 contained a white solid. After 10 min stirring at room temperature, the reaction mixture turned clear. A fine precipitation formed. An NMR sample was collected after 1 h showing the formation of the product
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ and excess PSEPVE.

EXAMPLE 10

15 Following the procedure of Example 11, inside the dry-box, the round bottom flask was charged with 0.633 g of the $\text{CF}_3\text{SO}_2\text{NHNa}$ of Example 11. The material was dissolved in 100 ml of anhydrous acetonitrile prepared as in Example 1. 0.103 g of NaH was placed in the SRAD. After the required connections were made, the reaction mixture was stirred and heated by immersing

the flask in an oil-bath set at 50°C. The reaction mixture was heated for 2 h and the pressure was allowed to equalize inside the flask. No pressure was released through the bubbler for 30 min. After 2 h of heating, the NaH was added to the solution. No obvious reaction could be observed for 20 min.. After 20 min., gas 5 was released from the reaction mixture. Evolution of ca. 83 ml of gas was calculated to correspond to complete conversion.

TABLE 2	
Elapsed time (after addition of NaH)	Gas Collected (ml)
0 h 20 min	0
0 h 25 min	25
0 h 30 min	71
0 h 35 min	85
1 h 0 min	91

10 The formation of gas stopped after 1 hour. The gas collection record is shown in Table 2. The reaction mixture was stirred for another hour at 50°C oil bath temperature with no further accumulation of gas. The reaction flask was brought inside the dry-box and an NMR sample was taken from the clear solution above the white residue. Only a trace of a fluorine signal at -80.6 ppm could be detected in the noise of the NMR spectrum, indicating the conversion of 15 $\text{CF}_3\text{SO}_2\text{NHNa}$ into insoluble $\text{CF}_3\text{SO}_2\text{NNa}_2$.

1.740 g PSEPVE was added to the colorless reaction mixture that contained a white solid. The reaction mixture turned yellow and after 10 min stirring at room temperature, the reaction mixture turned clear. A fine precipitation formed. An NMR sample was collected after 1 h showing the 20 formation of the product $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ and excess PSEPVE.

EXAMPLE 11

25 Following the procedure of Example 10, the flask was charged with 1.195 g of the $\text{CF}_3\text{SO}_2\text{NHNa}$ which was dissolved in a mixture of 95 ml of THF and 5 ml of anhydrous acetonitrile. 0.195 g of the NaH were placed in the SRAD. After connection to the remainder of the apparatus of Example 10, the NaH was added to the reactants in the flask. No immediate reaction could be observed. Over the first 1 h, only a total of 4 ml of gas was evolved. Over the next 5 h, only a total of 7 ml of the expected 157 ml. Hydrogen gas had been

collected. The reaction mixture was stirred for a total of 25 h at room temperature without further observation. 160 ml of gas were collected during this period.

4.500 g PSEPVE was added to the colorless reaction mixture that contained a white solid. The reaction mixture did not change its color and after 5 10 min stirring at room temperature, the reaction mixture turned clear. A fine precipitation formed. An NMR sample was collected after 1 h showing the formation of the product $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ and excess PSEPVE.

EXAMPLE 12

10 Employing the reagents and equipment of Example 1, inside the dry-box 3.033 g of the sublimed $\text{CF}_3\text{SO}_2\text{NH}_2$ was placed in a round bottom flask and dissolved in 50 ml of the anhydrous acetonitrile. 1.511 g of CaH_2 (Aldrich; 90-95%) was added. The reaction mixture was stirred with a magnetic stir bar at room temperature for 48 h. No fluorine could be detected in the reaction mixture 15 after this time period by NMR, indicating the complete conversion of $\text{CF}_3\text{SO}_2\text{NH}_2$ to $(\text{CF}_3\text{SO}_2\text{N}\text{Ca})_2$.

16 9.461 g of distilled PSEPVE was added and the reaction mixture was stirred at room temperature. No conversion to the product could be observed after 24 h at room temperature.

20 The reaction mixture was heated to 60°C for 7 days. The reaction mixture was filtered inside the dry-box through a glass filter (medium porosity) and the flask with the collected solution was brought outside the dry-box. All volatiles were removed under vacuum (10^{-3} Torr) and the beige residue was heated to 100°C at 10^{-3} Torr for 16 h. ^{19}F NMR in CD_3CN confirmed the structure 25 $(\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{NSO}_2\text{CF}_3)_2\text{Ca}$. Yield was 1.729 g.

^{19}F NMR in CD_3CN

26 $(\text{CF}_2\text{A},\text{A}'=\text{CF}\text{B}\text{OCF}_2\text{C}\text{CF}\text{D}(\text{CF}_3\text{E})\text{OCF}_2\text{F}\text{CF}_2\text{G}\text{SO}_2\text{NSO}_2\text{CF}_3\text{H})_2\text{Ca}$: -114.3, -122.7 ppm (A, 1F, A', 1F), -137.3 ppm (B, 1F), -79.5 ppm (CF₂, C, 2F), -145.9 ppm (CF, D, 1F), -80.9 ppm (CF₃, E, 3F), -85.5 ppm (CF₂, F, 2F), -117.6 (CF₂, G, 2F), -80.6 ppm (CF₃, H, 3F).

27 MS: Negative electron spray; 573.98, (M-Ca)/2.

EXAMPLE 13

28 Inside the dry-box, a round bottom flask was charged with 3.051 g, of the 35 $\text{CF}_3\text{SO}_2\text{NH}_2$ prepared in the manner of Example 1 and 100 ml of anhydrous acetonitrile prepared as in Example 1. 1.068 g of the NaH (Aldrich) was added slowly over a period of 5 min. The mixture was stirred at room temperature for 26 h inside the dry-box and checked periodically by fluorine NMR until no

fluorine could be detected. 3.27 g C₆H₅SO₂F used as received from Aldrich was added to the flask. The reaction mixture thus formed was stirred at room temperature for 144 h. The reaction mixture was centrifuged and all volatiles were removed from the reaction solution. The residue was dried at 110°C for 24 h 5 at 10⁻³ Torr. The residue was redissolved in 100 ml of anhydrous acetonitrile and filtered through a paper filter. All volatiles were removed from the solution. The residue was dried at 110°C for 16 h at 10⁻³ Torr.

NMR in CD₃CN and mass spec. confirmed the structure PhSO₂N(Na)SO₂CF₃. Yield was 4.284 g.

10 ¹⁹F NMR in CD₃CN: -79.9 ppm (CF₃, 3F). ¹H NMR in CD₃CN: 7.90 ppm (2H), 7.54 ppm (3H).

MS: negative electron spray; 288.09, M-Na.

EXAMPLE 14

As in Example 1, a round bottom flask was charged with 3.082 g of the 15 CF₃SO₂NH₂ prepared as in Example 1 and 100 ml of anhydrous acetonitrile prepared as in Example 1. 1.134 g of the NaH (Aldrich) was added slowly over a period of 5 min. The mixture was stirred at room temperature for 16 h inside the dry-box. No fluorine could be detected by NMR. 2.025 g of CH₃SO₂F (Aldrich, as received) was added. The reaction mixture thus formed was stirred at room 20 temperature for 2 h. The reaction mixture was centrifuged and all volatiles were removed. The residue was dried at 110°C for 24 h at 10⁻³ Torr. The residue was redissolved in 100 ml of anhydrous acetonitrile and filtered through a paper filter. All volatiles were removed from the solution. The residue was dried at 110°C for 16 h at 10⁻³ Torr. Yield was 4.20 g.

25 NMR in CD₃CN and mass spec. confirmed the structure CH₃SO₂N(Na)SO₂CF₃. ¹⁹F NMR in CD₃CN: -79.7 ppm (CF₃, 3F). ¹H NMR in CD₃CN: 2.966 ppm (3H). MS: negative electron spray; 226.06, M - Na.

EXAMPLE 15

A 400 mL Hastelloy autoclave prechilled to <-20°C was charged with 30 PSEPVE (150 g) and 15 mL of 0.17 M hexafluoropropylene oxide dimer peroxide. The vessel was closed, evacuated, then further charged with vinylidene fluoride (64 g) and CO₂ (150 g), and shaken at room temperature for 18 hr. Excess pressure was released and the viscous residue was analyzed by ¹⁹F NMR (acetone d₆) which clearly indicated residual monomer. Estimated conversion of 35 PSEPVE was ca. 60%. The entire sample was devolatilized at 100°C (0.5 mm) for several hours. Sample was a rather tough rubber, deformable by application of force. It did not flow significantly at room temperature under its own weight.

¹⁹F NMR (acetone d₆): +45.5 (s, a=0.91), -77.5 to -79.8 (m, a=7.00), -91 to -95.5 (m, a = 4.038), -108 to -115.9 (m, a = 4.680), -121.8, -122.3, and -122.8 (series of broadened m's. a = 1.651), -124 to -127 (bd m's, a = 0.766), -129.5 (s, a = 0.0244, assigned to internal CF₂ of CF₃CF₂CF₂OCF(CF₃)- fragment (end group), -144 (bd m, CF from PSEPVE side chains). Integration was consistent with 24.5 mol % PSEPVE. Integration of end groups from dimer peroxide fragments, assuming that all ends are of this type, gives an estimate of M_n for the copolymer as 106,000. ¹H NMR showed only broad signal 3.5-2.7.

4.47 g of the copolymer so prepared was dried at 10⁻³ Torr for 24 h at 10 100°C. 100 ml of anhydrous THF was added to the polymer and the reaction mixture was refluxed for 16 h to dissolve the polymer. 1.344 g of the CF₃SO₂NNa₂ prepared in Example 1 were added at room temperature over a period of 2 h. The reaction mixture was stirred at room temperature. The reaction mixture turned cloudy after 3 h. An additional 0.418 g of CF₃SO₂NNa₂ was 15 added over the next 6 days. After all the CF₃SO₂NNa₂ was added, the reaction mixture so formed was heated to 50°C. After 3 days at 50°C, ¹⁹F NMR indicated that the reaction was complete.

The reaction mixture was brought outside the dry-box and centrifuged. A slightly brown solution could be separated from a dark brown residue. Analysis 20 of the residue showed that it was mostly NaF and excess CF₃SO₂NHNa starting material. All volatiles were removed from the combined solutions and the beige residue was heated to 110°C at 10⁻³ Torr for 16 h. Yield is 3.8 g. ¹⁹F NMR in d₈-THF confirmed complete conversion of the sulfonyl fluoride groups of the polymer to imide. ¹⁹F NMR Residue in d₈-THF; -79 to -85 ppm (CF₃SO₂, 25 CF₃(CF), 2 x CF₂O, 10 F), -90 to -135 ppm (CF₂SO₂, VF₂ fluorines), -146.0 ppm (CF(CF₃), 1F); integration gives 28 mol % PSEPVE-imide in the polymer. ¹H NMR Residue in d₈-THF: 2 to 3.8 ppm VF₂ protons.

EXAMPLE 16

CH₂=CHCH₂CF₂CF₂OCF₂CF₂SO₂F was synthesized according to the 30 teachings of Guo et al., Huaxue Xuebao (1984), 42(6), 592-5.

As in Example 1, a round bottom flask was charged with 2.02 g of CF₃SO₂NNa₂ prepared as in Example 1 and 60 ml of anhydrous acetonitrile prepared as in Example 1. 3.73 g CH₂=CHCH₂CF₂CF₂OCF₂CF₂SO₂F was added drop wise over a period of 5 min. After 20-25 min, the mixture turned clear 35 and then generated a precipitation. The mixture was stirred for 3 h at room temperature. The reaction mixture was filtered through a paper filter inside the dry box. All volatiles were removed and the white residue was heated to 100°C

for 16 h at 10^{-3} Torr. Yield was 3.635 g. ^{19}F NMR in CD_3CN confirmed the structure $\text{CH}_2=\text{CHCH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$.

^{19}F NMR in CD_3CN :

5 $\text{CH}_2=\text{CHCH}_2\text{CF}_2\text{ACF}_2\text{BOCF}_2\text{CCF}_2\text{DSO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3\text{E}$: -80.60 ppm (CF_3 , **E**, 3F), -82.77 ppm (CF_2 , **C**, 2F), -88.90 ppm (CF_2 , **B**, 2F), -118.31 ppm (2 X CF_2 , **A** + **D**, 4F).

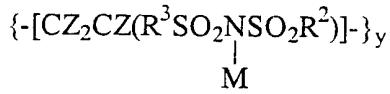
^1H NMR in CD_3CN : $\text{CH}_2\text{A}=\text{CHBCH}_2\text{CCF}_2\text{CF}_2\text{OCF}_2\sim$: 2.87 ppm (CH_2 , **C**, tdt, 2H), 5.26 ppm (CH_2 , **A**, 2F) and 5.74 ppm (CH_2 , **B**, 1F).

I claim:

1. A process comprising:

contacting in a liquid dispersion or solution
a composition comprising a dimetal sulfonyl amide salt represented by
5 the formula $(R^2SO_2NM_b)_{3-b}M'_c$
wherein R^2 is aryl, fluoro-aryl, or XCF_2 — where X is H, halogen,
fluorinated or non-fluorinated linear or cyclic alkyl radicals having
1-10 carbons, optionally substituted by one or more ether oxygens,
10 M' is an alkaline earth metal, $b = 1$ or 2 , $c = 0$ or 1 , M is an alkaline
earth where b is 1 or an alkali metal where b is 2 and $c = 0$, and M
is alkali metal when $b = 1$ and $c = 1$, with the proviso that $c = 1$
when $b = 2$

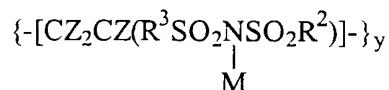
with
15 a non-polymeric sulfonyl fluoride composition represented by the
formula $R^1(SO_2F)_m$
wherein $m = 1$ or 2 , where when $m = 1$ R^1 is a fluorinated or non-
fluorinated, saturated or unsaturated hydrocarbyl radical except
perfluoroolefin having 1-12 carbons optionally substituted by one
or more ether oxygens, or tertiary amino; or, when $m = 2$, R^1 is a
20 fluorinated or non-fluorinated, saturated or unsaturated
hydrocarbenyl radical having 1-12 carbons optionally substituted
by one or more ether oxygens;
or with a polymeric sulfonyl fluoride composition comprising monomer
units represented by the formula
25 $-[CZ_2CZ(R^3SO_2F)]-$
wherein R^3 is a diradical selected from the group consisting of
fluorinated or non-fluorinated alkenyl, including oxyalkenyl or
30 fluorooxyalkenyl, and each Z is independently hydrogen or
halogen, and need not be the same; and,
causing them to react to form a non-polymeric imide composition represented by
the formula



35

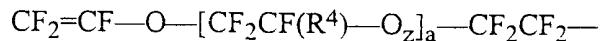
wherein $y = 1$ or 2 , M is alkali or alkaline earth metal when y is 1 or 2 respectively, $m = 1$ or 2 , where, when $m = 1$, R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbyl radical, except perfluoroolefin, having 1 - 12 carbons optionally substituted by one or more ether oxygens, or tertiary amino; or, when $m = 2$, R^1 is a fluorinated or non-fluorinated, saturated or unsaturated hydrocarbenyl radical having 1 - 12 carbons optionally substituted by one or more ether oxygens, with the proviso that when $y = 2$ and $m = 2$, M may represent a combination of alkali and alkaline earth metals;

or, in the alternative, a polymeric imide composition comprising monomer units represented by the formula



wherein $y = 1$ or 2 ; R^3 is a diradical selected from the group consisting of fluorinated or non-fluorinated alkenyl, including oxyalkenyl or fluoroxyalkenyl, each Z is independently hydrogen or halogen, wherein the Z s need not be the same; R^2 is aryl, fluoro-aryl, or XCF_2 - where X is H, halogen, fluorinated or non-fluorinated linear or cyclic alkyl radicals having 1 - 10 carbons, optionally substituted by one or more ether oxygens; M is an alkali when y is 1 or an alkaline earth metal when y is 2 .

2. The process of Claim 1 wherein $m = 1$.
- 25 3. The process of Claim 1 further comprising an inert, aprotic organic liquid.
4. The process of Claim 3 wherein the organic liquid is an ether.
5. The process of Claim 4 wherein the ether is tetrahydrofuran.
6. The process of Claim 1 wherein R^2 is a perfluoroalkyl radical.
- 30 7. The process of Claim 6 wherein R^2 is a trifluoromethyl radical.
8. The process of Claim 1 wherein M is an alkali metal, $b = 2$ and $c = 0$.
9. The process of Claim 8 wherein M is sodium.
10. The process of Claim 2 wherein R^1 is a perfluorovinyl ether radical.
11. The process of Claim 10 wherein the perfluorovinyl ether radical is represented by the formula



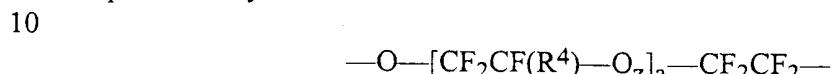
wherein R^4 is F or perfluoroalkyl having 1-4 carbons, $z = 0$ or 1, and $a = 0$ -3.

12. The process of Claim 11 wherein R^4 is trifluoromethyl, $z = 1$, and
5 $a = 0$ or 1.

13. The process of Claim 1 wherein Z is F.

14. The process of Claim 1 wherein R^3 is a perfluorooxyalkenyl radical.

15. The process of Claim 14 where R^3 is a perfluorooxyalkenyl radical
represented by the formula



wherein R^4 is F or perfluoroalkyl having 1-4 carbons, $z = 0$ or 1, and $a = 0$ -3.

16. The process of Claim 15 wherein R^4 is trifluoromethyl, $z = 1$, and
15 $a = 0$ or 1.

17. The process of Claim 1 wherein the sulfonyl fluoride polymer
composition further comprises comonomer units derived from the group
consisting of fluorinated, but not perfluorinated, olefins, non-fluorinated olefins,
fluorinated vinyl ethers, non-fluorinated vinyl ethers, and mixtures thereof.

20 18. The process of Claim 17 wherein the comonomer units are derived
from the group consisting of ethylene, perfluoroalkyl vinyl ether, vinylidene
fluoride, and vinyl fluoride, and mixtures thereof.

19. The process of Claim 18 wherein the comonomer units comprise
vinylidene fluoride.

25 20. The process of Claim 19 wherein the vinylidene fluoride is at a
concentration of at least 50 mol % in the sulfonyl fluoride polymer composition.

21. The process of Claim 1 wherein the monomer units represented by the
formula $-\text{[CZ}_2\text{CZ}(\text{R}^3\text{SO}_2\text{F})]-$ are present in the sulfonyl fluoride polymer at a
concentration of up to 50 mol %.

30 22. The process of Claim 21 wherein the monomer units represented by
the formula $-\text{[CZ}_2\text{CZ}(\text{R}^3\text{SO}_2\text{F})]-$ are present in the sulfonyl fluoride polymer at
a concentration of up to 20 mol %.

23. The process of Claim 9 further comprising the step of performing an
ion exchange to form the lithium imide.

35 24. The process of Claim 23 wherein the ion exchange is performed by
contacting the sodium imide with organic lithium chloride solution.

25. The process of Claim 1 wherein the composition comprising the dimetal sulfonyl amide salt comprises at least 50 mol % of said dimetal sulfonyl amide salt.

26. The process of Claim 25 wherein the composition comprises at least 5 90 mol % of said dimetal sulfonyl amide salt.

27. The process of Claim 1 wherein the dimetal sulfonyl amide salt is contacted with the non-polymeric sulfonyl fluoride composition causing them to react to form the non-polymeric imide composition.

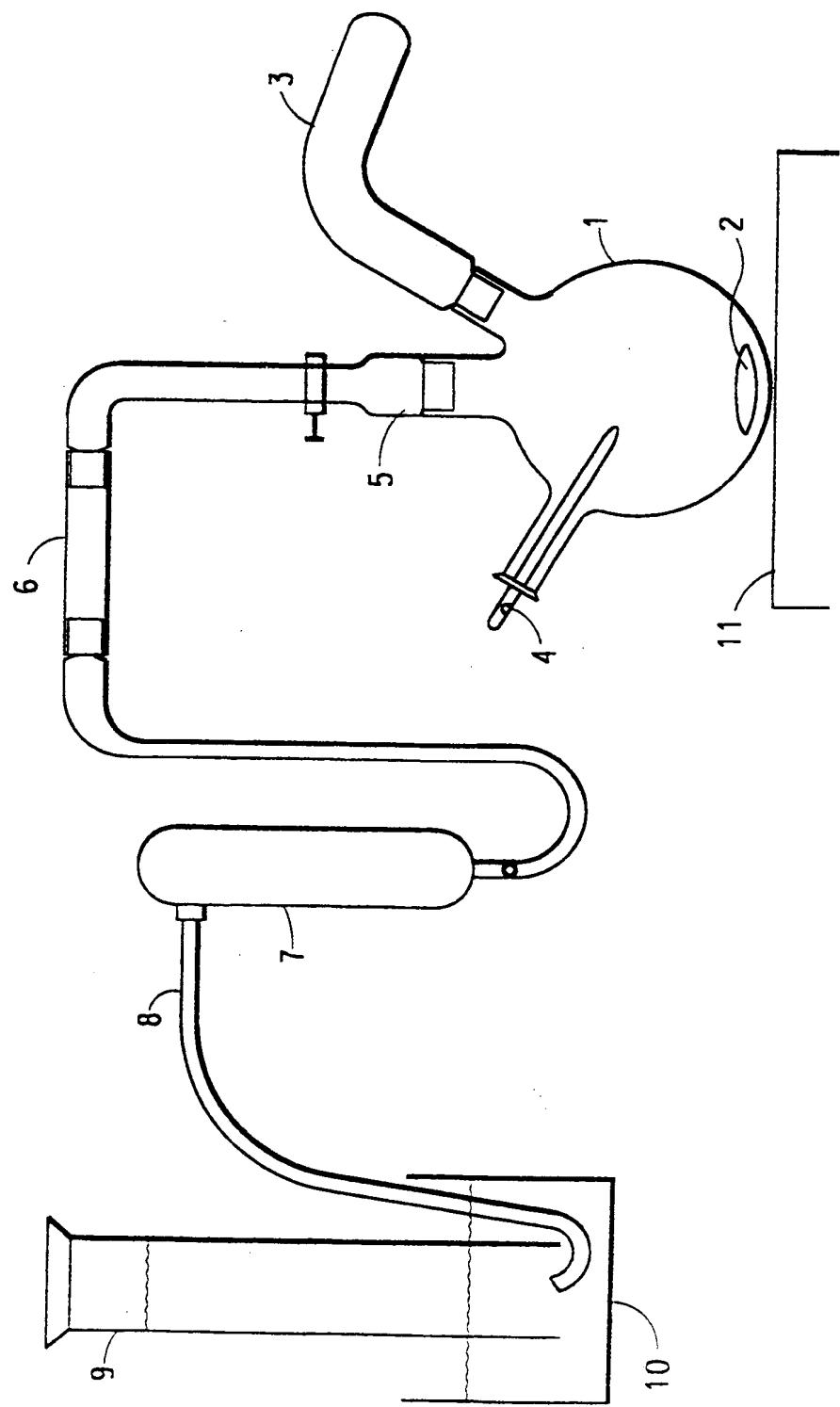
28. The process of Claim 1 wherein the dimetal sulfonyl amide salt is 10 contacted with the polymeric sulfonyl fluoride composition causing them to react to form the polymeric imide composition.

29. The process of Claim 18 wherein the sulfonyl fluoride polymer composition further comprises a termonomer unit derived from a perfluoro-olefin.

30. The process of Claim 29 wherein the perfluorolefin is 15 tetrafluoroethylene, hexafluoropropylene or a combination thereof.

1/1

FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/32672

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C07C311/48 C08F214/22 C07C303/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C07C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 850 920 A (HYDRO QUEBEC ; CENTRE NAT RECH SCIENT (FR)) 1 July 1998 (1998-07-01) cited in the application claims; examples ---	1-30
A	US 5 463 005 A (DESMARTEAU DARRYL D) 31 October 1995 (1995-10-31) cited in the application column 5, line 65 -column 6, line 15 column 8, line 1 - line 35; claims; examples ---	1-30
A	WO 99 45048 A (FARNHAM WILLIAM BROWN ; FEIRING ANDREW EDWARD (US); ROELOFS MARK GE) 10 September 1999 (1999-09-10) cited in the application claims; examples ---	1-30
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

21 February 2001

16/03/2001

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Seufert, G

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/32672

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 90 11999 A (CENTRE NAT RECH SCIENT ;HYDRO QUEBEC (CA)) 18 October 1990 (1990-10-18) claims; examples -----	1-30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/32672

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
EP 0850920	A 01-07-1998	CA 2194127	A	30-06-1998	
		CA 2199231	A	05-09-1998	
		CA 2244979	A	09-07-1998	
		CA 2248242	A	09-07-1998	
		CA 2248244	A	09-07-1998	
		CA 2248246	A	09-07-1998	
		CA 2248303	A	09-07-1998	
		CA 2248304	A	09-07-1998	
		WO 9829358	A	09-07-1998	
		WO 9829399	A	09-07-1998	
		WO 9829389	A	09-07-1998	
		WO 9829396	A	09-07-1998	
		WO 9829877	A	09-07-1998	
		WO 9829388	A	09-07-1998	
		EP 0850933	A	01-07-1998	
		EP 0850921	A	01-07-1998	
		EP 0850932	A	01-07-1998	
		EP 0889863	A	13-01-1999	
		EP 0890176	A	13-01-1999	
		JP 2000508676	T	11-07-2000	
		JP 2000508677	T	11-07-2000	
		JP 2000508346	T	04-07-2000	
		JP 2000508114	T	27-06-2000	
		JP 2000508678	T	11-07-2000	
		US 6120696	A	19-09-2000	
US 5463005	A 31-10-1995	NONE			
WO 9945048	A 10-09-1999	AU 2978199	A	20-09-1999	
		EP 1060200	A	20-12-2000	
		NO 20004334	A	30-10-2000	
WO 9011999	A 18-10-1990	FR 2645533	A	12-10-1990	
		AT 93844	T	15-09-1993	
		CA 2030809	A	07-10-1990	
		DE 69003063	D	07-10-1993	
		DE 69003063	T	17-03-1994	
		EP 0419647	A	03-04-1991	
		ES 2044587	T	01-01-1994	
		JP 4501118	T	27-02-1992	
		US 5072040	A	10-12-1991	