Hydrogen Fluoride

This fact sheet is part of a series of chemical fact sheets developed by TURI to help Massachusetts companies, community organizations and residents understand a chemical's use and health/environmental effects, as well as the availability of safer alternatives.

Overview

Hydrogen fluoride (HF), also known as hydrofluoric acid, is used primarily for metal cleaning and etching in Massachusetts. Nationally, HF is mainly used to manufacture chemical refrigerants.

HF is highly corrosive to all tissues and any contact with HF liquid or vapor can cause severe burns (sometimes with delayed onset), necrosis, and death. Skin contact with HF may not cause immediate pain, so systemic poisoning can begin before the person is aware of the exposure.

In 2017, Massachusetts facilities subject to TURA reported the use of over 230,000 pounds of HF. **HF is designated as a Higher Hazard Substance (HHS) under the Toxics Use Reduction Act (TURA), which lowered the reporting threshold to 1,000 pounds/year, effective January 2016.**

Hazards

Acute Health Effects

HF is highly corrosive to all tissue. Skin contact results in burns and necrosis, and underlying bone may be decalcified.[1]

Skin contact with HF may not cause immediate pain, so systemic poisoning can begin before the person is aware of the exposure.[2] In addition, the HF penetrates the skin and causes systemic toxicity through binding with calcium and magnesium, which induces metabolic disorders and further tissue necrosis.[3] Systemic effects are potentially lethal.

Inhalation of, and exposure to, HF mist can cause severe irritation and damage to the eye, nose and skin. Acute exposure to HF through inhalation or skin contact (for example, through a facial splash) can be fatal due to effects on the heart and lungs, including pulmonary hemorrhage, pulmonary edema, and bronchiolar ulceration. Deaths associated with HF exposure generally result either from pulmonary edema or from cardiac arrhythmias.[2]

Accidental releases have caused severe respiratory and gastrointestinal symptoms among residents that live near the facility.[2]

TABLE 1: HF Facts	
Chemical Formula	HF
CAS Number	7664-39-3
Vapor Pressure	760 mm Hg at 68ºF (20ºC)
Solubility	Miscible in water; soluble in ether, soluble in many organic solvents
Flash point	Nonflammable
Reactivity	Reacts violently with strong bases and many other compounds; reacts with water and steam to produce toxic and corrosive gases
Description	Colorless, fuming liquid or gas at room temperature with a sharp, irritating odor that humans can detect at low concentrations (0.04-0.13ppm)[4]

Chronic Health Effects

Individuals who breathe in hydrogen fluoride and survive the resulting severe acute injuries may suffer lingering chronic lung disease.

Chronic inhalation of fluoride (either in the form of hydrogen fluoride or in the form of fluoride dusts) is associated with skeletal fluorosis, a disease associated with accumulation of fluoride in the bones and characterized by abnormal bone density, joint pain, and problems with joint movement.[2]

Animal studies also show evidence of liver and kidney damage associated with HF inhalation exposure.[2]

Exposure Routes

The main routes of exposure to HF are inhalation or dermal exposure in occupational settings.[2]

Worker Health

Facilities using HF must minimize worker exposure. To protect against adverse effects from exposure to hydrofluoric acid in the workplace, the most protective occupational exposure limit has been set by the California Occupational Safety and Health Administration (Cal/OSHA). California's permissible exposure limit (PEL) is 0.4 ppm averaged over an eight-hour work shift; the federal OSHA PEL is 3 ppm.[5,6] At 30 ppm, the National Institute for Occupational Safety and Health (NIOSH) has determined that exposure to HF is "immediately dangerous to life or health" (IDLH).[7] These exposure limits are for air levels. When dermal exposure occurs, overexposure can occur rapidly even if air levels are less than the limits above.

In Massachusetts in 1993, a worker was killed as a result of a spill that occurred when transferring HF manually from one container to another.[8] Two spills requiring emergency response were reported in Massachusetts in 2019.[9,10]

Public Health

HF is primarily a concern for occupational health, but community exposures through accidental releases are a serious matter. Exposure is possible among those that live, work or play near industrial facilities where HF is used or stored.

A large-scale accident in South Korea in 2012 led to deaths and severe injuries among workers and emergency personnel, as well as harmful health effects among thousands of people living in the area.[11]

Uses and Releases

Use in the United States

HF is commercially available either in an anhydrous form, hydrogen fluoride, or as a 70% aqueous solution, hydrofluoric acid.

The primary use of HF in the US is for manufacture of fluorocarbons (82% of the 314,000 metric tons used in 2014); uses of fluorocarbons include refrigerants, blowing agents, and fluoropolymers. Approximately 4% is used for metal treatment, 8% for uranium fuel processing and petroleum catalysts, 3% for semiconductor etching, and 2% for glass etching.[12]

Use in Massachusetts

The major uses of HF in Massachusetts are metal cleaning and etching (see Table 2).

TABLE 2: HF Use Reported Under TURA, 1990 and 2017

Facility Name	Location	Use (pounds), 1990[a]	Use (pounds), 2017[a]
Semiconductor Etching[b]			
Allegro Microsystems	Worcester	52,011	
Analog Devices	Wilmington	26,000	54,105
Digital Equipment Corp	Hudson	15,603	
IXYS Integrated Circuits	Beverly		2,452
Lucent Technologies	North Andover	20,100	
MACOM Technologies	Lowell		3,185
Microsemi Inc.	Watertown	14,000	5,673
North East Silicon Technologies	New Bedford		4,850
Skyworks Solutions	Woburn		4,572
Glass Etching			
Ardagh Glass Inc.	Milford		3,607
Karl Storz	Charlton		2,143
OFS Fitel	Sturbridge		6,842
Osram Sylvania Inc.	Ipswich	98,706	
Metal Treatment & Etching			
Cleanpart East	Southbridge		7,840
Coorstek Worcester	Worcester		1,413
Crown Cork and Seal	Lawrence	56,679	10,325
Electropolishing Systems	Randolph		1,623
FM Callahan	Malden		1,400
Fountain Plating	West Springfield		3,218
General Metal Finishing	Attleboro		2,279
MKS Instruments	Wilmington		1,274
PerkinElmer	Hopkinton		2,189
Photofabrication Engineering	Milford		1,715
Rodney Metals	New Bedford	49,600	
Tech-Etch	Plymouth		26,994
Tecomet	Woburn		25,862
Texas Instruments	Attleboro	10,040	
Westfield Electroplating	Westfield		2,012
Wyman Gordon (combined)	Grafton/ Worcester	323,200	19,894

Facility Name	Location	Use (pounds), 1990[a]	Use (pounds), 2017[a]
Chemical Products			
Cyalume Technologies	West Springfield		8,441
Trans Mate	Billerica		15,612
Transene	Danvers		14,629
Distribution			
George Mann	Stoneham	10,231	
Total HF Use		**676,170**	**234,150**

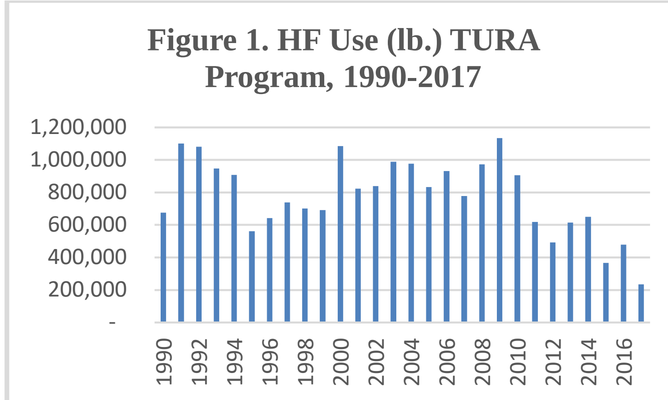
[a] Blank cells indicate that HF was not reported under TURA by that company for the corresponding year. Note that the HHS reporting threshold for 2017 is 1000 lbs.

[b] Use categories were assigned based on TURI's interpretation of facility-reported information under TURA.

Source: Massachusetts Toxics Use Reduction Act data, 2019.

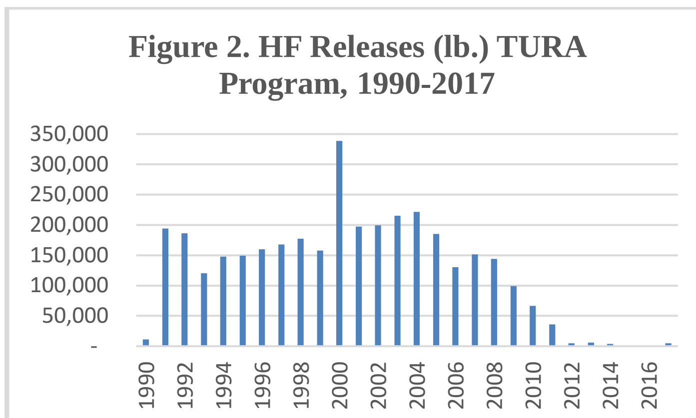
The following information is based on use reporting to the TURA program:

- *Quantity used.* Businesses subject to TURA reported a 65% decrease in the use of HF from 1990 to 2017, from 676,170 pounds in 1990 to 234,150 pounds in 2017 (Figure 1). From 1991 to 2017, total use decreased 79%. Utilities were not subject to TURA reporting until 1991.
- *Number of filers.* Eleven facilities reported using HF in 1990. In 2017 there were 26 filers. This includes 21 facilities that began reporting due to the HHS designation, which lowered the reporting threshold to 1,000 pounds per year. (The previous threshold was 25,000 or 10,000 pounds per year, depending on type of use.) In 2017, these 21 filers accounted for nearly 100,000 pounds (41%) of use and 4,500 pounds (94%) of releases.
- *Combustion byproducts.* Between 1990 and 2011, several utilities reported HF as a combustion byproduct from burning fossil fuels. This includes a spike in one utility's releases in 2000, observed in Figure 2.
- *Primary uses.* Etching (of glass, metal, and semiconductors combined) is the primary use in Massachusetts followed by metal treatment.



Environmental Releases in Massachusetts

Massachusetts facilities reported significant reductions in environmental releases of HF (Figure 2). Releases declined from 12,263 pounds in 1990 to 4,805 pounds in 2017. From 1991 (the first year that utilities reported under TURA) to 2017, there was a 98% reduction in HF releases.



Toxics Use Reduction Options

Due to the significant hazards associated with HF, facilities should seek out opportunities to reduce their use wherever possible. Opportunities include adopting safer alternatives for specific functions or applications where HF is used, and minimizing use through improved efficiencies if alternatives are not available.

Options for metal and glass cleaning and etching – the primary uses in Massachusetts – are reviewed below based on the TURA program's experience and a literature review of available options.

Etching Alternatives

Metal etching. Depending on the metal, other acids may function as viable etching substitutes. These other acids also have significant hazards, but do not have the poor warning properties and systemic effects of HF.

- Brigham Young University has developed a searchable list of chemical etchants used for 44 different metals and semiconductors (see https://cleanroom.byu.edu/wet_etch). Although HF is noted as an etchant for nearly all metals, other alternative acids used in specific proportions and concentrations are described. While these acids (such as hydrochloric and phosphoric acid) also exhibit corrosive hazard properties, they are typically easier to manage and are less hazardous than HF.
- Texas Instruments of North Attleboro, MA, moved to a metal spraying technique for coating ceramic parts that decreased the need for chemical acid etching of ceramic parts prior to metal application.[13]

Bathtub refinishing. Bathtub refinishers have described alternative etching techniques to prepare the surface of a bathtub to promote adhesion of new surface coatings.

- Mechanical abrasion, such as sanding, is an effective alternative for preparing acrylic fiberglass or enamel tubs for refinishing. Sanding typically takes more time and effort, and workers need to be protected from dust; however, chemical exposures are eliminated.

Metal Cleaning Alternatives

Surface treatment. When HF is used as a surface treatment to clean and activate metallic surfaces, low frequency plasma etching technologies may be a viable alternative but also typically use toxic etchants.

Vehicle washes. Some vehicle wash facilities use HF or ammonium bifluoride (which dissociates in water to form HF) to remove dirt, brake dust and road grime from wheels and to clean car wash equipment. A less hazardous solution—an alternative product with dodecyldimethylamine oxide and alcohol ethoxylates as the main ingredients—is available.[14] Other wheel brightener alternatives include oxalic acid surfactant-based products.

Gold jewelry manufacturing. Alternatives to using HF to remove the plaster from the casting mold in gold jewelry manufacturing include sulfuric acid, though it is not always capable of dissolving all plaster residues. In some cases, additional manual treatment is required to achieve the level of cleaning necessary. Sulfuric acid is also a toxic chemical, but is generally less hazardous than HF.[15]

Improved Efficiencies

Diffusion dialysis may be used in some cases to recycle spent hydrofluoric acid in mixed acid baths, reducing consumption of virgin HF.[16] Two regional suppliers currently offer diffusion dialysis units: Zero Discharge Technologies, Inc. of Chicopee, MA, and Pure Cycle Environmental, LLC in North Haven, CT.

In 1999, TURI sponsored a demonstration site event in which ASE Americas Inc. in Billerica, MA, demonstrated a hydrofluoric acid vapor acid etch process for silicon wafers using an ultra-small volume chamber. This new process reduced their use of hydrofluoric acid by nearly 99% compared to the liquid batch etching process. However, the use of HF in vapor rather than liquid form introduced new safety concerns to the process that had to be addressed by implementing strict procedures.[17]

Point of Use Generation of HF

There are also options to improve safety by generating HF at the point of use, although these options do not reduce the amount of HF used. For some applications, it is possible to generate HF at the point of use by using salt forms, such as ammonium or sodium bifluoride. These are solid materials that dissociate in water to form HF. Using the solid material reduces the potential for exposure related to transporting liquid HF within and outside the facility. While this approach does not eliminate HF, it is an important option to improve safety.

Glass etching. Preliminary research showed promising results using ammonium bifluoride in the presence of sulfuric acid in a heated bath, although the etched silica formed an ammonium silica fluoride complex which needed to be precipitated out by cooling the bath. Researchers thought this deserved further study.[18]

Regulatory Context

Due to its toxicity, HF is subject to a number of regulations. Selected federal and state regulations are noted in the tables below.

TABLE 3: Massachusetts Regulations & Guidelines	
Toxics Use Reduction Act	Listed under TURA. Designated as a Higher Hazard Substance under TURA, effective January 2016
Environmental & Public Health	Subject to Massachusetts Right-to-Know requirements[19] Massachusetts Ambient Air Guidelines: threshold effects exposure limit (TEL) 0.83 ppb (24 hr avg); allowable ambient limit (AAL) 0.42 ppb (annual avg)[20]
Releases & Waste Cleanup	Reportable under 310 CMR 40.0000, the Massachusetts Contingency Plan.[21]

TABLE 4: Other State Regulations (*Not Comprehensive*)	
California	Cal/OSHA has adopted more stringent occupational exposure limits for HF than those currently in force at the federal level and through ACGIH:[6] – Permissible Exposure Limit (PEL): 0.4 ppm (Time Weighted Average [TWA] over an 8 hr work shift) – Short-term Exposure Limit (STEL): 1 ppm (TWA over 15 min, not to be exceeded during the work day)

TABLE 5: U.S. Regulations And Guidance Values *(Not Comprehensive)*	
EPCRA	Reportable under TRI[22] Subject to US EPA Tier II reporting requirements[23] Regulated as an Extremely Hazardous Substance (EHS) under EPCRA Section 302][24,25]
Clean Water Act	Designated as a hazardous substance under section 311(b)(2)(A) of the Federal Water Pollution Control Act and further regulated by the Clean Water Act Amendments of 1977 and 1978[26]
RCRA	Must be managed as hazardous waste[27]
Clean Air Act	Regulated as a Hazardous Air Pollutant (HAP)[28] Clean Air Act Section 112(r) List of Substances for Accidental Release Prevention for concentrations 50% or greater (threshold quantity: 1,000 lb. per process)[29]
CERCLA	Reportable quantity: 100 lb[27,30]
OSH Act	Permissible Exposure Limit (PEL): 3 ppm (TWA over an 8 hr work shift)[28]
NIOSH	Recommended Exposure Limit (REL): TWA 3 ppm, Ceiling 6 ppm [15-minute][31] Immediately Dangerous to Life and Health (IDLH): 30 ppm[29]
ACGIH TLV	Threshold Limit Value (TLV) 8 hr TWA: 0.5 ppm (TWA over an 8 hr work shift) Ceiling: 2 ppm (not to be exceeded anytime)[32]

TABLE 6: International Policies	
Canada	Included on Canada's Toxic Substances List (Schedule 1) under the Canadian Environmental Protection Act[33] Also included on Canada's Environmental Emergencies: List of Exploding or Hazardous Substances, Part 2: substances hazardous when inhaled[34] Reportable under the National Pollutant Release Inventory, category 1A (10 ton threshold)[35]
European Union	Hydrogen fluoride is included in the EU Cosmetic Products Regulation, Annex II (list of substances prohibited in cosmetic products)[36]

Note: Information in this fact sheet should not be used for compliance purposes.

[1] International Programme on Chemical Safety, *Poisons Information Monograph 268*. 1990, World Health Organization.
[2] Agency for Toxics Substances and Disease Registry, *Toxicological Profile for Fluorides, Hydrogen Fluoride, and Fluorine*. September 2003.
[3] Burgher, F., et al., *Experimental 70% hydrofluoric acid burns: histological observations in an established human skin explants ex vivo model.* Cutan Ocul Toxicol, 2011. 30(2): p. 100-7.
[4] Emergency Response Planning Guideline Committee, *Emergency Response Planning Guidelines*. 1988, American Industrial Hygiene Association.
[5] Occupational Health and Safety Administration. *Annotated OSHA Z-2 Table*. [cited 2018 May 15]; Available from: https://www.osha.gov/dsg/annotated-pels/tablez-2.html.
[6] California Department of Industrial Relations. *Table AC-1. Permissible Exposure Limits for Chemical Contaminants*. [cited 2018 May 15]; Available from: https://www.dir.ca.gov/title8/5155table_ac1.html
[7] National Institute for Occupational Safety and Health. *NIOSH Pocket Guide to Chemical Hazards - Hydrogen Fluoride*. [cited 2018 May 15]; Available from: https://www.cdc.gov/niosh/npg/npgd0334.html.
[8] National Institute for Occupational Safety and Health (NIOSH). *Massachusetts plater dies following hydrofluoric acid spill exposure during transfer process*. 1993, April; Available from: https://www.cdc.gov/niosh/nioshtic-2/20028388.html.
[9] Alisa Bosma, "Milford Hazmat Spill Sends Four to Hospital." *The Milford Daily News*, January 15, 2019. https://www.milforddailynews.com/news/20190115/milford-hazmat-spill-sends-four-to-hospital
[10] Sabrina Schnur, "Chemical spill at lab sends 2 to hospital in Waltham." *Boston Globe* March 19, 2019. Available from: https://www.bostonglobe.com/metro/2019/03/19/chemical-spill-lab-sends-hospital-waltham/gSfZx1g2NejsW2EzM0nCXI/story.html.
[11] Stafford, N. *Questions remain after huge hydrofluoric acid leak*. 2012, November 8; Available from: https://www.chemistryworld.com/news/questions-remain-after-huge-hydrofluoric-acid-leak/5611.article.
[12] IHS Chemical, *Chemical Economics Handbook - Fluorspar and Inorganic Fluorine Compounds* January 2016. p. 69-70, 72.
[13] Ray Lizotte -Texas Instruments, Personal Communication. 2000.
[14] (SUBSPORT), S.S.P. *Case study: Car wheel cleaner based on alcohol ethyocylates and dodecyldimethylamine oxide as alternative to fluorine containing products*. 2012; Available from: http://www.subsport.eu/case-stories/317-en?lang=
[15] Substitution Support Portal (SUBSPORT). *Substituting hydrofluoric acid in gold jewelry production*. 2012; Available from: http://www.subsport.eu/case-stories/283-en?lang=
[16] Bonner F. and A. Donatelli. *Diffusion Dialysis and Acid Recovery in Metal Operations. Toxics Use Reduction Institute Technical Report No. 29*. 2001; Available from: http://www.turi.org/TURI_Publications/TURI-Technical-Reports/Diffusion_Dialysis_and_Acid_Recovery_in_Metal_Operations._20012.
[17] Toxics Use Reduction Institute, *Cleaner Technology Demonstration Site Fact Sheet: Acid Use Reduction in Photovoltaic Semiconductor Etching*. 1998.
[18] DeFosse, T., Demarey, D., *Hydrofluoric Acid Reduction Project – TURI Grant 2017*. 2017: OFS, Sturbridge, MA.
[19] *MGL Title XVI, Ch.111F, Sec 4: Substance List*. [cited 2018 May 15]; Available from: https://malegislature.gov/Laws/GeneralLaws/PartI/TitleXVI/Chapter111F/Section4.
[20] Massachusetts Executive Office of Energy and Environmental Affairs. *Ambient Air Toxics Guidelines*. 2015 [cited 2016 November 7]; Available from: http://www.mass.gov/eea/agencies/massdep/toxics/sources/air-guideline-values.html#CurrentAALsTELs.
[21] Massachusetts Department of Environmental Protection. *310 CMR 40.0000: Massachusetts Contingency Plan*. [cited 2016 November 7]; Available from: http://www.mass.gov/eea/agencies/massdep/cleanup/regulations/massachusetts-contingency-plan.html.
[22] United States Environmental Protection Agency (USEPA). *List of Lists: Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-To-Know Act (EPCRA), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and Section 112(r) of the Clean Air Act*. 2012, October [cited 2014 May 29]; Available from: https://www.epa.gov/sites/production/files/2013-08/documents/list_of_lists.pdf.
[23] United States Environmental Protection Agency (USEPA). *Emergency Planning and Community Right-to-Know Act (EPCRA) Hazardous Chemical Storage Reporting Requirements*. 2014; Available from: http://www.epa.gov/emergencies/content/epcra/epcra_storage.htm#msds.
[24] U.S. Environmental Protection Agency. *40 CFR Part 355, Appendix A. ("Appendix A to Part 355: The List of Extremely Hazardous Substances and their Threshold Planning Quantities")*. 1999; Available from: http://www.gpo.gov/fdsys/pkg/CFR-2002-title40-vol24/pdf/CFR-2002-title40-vol24-part355-appA.pdf.
[25] U.S. Environmental Protection Agency. *Emergency Planning and Community Right-To-Know Act*. 2012 [cited 2014 May 29]; Available from: http://www.epa.gov/oecaagct/lcra.html.
[26] Hazardous Substances Data Bank (HSDB). *40 CFR 116.4*. 2012; Available from: http://toxnet.nlm.nih.gov.
[27] Hazardous Substances Data Bank (HSDB). *40 CFR 261.22 and 40 CFR 261.33*. 2012; Available from: http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~WhnmH3:1.
[28] U.S. Environmental Protection Agency. *Clean Air Act Amendments of 1990 List of Hazardous Air Pollutants*. 1990 [cited 2014 May 29]; Available from: http://www.epa.gov/ttn/atw/orig189.html.
[29] U.S. Environmental Protection Agency. *List of Lists ….* 2012, October [cited 2014 May 29]; Available from: http://www2.epa.gov/sites/production/files/2013-08/documents/list_of_lists.pdf.
[30] U.S. Centers for Disease Control and Prevention - National Institute for Occupational Safety and Health (NIOSH). *NIOSH Pocket Guide to Chemical Hazards entry for hydrogen fluoride*. 2017, March [cited 2017 March 6]; Available from: https://www.cdc.gov/niosh/npg/npgd0334.html.
[31] National Institute for Occupational Safety and Health. *NIOSH Pocket Guide to Chemical Hazards: Hydrogen fluoride*. 2011, April; Available from: http://www.cdc.gov/niosh/npg/npgd0334.html.
[32] Occupational Safety and Health Administration. *Hydrogen Fluoride*. 2005 [cited 2014 May 29]; Available from: https://www.osha.gov/dts/chemicalsampling/data/CH_246500.html.
[33] Environment and Climate Change Canada. *Toxic Substances List – Schedule 1*. [cited 2017 March 10]; Available from: http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=0DA2924D-1&wsdoc=4ABEFFC8-5BEC-B57A-F4BF-11069545E434.
[34] Government of Canada. *Environmental emergencies: list of exploding or hazardous substances*. 2016, January 14; Available from: https://www.canada.ca/en/environment-climate-change/services/environmental-emergencies-program/regulations/list-exploding-hazardous-substances.html.
[35] Government of Canada. *National Pollutant Release Inventory (NPRI)*. 2016, July 11; Available from: https://pollution-waste.canada.ca/substances-search/Substance/DisplaySubstanceDetails?Id=%20%097664-39-3.
[36] European Union. *Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products*. 2009, December 22 [cited 2016 November 7]; Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:342:0059:0209:en:PDF