

New POPs in Articles -Case study of PBDEs and PFOS



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Outline

- ① Production and application
- ② Analysis
- ③ Treatment of PBDEs containing articles
- ④ Some alternatives to PFOS



Production and application

1.1 Production of PBDEs in China

- ❑ China has never produced octaBDE.
- ❑ With the impact of the international conventions and changes in market demand, the production of PentaBDE was ceased in 2003.
- ❑ DecaBDE is producing from the late of 1990. Historically, 15 enterprises produce Deca-BDE, up to now, only four companies still produce Deca-BDE. The actual annual production capacity of Deca-BDE is about 23,000 tons



Production and application

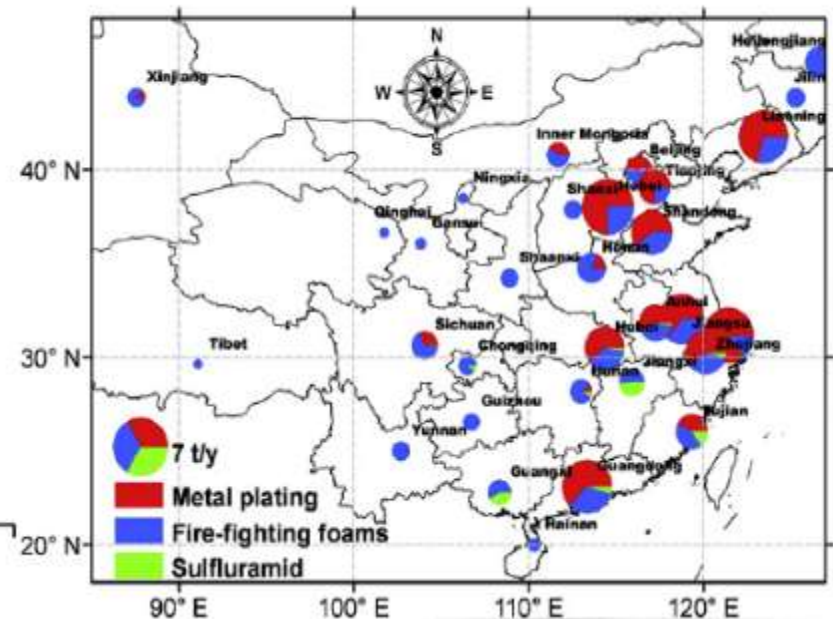
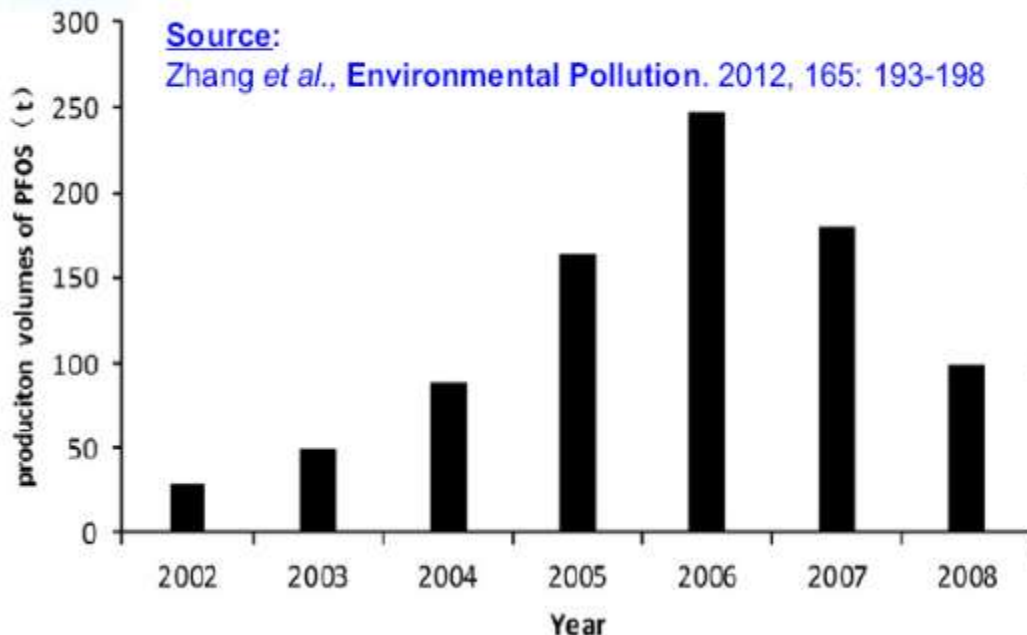
1.2 PBDEs usage status in China

- ❑ Deca-BDE is a general purpose flame retardant and is used in virtually any type of polymer in China, including: polycarbonates, polyester resins, polyolefins, ABS, polyamindes, polyvinyl chloride, and rubber.
- ❑ 99% Deca-BDEs are supplied to plastic modification companies for producing flame retardants plastic.
- ❑ 70% flame retardants plastic are used in electric and electronic equipment including computer, air condition, wash-machine, television, refrigerator, housings of equipment, high-voltage coil etc.

Production and application

1.3 Production of PFOS in China

- Average production of PFOS in 2009-2012: 100-140 t/a (PFOSF)
- About 1/4-1/3 was exported (esp. to Brazil)



Production and application

1.4 PFOS application in China

- ❑ Sulfluramid as A. I. in
 - ❑ Bait for termite control
 - ❑ Bait for cockroach control
- ❑ Mist suppressant in hard chrome plating industry
- ❑ Fluorocarbon surfactant in fire-fighting foam
- ❑ Surfactants for oil production
 - ❑ Surfactant for Chemical EOR
 - ❑ Cleanup agent in oil production
 - ❑ Viscosity reducer in oil transportation

Analysis

2.1 PBDEs Analysis technique

- ❑ Sliding spark spectroscopy: is a surface screening destructive method capable to rapidly detect halogens in plastic without prior sample preparation. The scanning time takes only a few seconds. The lowest detection limit for bromine with this technology is 0.1%.
- ❑ X-ray fluorescence (XRF): is a non-destructive method and can be used for detection of bromine in polymers and other materials with a detection limit for bromine of 10 to 100 ppm. The time requirement for a measurement when applying handheld items is less than a minute.



Analysis

2.1 PBDEs Analysis technique

- ❑ X-ray transmission technology (XRT): The XRT is non-mobile equipment applied in dismantling plants to sort scrap plastic by automatically monitoring the atomic density of materials. Industrial machines sort up to 1 tonne of scrap per hour.
- ❑ Sink and float technology: Polymer types exhibit different specific weights, and therefore liquid media with appropriate densities allow for separation of different thermoplastics into density groups.
- ❑ Raman spectroscopy: is mainly implemented in an experimental stage.
- ❑ Neutron activation analysis: this technique can only be applied in laboratory, the instruments are rather expensive and of limited practicability as nuclear expertise is required.

Analysis

2.1 PBDEs Analysis technique

- ❑ Gas chromatography/mass spectrum(GC/MS): is the most popular method to analyze PBDE in plastic and environmental media.
- ❑ High performance liquid chromatography/mass spectrum(LC/MS): is another popular method to analyze PBDE in plastic and environmental media.
- ❑ Other detection techniques: Sensitive electron ionization mass spectrometry



Analysis

2.2 PFOS Analysis technique

Standard methods in China

□ GB/T 24169-2009

- Determination of perfluorooctane sulfonates (PFOS) in the fluorinecontaining products and consumer products – High performance liquid chromatography-tandem mass spectrometry

□ GB/T 23243-2009

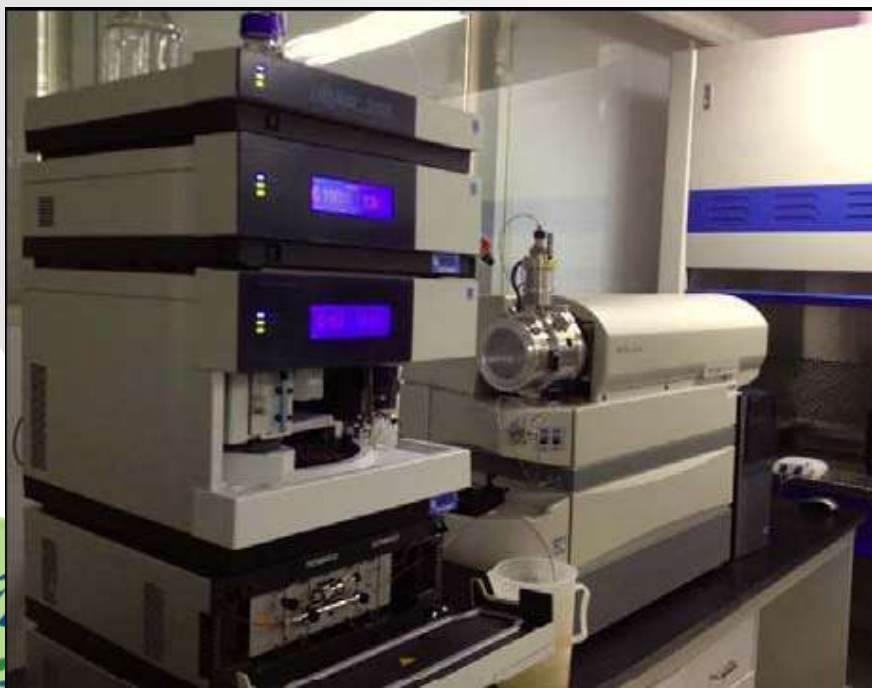
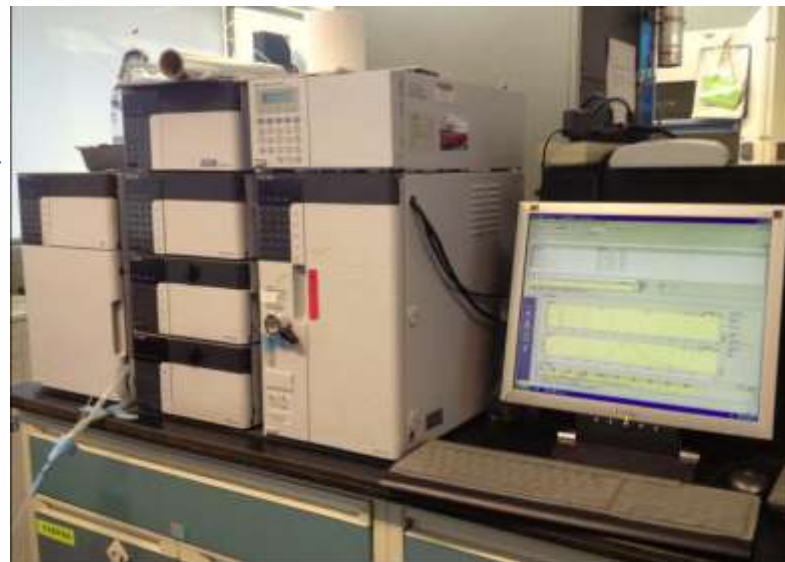
- Determination of perfluorooctane sulfonates (PFOS) in the food packaging material - High performance liquid chromatography-tandem mass spectrometry



Analysis

2.2 PFOS Analysis technique

□ LC-CDD:
for rough analysis



□ LC-MS/MS:
for quantification

Analysis

2.3 Some results of PFOS Analysis

	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
VF-570 (for AFFF)	293	10.8	55.8	36.9	25.5	11,500
VF-830 (for oil production)	122	0.131	23.4	0.384	9.94	11,300

	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
VF-9128 (for AFFF)	19.4	0.833	3.82	13.1		
VF-9126 (for AFFF)	27		2.54	1,050		
VF-6119 (for AFFF)	6.83			9.39		5.28
VF-230 (for AFFF)	95.4					



Treatment of PBDE containing articles

□ Treatment of PBDEs containing plastic production from WEEE

- According to the “old for new” policy. Up to Nov., 30, 2011, 8373×10^4 units waste household electric appliance are collected, generating 21.1×10^4 tons flame retardant plastic produced from TV plastic, refrigerator plastic wash machine plastic, air condition plastic and computer plastic.

□ Treatment of plastic waste and printed circuit board (PCB) from WEEE

- if the plastic can be separated according to different type, each kind of waste plastic can be reused in electric and electronic equipment. As for the mixed plastics, incineration is always used.
- PCB is always crushed mechanically, and the polymer from printed circuit board is usually incinerated. There are some cases of using polymer with thermoplastic to produce articles such as dustbin and garden building.

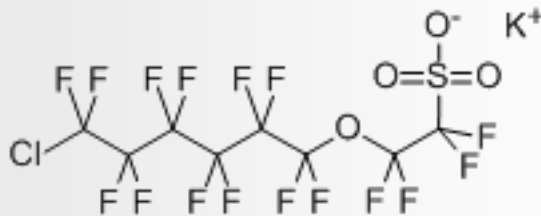


Some alternatives to PFOS

- Example: non-PFOS chrome mist suppressant



•F-53B: $C_8ClF_{16}O_4SK$
CAS: 73606-19-6

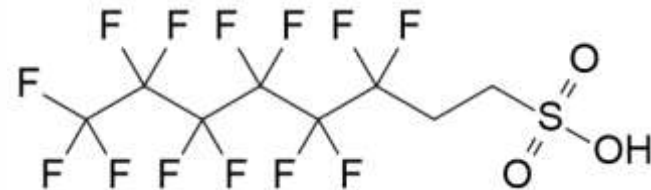


Local product



Hard Chrome Bath with Fumetrol® 21
(non-PFOS mild foaming mist suppressant)

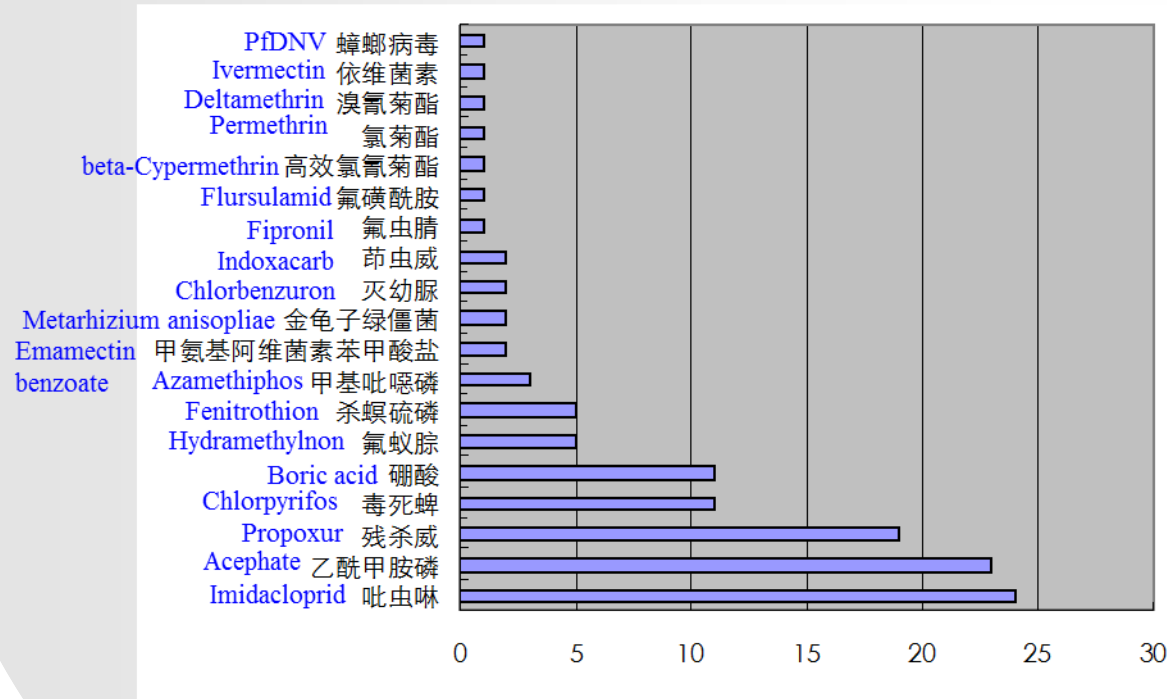
•Fumetrol 21: 6:2 FTS
CAS: 27619-97-2



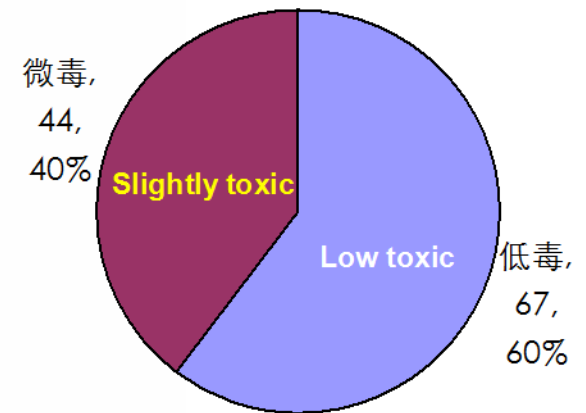
Imported product

Some alternatives to PFOS

- Example: non-PFOS A.I. in baits for termite or cockroach



Number of registered products using such A.I.



Some alternatives to PFOS

- Example: non-PFOS A.I. in baits for termite or cockroach

序号 No.	中文名 Chinese Name	英文名 English Name	CAS号 CAS No.	t _{1/2} (d)				分配平衡百分数 (%)				BCF	ChV (Fish) mg/L	logK _{ow}
				水 Water	土壤 Soil	底泥 Sediment	大气 Air	水 Water	土壤 Soil	底泥 Sediment	大气 Air			
1	乙酰甲胺磷	Acephate	30560-19-1	38	75	340	1.4	46	54	0	0	3.2	5,800	0
2	杀螟硫磷	Fenitrothion	122-14-5	38	75	340	0.27	18	81	1	0	69	NA	3.3
3	吡虫啉	Imidacloprid	138261-41-3	60	120	540	0.1	47	53	0	0	3.2	440	0.57
4	残杀威	Propoxur	114-26-1	38	75	340	0.5	33	67	0	0	3	15	1.5
5	毒死蜱	Chlorpyrifos	2921-88-2	180	360	1,600	0.18	4	76	20	0	1,300	NA	5
6	氟虫腈	Fipronil	120068-37-3	180	360	1,600	0.17	5	93	2	0	240	0.00094	4
7	氟蚁腈	Hydramethylnon	67485-29-4	180	360	1,600	0.096	1	49	50	0	550	NA	8.5
8	高效氯氰菊酯	Beta-cypermethrin	65731-84-2	180	360	1,600	0.75	1	52	47	0	210	0.006	6.1
9	甲基吡啶磷	Azamethiphos	35575-96-3	60	120	540	0.11	43	57	0	0	1.3	130	1
10	氯菊酯	Permethrin	52645-53-1	60	120	540	0.71	2	40	58	0	450	0.00073	6.5
11	灭幼脲	Chlorbenzuron	35409-97-3	60	120	540	1.1	8	85	7	0	560	NA	4.5
12	溴氰菊酯	Deltamethrin	52918-63-5	60	120	540	0.67	2	40	57	0	270	0.01	6.2
13	氟啶脲	Chlorfluazuron	71422-67-8	180	360	1,600	0.83	2	58	40	0	5,800	NA	5.8
14	氟铃脲	Hexaflumuron	86479-06-3	180	360	1,600	0.75	2	66	32	0	4,700	NA	5.7
15	胺菊酯	Tetramethrin	7696-12-0	38	75	340	0.019	14	69	17	0	20	0.023	4.7
16	顺式氯氰菊酯	Alpha-cypermethrin	67375-30-8	180	360	1,600	0.75	1	52	47	0	210	0.006	6.1

Evaluation of PBT Profiles of A.I.

Thanks !

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