



Access to Poly-Fluorinated Building Blocks via ElectroChemical Fluorination

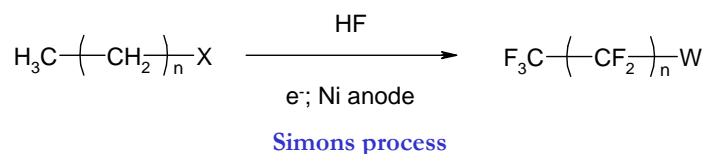
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Berlin, 9 – 10 June 2010

A. Missio
M. Bertola



ElectroChemical Fluorination Basic Principles

In its simplest formulation, ECF performs the conversion of an hydrogenated substrate to its perfluorinated derivative. The reagents are anhydrous hydrofluoric acid (HF) and electricity.



“A remarkable fluorination process” (R.D. Chambers, Durham University)

“... An art in many respects” (J.C. Tatlow, Birmingham University)

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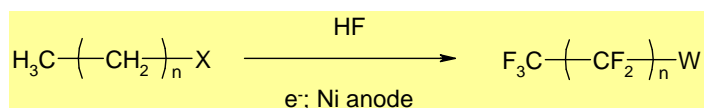
Mechanism of ECF

1. Radical mechanism Fluorine homolysis
2. EC_bEC_n mechanism
Electrochemical oxidation of substrate to radical cation,
Chemical abstraction of proton to radical (C_{\cdot}),
Electrochemical oxidation to carbocation,
Reaction with F^- (C_n) to form C-F bond.
3. NiF_2/NiF_3 mediated mechanism Formation of high valence Nickel Fluorides (NiF_2/NiF_3) at anode.

The ECF process performs an exhaustive fluorination of each molecule of substrate



ECF: Advantages



Advantages

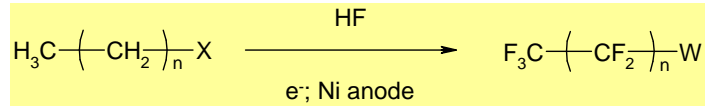
Cheap reagents
Simple design of reactors
Functional group tolerance

Electrical conductivity is critical:
Nitrogen, Oxygen, Phosphorus and Sulfur containing compounds are **OK**.
Hydrocarbons may require conductivity aids.
Optional use of mixtures.

X	W
$CO_2H/COCl$	COF
CH_3	CF_3
SO_3H/SO_2Cl	SO_2F
$N(R_H)_2$	$N(R_F)_2$
$P(R_H)_2$	$(F)_2P(R_F)_2$



ECF: Disadvantages



Disadvantages

ECF run takes time (weeks/months)
Low yields
Conversion / Selectivity
Product purification
Explosion hazard (F₂O)

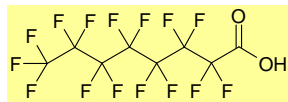
X	W	n	Y (%)*
CO ₂ H	COF	6	10
COCl	COF	6	15-20
COCl	COF	4	18
COCl	COF	2	35
SO ₂ Cl	SO ₂ F	7	25
SO ₂ Cl	SO ₂ F	5	36
SO ₂ Cl	SO ₂ F	3	58

*: isolated carboxylic/sulfonic acid

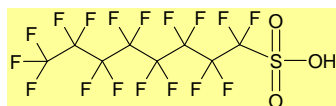


Main Products from ECF

- *PerFluorinated Carboxylic Acids (PFCAs):*
 - e.g.: *PerFluoroOctanoic Acid (PFOA)*



- *PerFluorinated AlkylSulfonates (PFASs):*
 - e.g.: *PerFluoroOctaneSulfonate (PFOS)*



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≥ C8



Main Properties

(in final products)

- Low surface energy
- Chemical & moisture resistance
- Oil & grease resistance
- Soil & dirt resistance
- Low refractive index
- Surface lubricity
- Adhesion to low-energy surfaces



Main Uses

- Fluoropolymers
- Coatings
- Fire-fighting foams
- Paper
- Textiles, fabrics
- Carpets
- Metal plating
- Soldering systems
- Floor & shoe polish
- Thermal fluids
- Photographic processes



The Legacy of Older Products

Research has produced evidence that some perfluorinated substances are:

- Resistant to degradation
- Present in the environment
- Subject to long range transport
- Widespread presence in humans and wildlife
- Biopersistent & Bioaccumulative

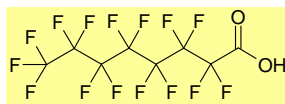


Regulatory Environment

United States Environmental Protection Agency Stewardship Program (2006)

Program requires corporate commitment to two goals:

- To commit to achieve, no later than 2010, a 95% reduction (baseline: year 2000) in facility emissions of PFOA, longer chain PFCAs and their precursors, and in residuals in commercial products.
- To commit to working toward the elimination of PFOA, longer chain PFCAs and their precursors from facility emissions and from residuals in commercial products by 2015.





Regulatory Environment

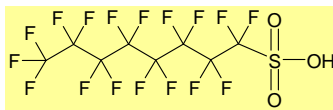
DIRECTIVE 2006/122/EC of the EUROPEAN PARLIAMENT and of the COUNCIL
of 12 December 2006

amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates)

(Text with EEA relevance)

L 372/32 EN Official Journal of the European Union 27.12.2006

Restrictions on the marketing and use of PFOS and related products



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Novel Building Blocks

• **Convert ECF product line from C8 to environmentally acceptable products**

- ✓ RM 60 series (perfluorobutanesulfonyl derivatives; C4)
- ✓ RM 70 series (perfluorohexanesulfonyl derivatives; C6)
- ✓ **RM 600 series (perfluoroalcohols C3-C6)**
- ✓ C6-based chemistry

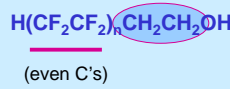
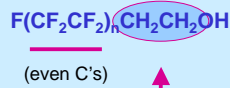
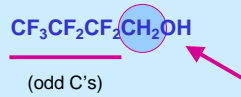
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MITENI Novel Building Blocks

RM 600 series (perfluoroalcohols C3-C6)

- technology / product differentiator



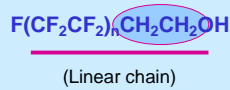
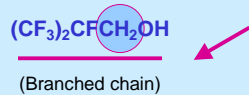
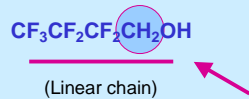
Miteni

Competitors

MITENI Novel Building Blocks

RM 600 series (perfluoroalcohols C3-C6)

- technology / product differentiator



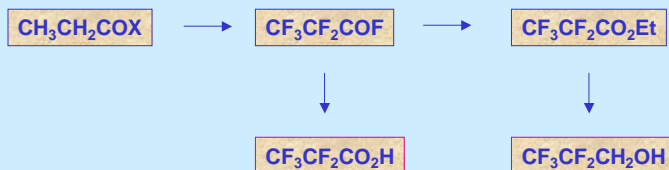
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Competitors



Synthesis of PolyFluorinated Building Blocks

C3 Building Blocks



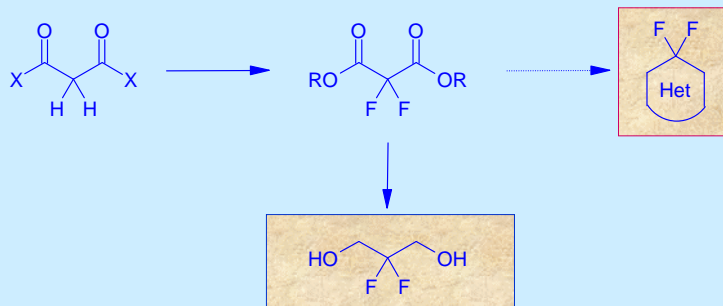
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Synthesis of PolyFluorinated Building Blocks

C3 Building Blocks



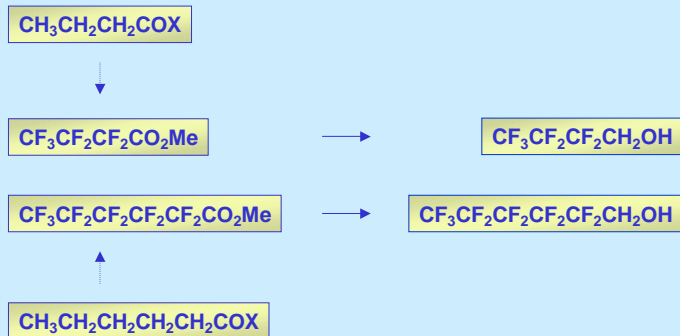
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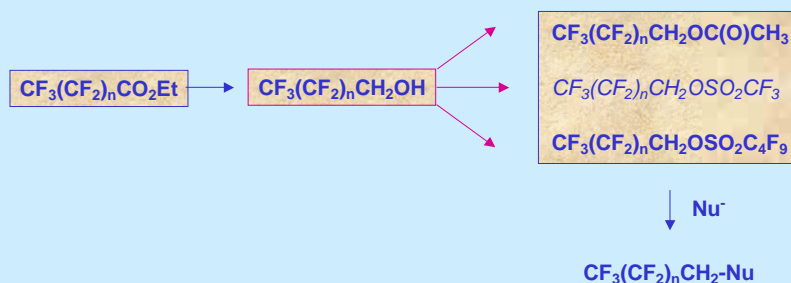
Synthesis of PolyFluorinated Building Blocks

C4 & C6 Building Blocks



Synthesis of PolyFluorinated Building Blocks

C3-C6 Building Blocks





Acknowledgements

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THANK YOU