

*Side event in the 4<sup>th</sup> meeting of Persistent  
Organic Pollutants Review Committee*

# **Substitution and Alternatives - focusing on PFOS alternatives -**

14 October 2008 in Geneva, Switzerland

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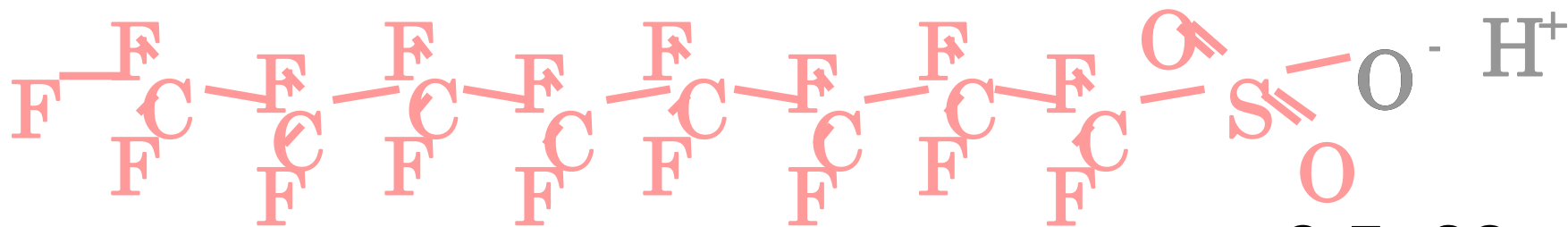
*Chemical Management Policy Division, Manufacturing Industries Bureau  
Ministry of Economy, Trade and Industry (METI) of Japan*

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1. Advantages of PFOS
2. Identify PFOS uses in the supply chain
3. Examples of substitution and alternatives
4. Difficulties of substitution and alternatives
5. Sound management of acceptable uses
6. Summary points for discussion

- 1. Advantages of PFOS -

# Perfluorooctane Sulfonate (PFOS)



- Thermal stability and chemical resistance
- Water and oil repellent (insoluble with water and oil)

• Low surface tension *for example*

- Low friction factor
- Anti-adhesive
- Low inflection
- High electro-isolation

Beneficial effects on application of surfactants and dispersing

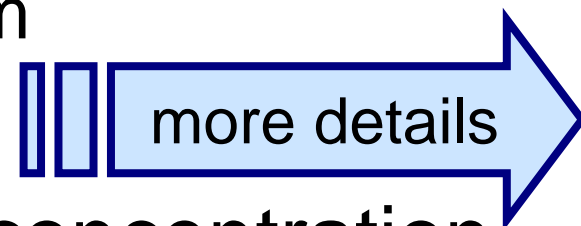
Keep beneficial effects under the strong acid and high temperature

Essential chemical in wide range of industries  
PFOS is a **LIVING Chemical**, not dead

- 1. Advantages of PFOS -

# Perfluorinate Surface-active Agent (e.g. PFOS)

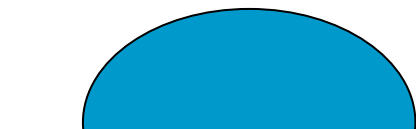
- Reduce surface tension up to 15 dyn/cm, increase wettability and permeability
  - Hydrocarbon base: 27 dyn/cm
  - Silicone base: 22 dyn/cm
- High surface activity at low concentration
- Thermal stability and chemical resistance



- 1. Advantages of PFOS -

# Surface tension and permeability

Hydrocarbon surfactant

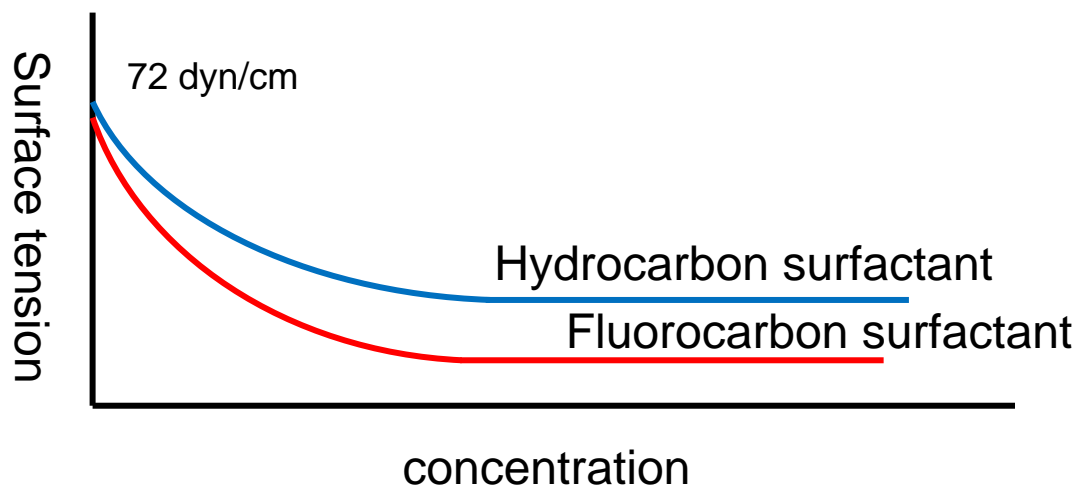


High surface tension

Fluorocarbon surfactant



Low surface tension

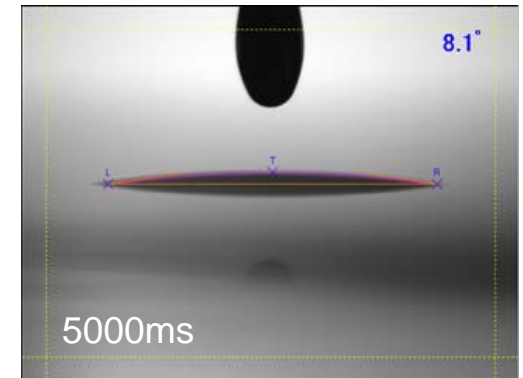
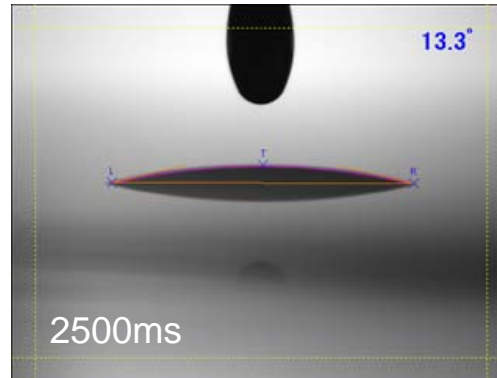
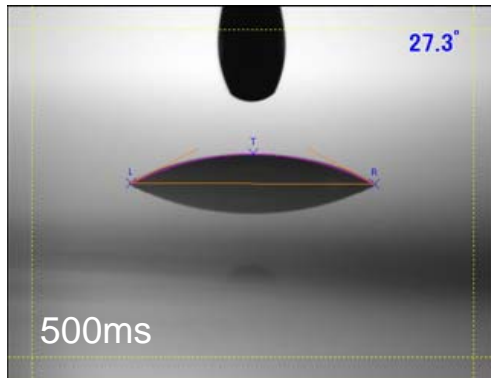


- 1. Advantages of PFOS -

# Surface tension and permeability (example photo)

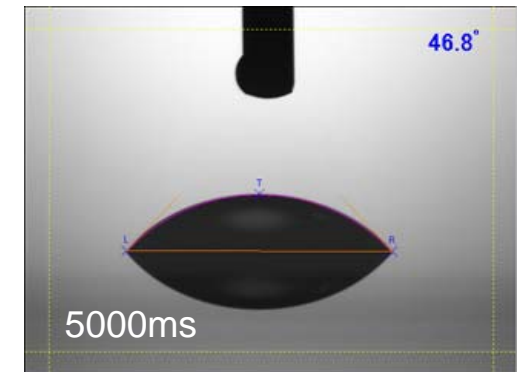
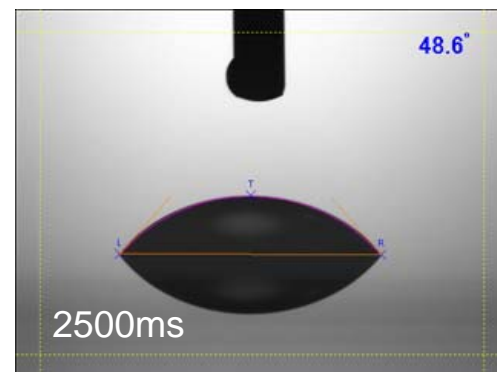
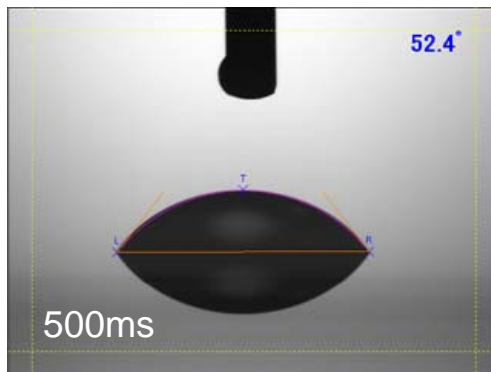
◆ PFOS

time →



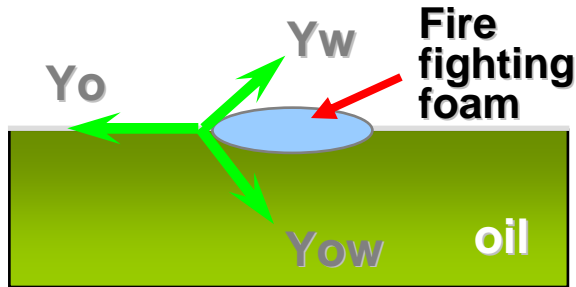
◆ PFAS: C=4

time →

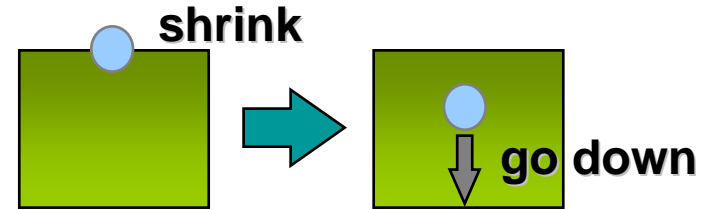


- 1. Advantages of PFOS -

# Example of fire fighting foam (AFFF)



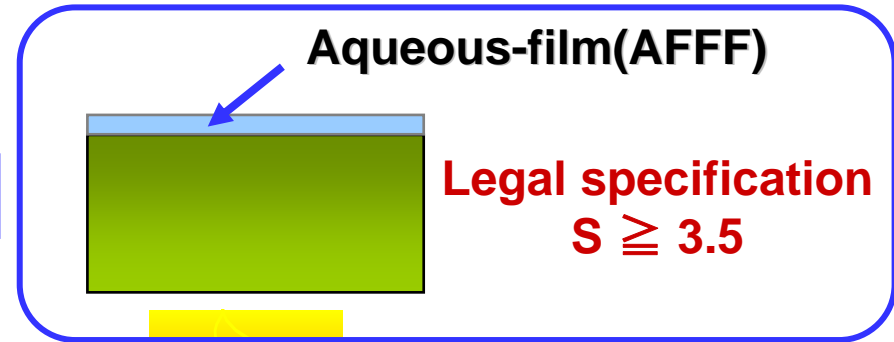
$$S < 0$$



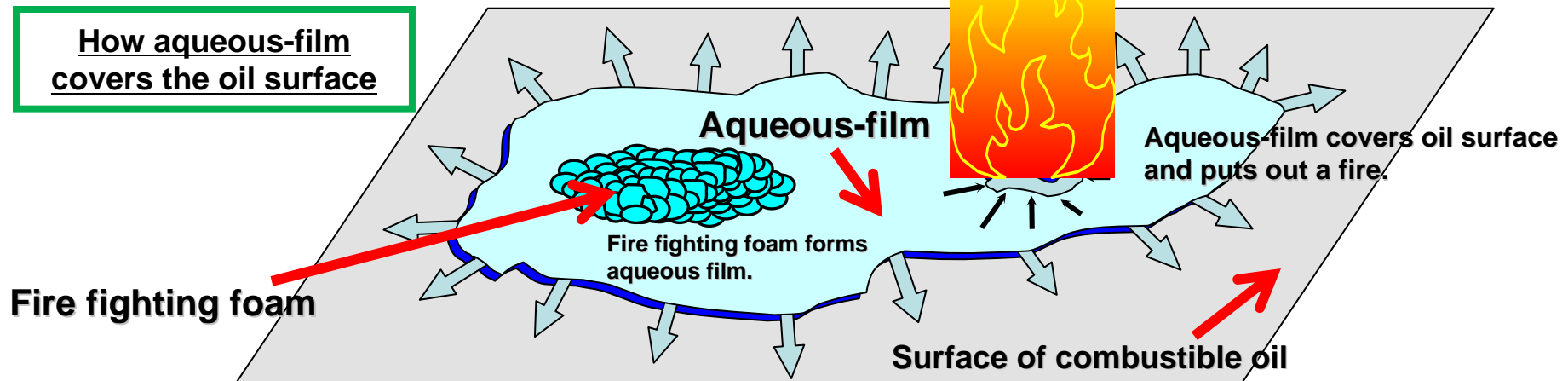
Water is heavier than oil

Yo : surface tension of oil  
Yw: surface tension of fire fighting foam  
Yow: interfacial tension  
between oil and water  
 $S = Y_o - (Y_w + Y_{ow})$   
S: diffusion coefficient

$$S > 0$$

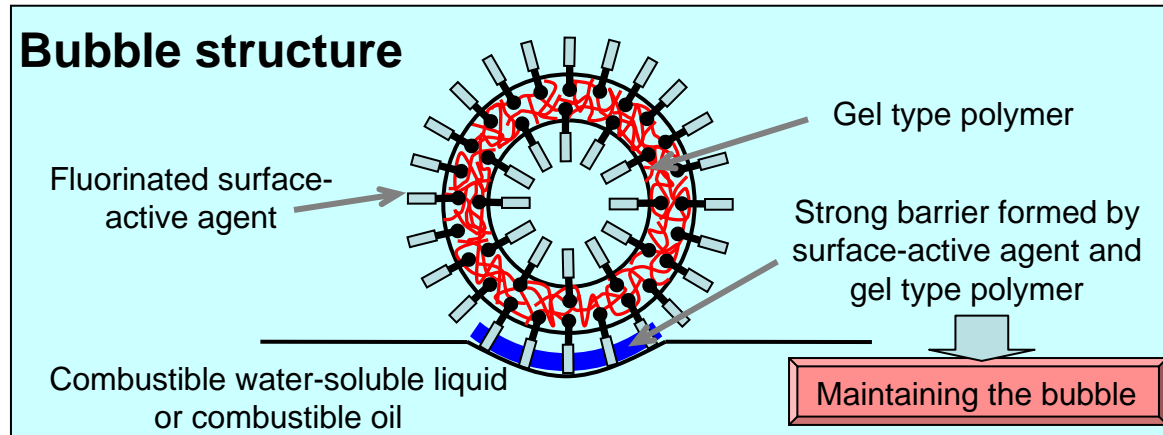


How aqueous-film covers the oil surface



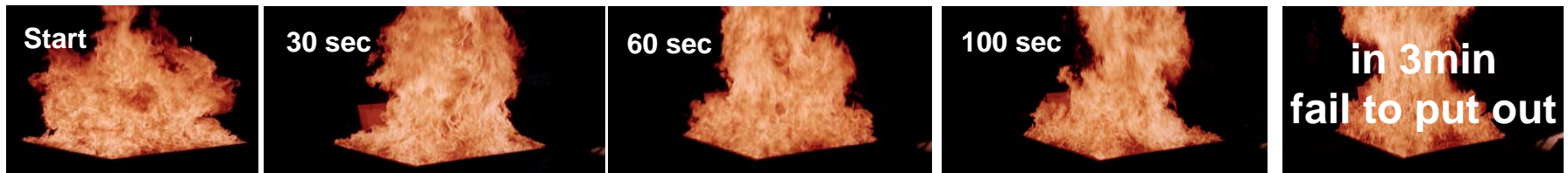


# - 1. Advantages of PFOS - Example of fire fighting foam (AR)



## Experiment using combustible water-soluble liquid (acetone)

### Non-PFOS protein foam (fail to satisfy the legal requirement)



### PFOS gel type fire fighting foam (satisfy the legal requirement)

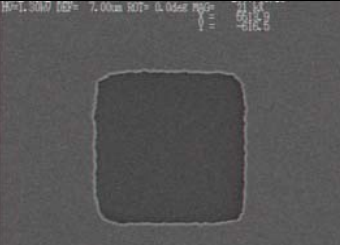
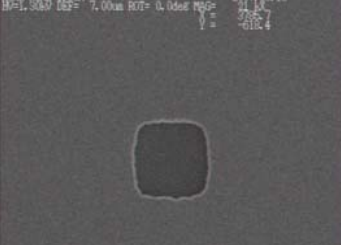
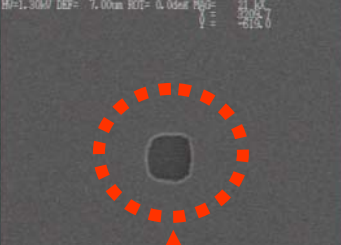
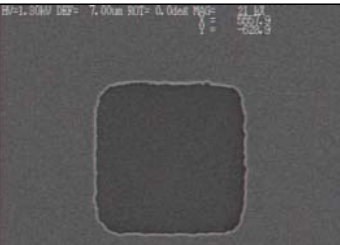
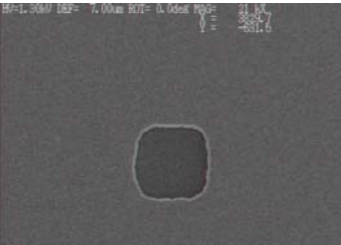
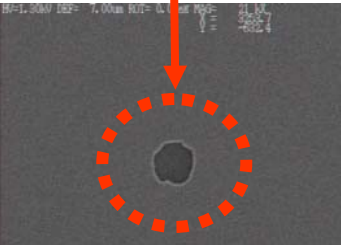




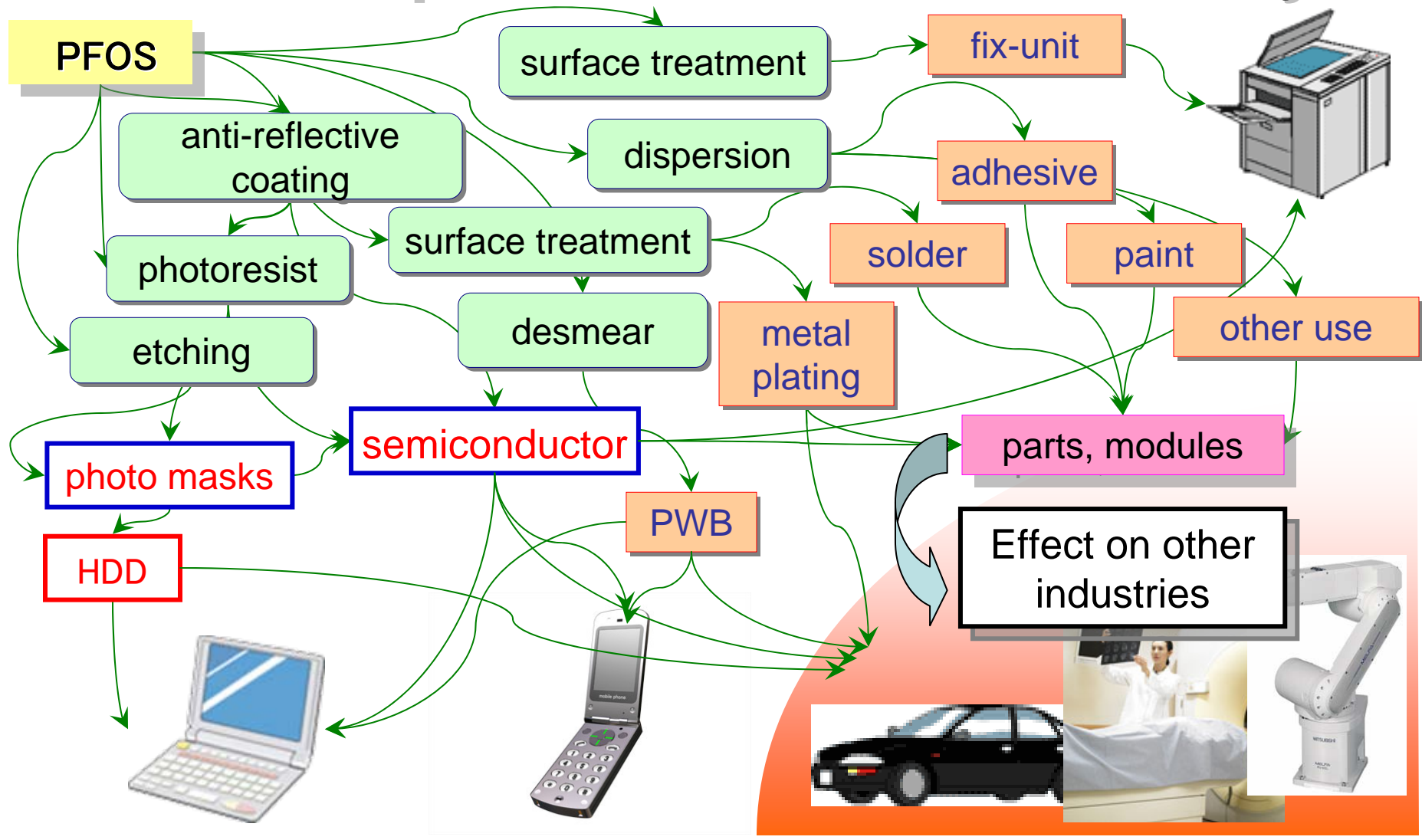
- 1. Advantages of PFOS -

# Example of photo masks

- Surfactant containing PFOS can realize ultra-fine patterning in the photo-lithography process

		target		
PRE WET liquid	Chrome Etcher	3um	1.5um	1um
PFOS	PFOS	 <p>3.0191um</p>	 <p>1.4841um</p>	 <p>0.8754um</p>
PFAS	PFAS	 <p>2.9963um</p>	 <p>1.4551um</p>	 <p>0.7753um</p>

- 2. Identify PFOS uses in the supply chain -  
**Example in electronics industry**

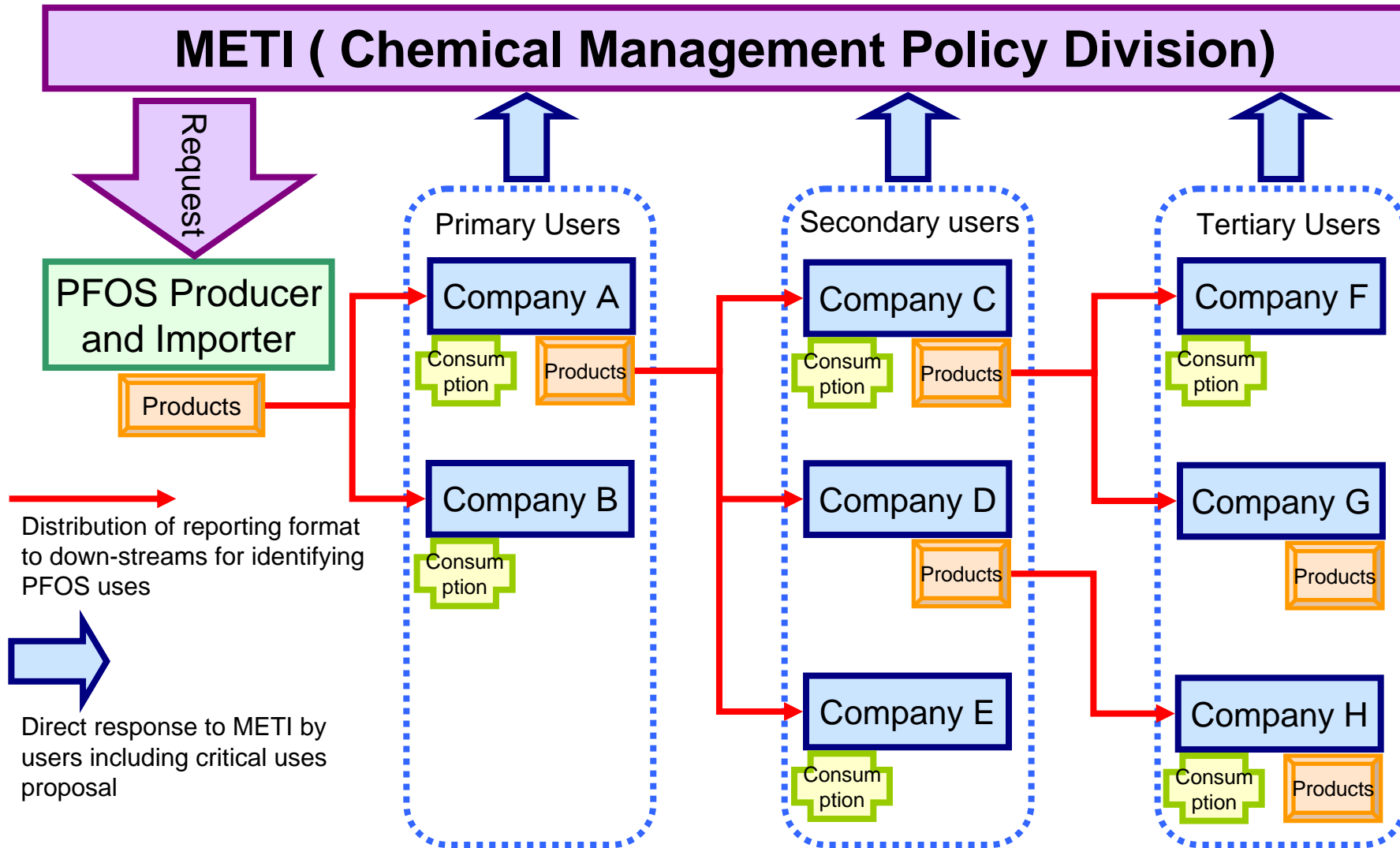


## - 2. Identify PFOS uses in the supply chain - PFOS uses (e.g. electronics industry)

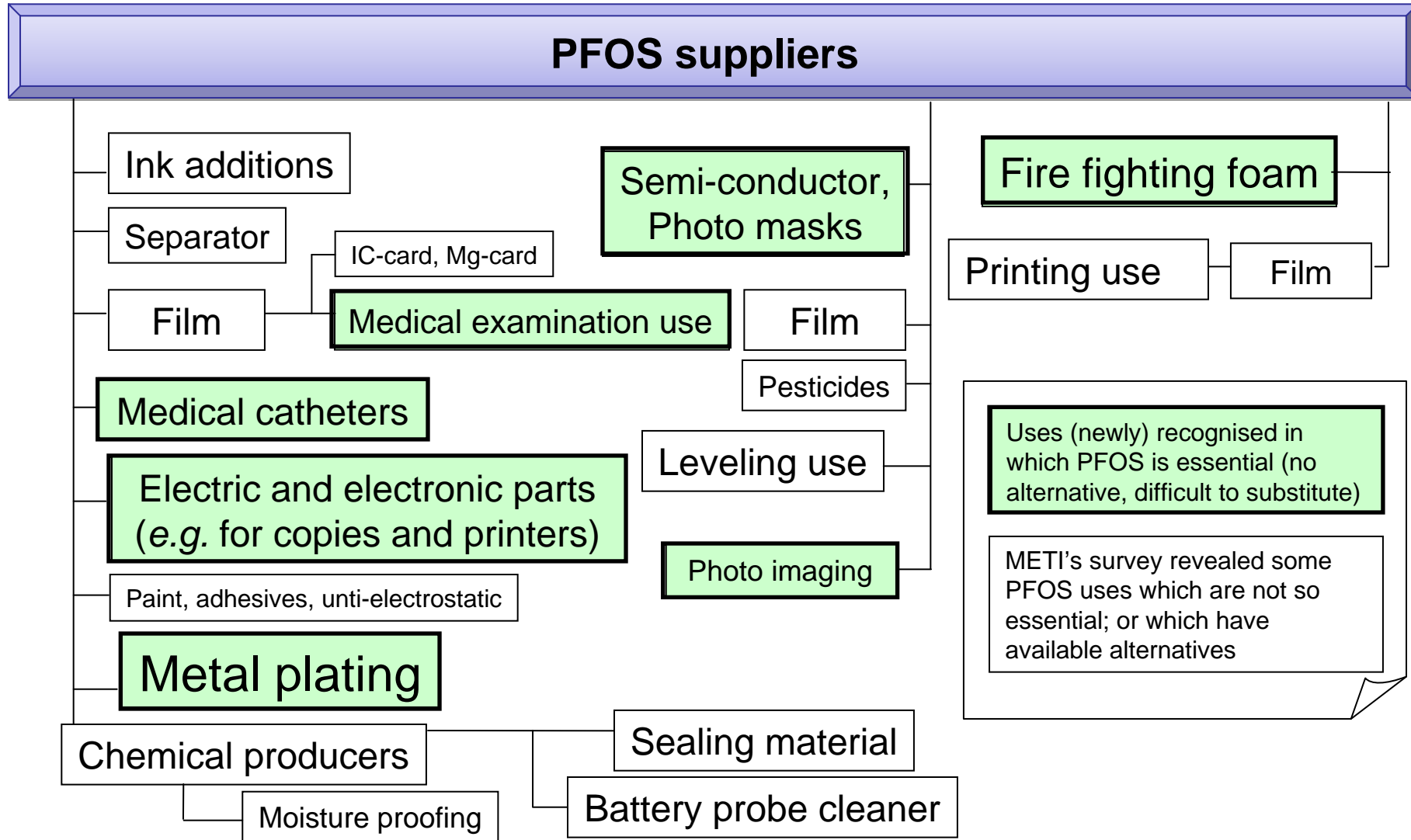
	PFOS uses	Component
1	Etchant for photolithography processes	Etching
2	Etchant for metal-plating processes	Etching
3	Seal aperture treatment agent	Post process
4	Fluxes for soldering	Pre treatment
5	Etchant for desmear processes	Etching
6	Pre-treatment agent used for PWB production process	Permeate
7	Wax for temporary end use	Pre treatment
8	Surface treatment agent	Pre treatment
9	Surface treatment agent for water-repellent	Pre treatment
10	Moisture proofing agent for PWB	PWB
11	Bearing grease for small motor	Shaft bearing
12	Grease for dye use	Dye
13	Raw materials for paint	Paint
14	Painting film for PCM steel sheet	Wax
15	UV ink for wax	Surfactant
16	UV vanish for was	Surfactant

	PFOS uses	Component
17	Glue for engine oil	Fibre
18	Raw materials for PWB	Etching
19	Polycarbonate resin additive	Drip protection
20	PBT resin additive	Assembly
21	PPS resin additive	Fluoric resin
22	9T nylon additive	Housing
23	Epoxy resin additive	Resin
24	Rubber sheet	Rubber
25	Filter	Membrane
26	PTFE/FEP tube	Motor parts
27	Fluoric resin coating	Coating
28	Raw material for PTFE	Filter module
29	Water-repellent filter	Filter
30	Molybdenum coating	Coating
31	Tantalum electrolytic capacitor	Water repellent
32	Copper clad laminate	Material
33	Paper windshield wiper	Wiper

- 2. Identify PFOS uses in the supply chain -  
**METI's survey of PFOS uses**



## - 2. Identify PFOS uses in the supply chain - Results of METI's survey



- 2. *Identify PFOS uses in the supply chain* -

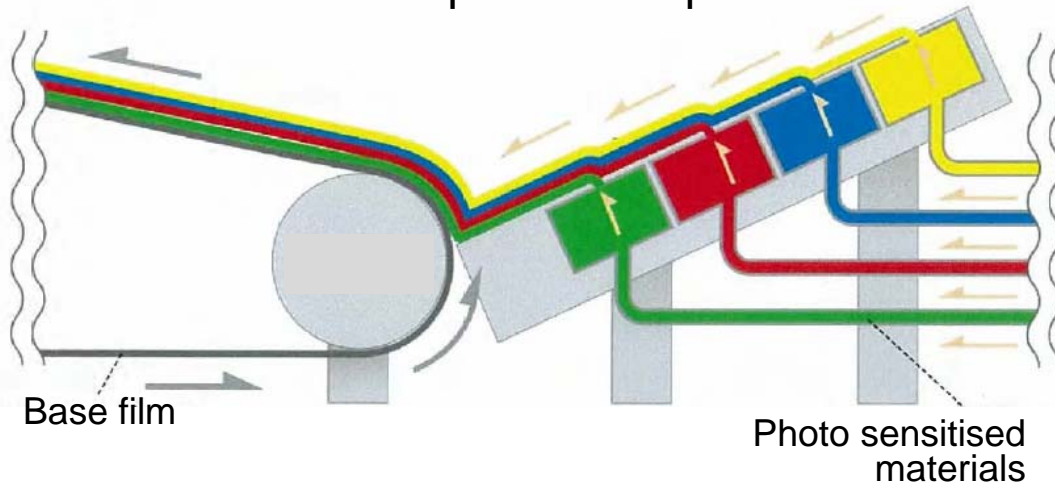
## **Benefits of supply-chain survey**

- Identifying essential uses
  - Japan reported 7 essential uses to POPRC3, all of which are listed on the RME report
- Drawing PFOS users' attention to their PFOS uses
  - PFOS is used in a wide range of industries
  - Very small amount is used in many cases
  - Not contained in products but in materials for processes (e.g. Surfactants)
- Inducing PFOS users to make efforts to search for substitutes and develop alternatives

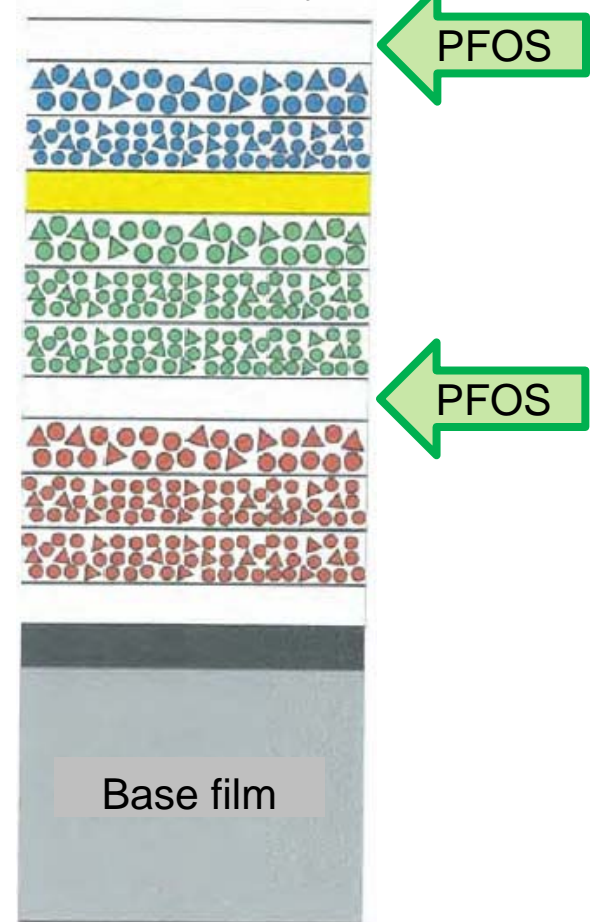


## - 3. Examples of substitution and alternatives - **Photo imaging industry (PFOS use)**

Colour film production process



Colour film layer

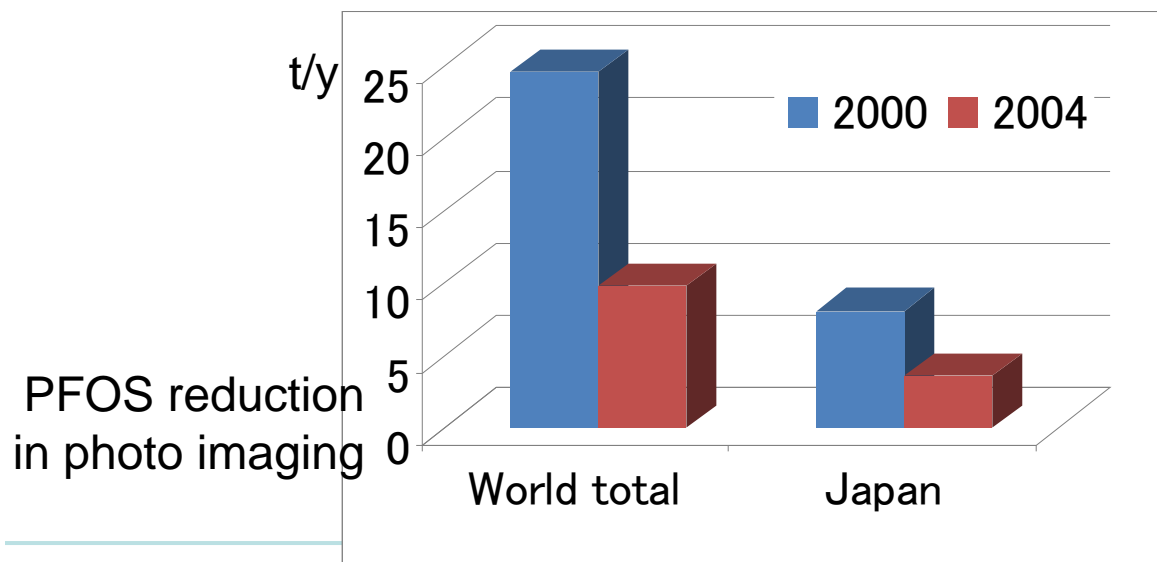


- Some kinds of photo-sensitised materials are layered on the base film using PFOS
- Surfactant and antistatic properties are required with:
  - Dynamic surface tension capability
  - Solubility
  - Photo-inactivity
  - Heat and chemical stability

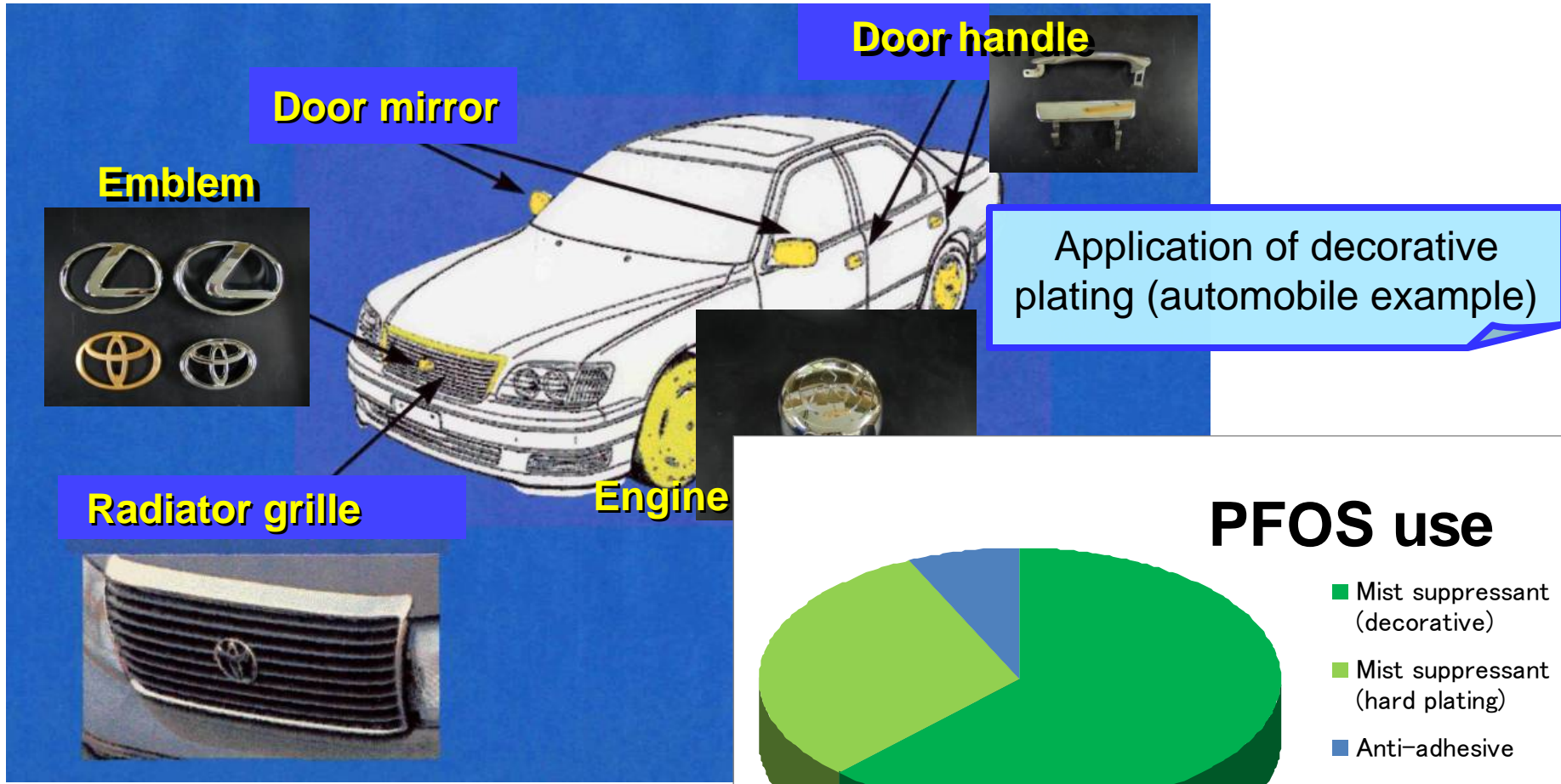


## - 3. Examples of substitution and alternatives - Photo imaging industry (alternatives)

Alternatives	Properties
Non-fluorinated	<ul style="list-style-type: none"> <li>• Less antistatic</li> </ul>
Shorter-length chain	<ul style="list-style-type: none"> <li>• Less surface active</li> <li>• Soluble to water</li> </ul>
Telomers	<ul style="list-style-type: none"> <li>• Less surface active</li> <li>• Better antistatic</li> </ul>
Silicones	<ul style="list-style-type: none"> <li>• Less surface active</li> </ul>

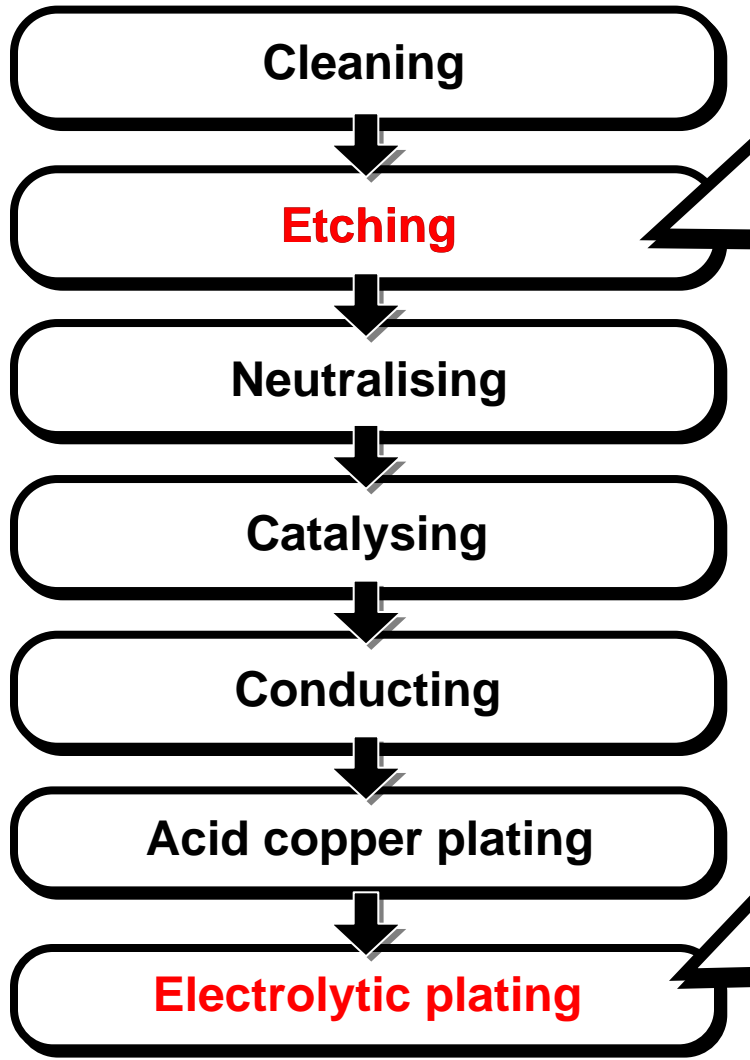


# - 3. Examples of substitution and alternatives - Metal plating industry (PFOS use)



Mist suppressant for using hexa-valent Cr shares 93%

# - 3. Examples of substitution and alternatives - Metal plating process (substitution)



**Hexa-valent Cr etching substitution**

- **Permanganic acid etching**

⇒ Study for practical use

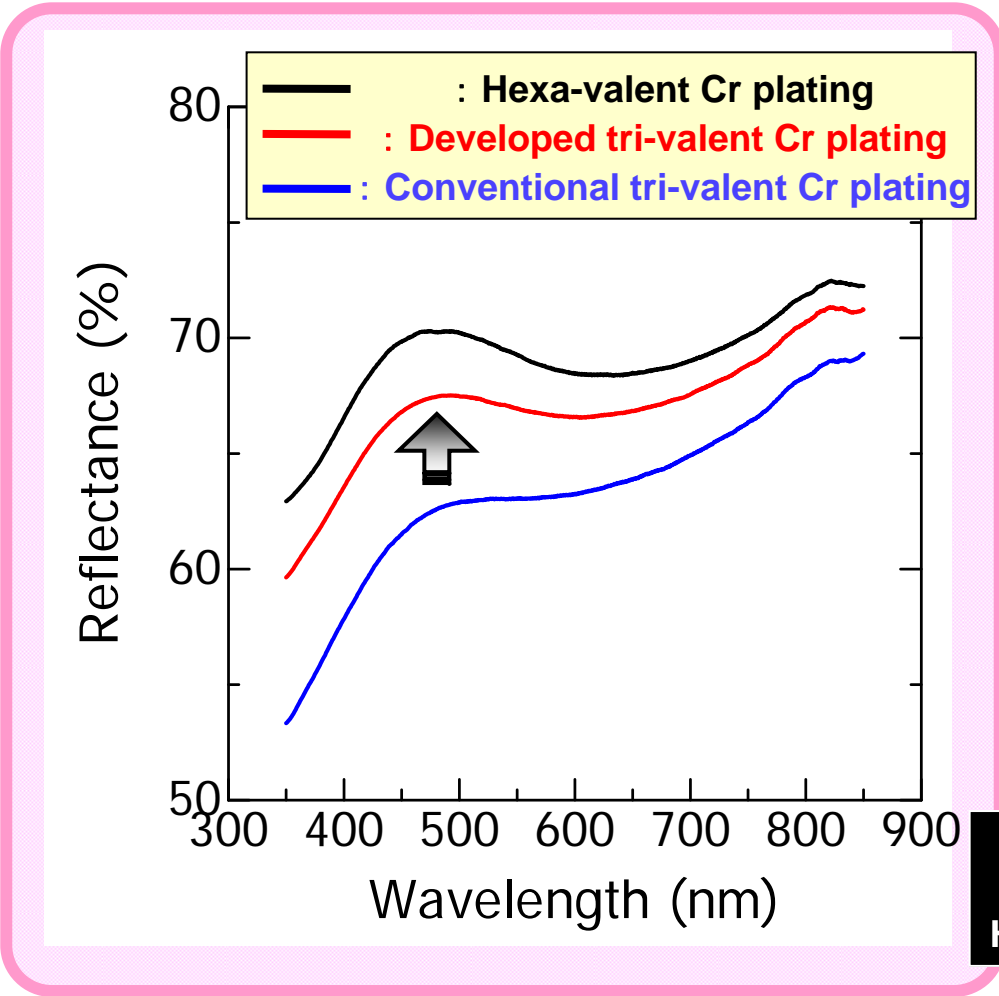
**Hexa-valent Cr plating substitution**

- **Tri-valent Cr plating**

⇒ Practical use

- 3. Examples of substitution and alternatives -

# Metal plating process (technology breakthrough for substitution)



Hexa-valent Cr etching & Hexa-valent Cr plating

Permanganic acid etching & Tri-valent Cr plating

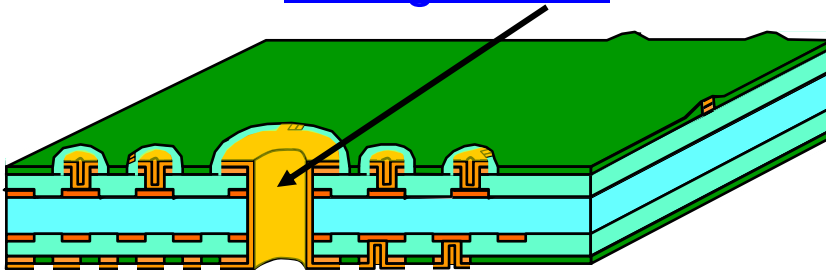
- 3. *Examples of substitution and alternatives -*

# Alternatives in semiconductor industry

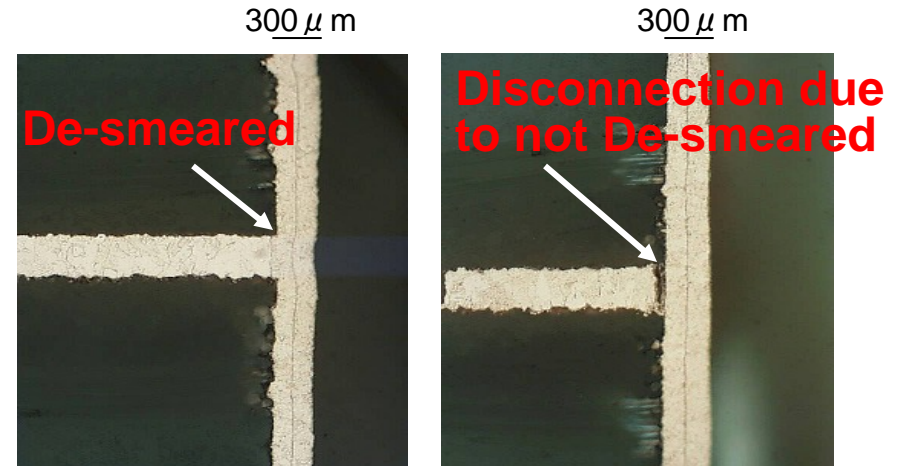
## ● Desmear process for PWB\* fabrication

- Desmear\* is to remove smears on the through-hole walls (diameter = c.a.300um)
- PFOS reduces the surface tension of the etching solution (pH=12-13) to infuse into the through-holes
- Suppliers apply alternatives

\*smear: melted and remaining resins on the wall of through-holes



Printed Wired Board composes a inner-circuit to enable High-Density Packaging via through-holes



Cross-section of through-hole

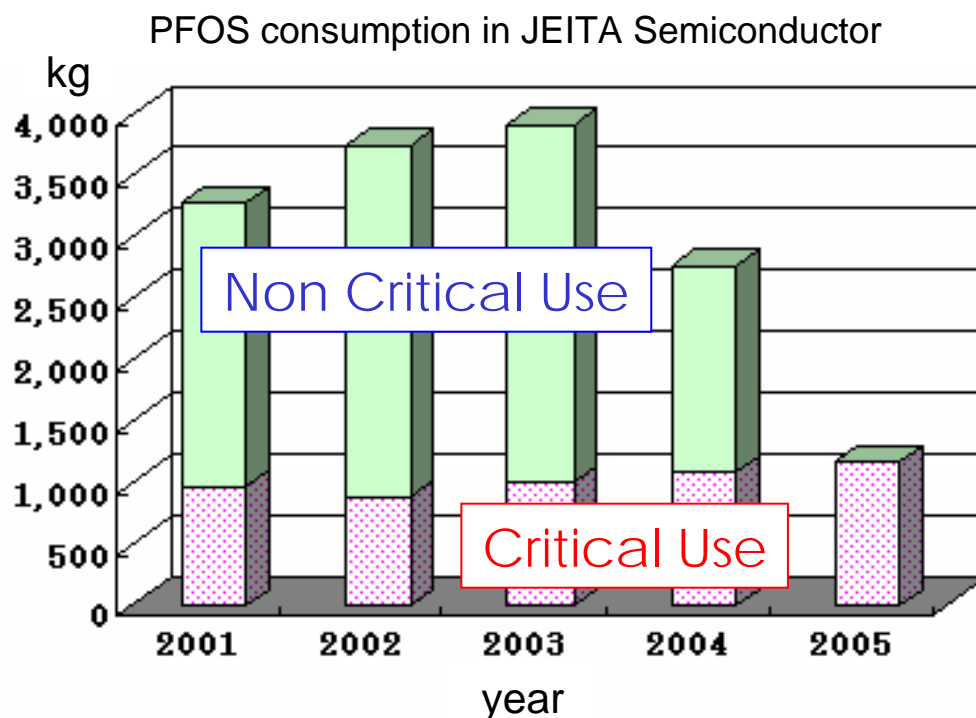


### - 3. Examples of substitution and alternatives -

# PFOS reduction in semiconductor industry

WSC/SEMI Agreement PFOS 2006

Commitments	
C1.	<b>End all non-critical PFOS uses and emissions</b> ESIA, JSIA, KSIA, SIA- May, 2007 TSIA- May, 2009
C2.	Send all solvent wastes from remaining critical uses to incineration for destruction Date: December 31, 2006.
C3.	Periodically collect PFOS use data for a mass balance model Date: 2005 baseline data; evaluate and update every 2 years.
Intentions	
I1.	Work towards PFOS substitutes for critical applications
I2.	Evaluate potential segregation of PFOS effluent streams in new and existing tools
I3.	Evaluate potential PFOS wastewater discharge control technologies
I4.	Periodically make available aggregated industry information for above commitments and intentions Date: Every 2 years.



JEITA: Japan Electronics & Information Technology Industries Association

WSC: World Semiconductor Council

SEMI: Semiconductor Equipment and Materials Institute

- 4. *Difficulties of substitution and alternatives* -

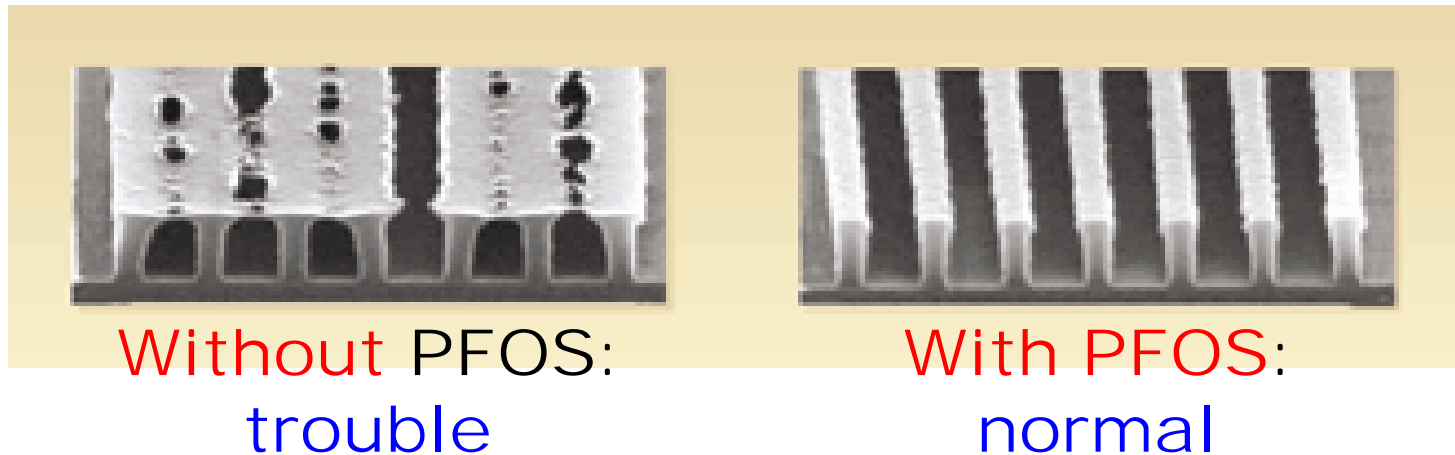
## Photo imaging industry (X-ray film example)

	Medical use	Industrial use
User	hospital, medical institute	public construction, energy plant, aviation industry, etc.
Requirement	Need to prepare a wide range of films by body parts and diagnostic purpose. No static mark.	Used for very detailed non-destructive test, different by scanning materials
Difficulties	High contrast and higher photographic density is required in minimum exposure. Antistatic property.	High quality is required in order to identify an ultra-small defect (e.g. crack)
Potential digitalization	Cost is too high esp. for small hospitals in local areas	Missing very precise picture information by digitalization

PFOS alternatives cannot achieve such high quality in X-ray film production

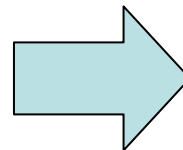


- 4. Difficulties of substitution and alternatives -  
**Semiconductor industry  
(Anti-reflective coating)**



Requirement for precise lithography

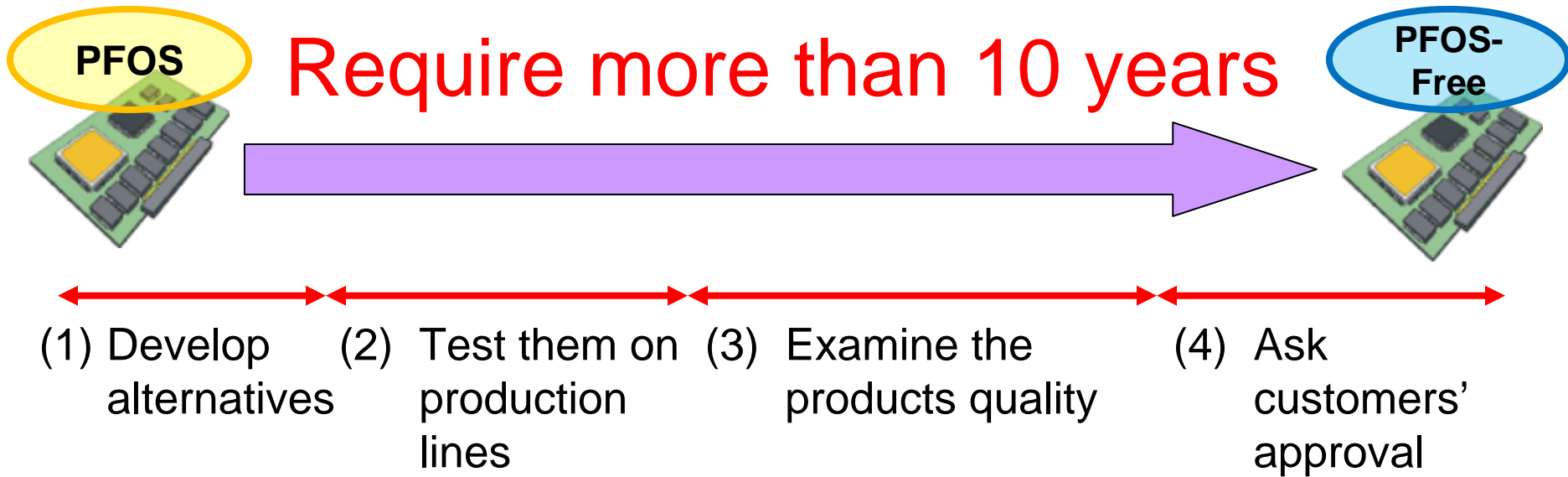
1. Low surface tension
2. Low reflection
3. High acid durability
4. Thermal stability
5. High UV durability
6. Dispersible



**No alternatives  
for PFOS**

- 4. Difficulties of substitution and alternatives -

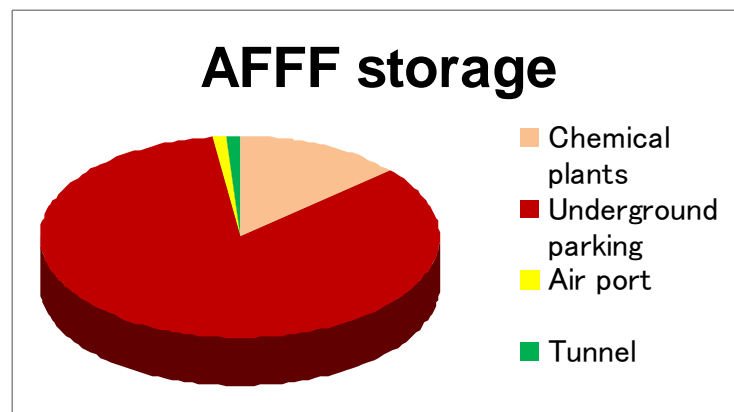
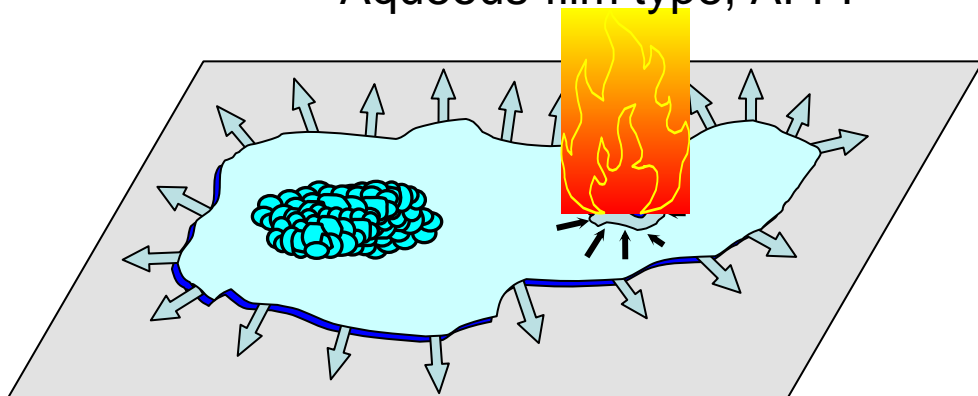
# Time requirement for replacement (example in semiconductor industry)



According to industries' experiences, substitutions without customers' approval tend to stop customer's production lines, which eventually results in half to one year delay for recovery.

# - 4. Difficulties of substitution and alternatives - Time requirement for replacement (example in fire fighting foam)

Aqueous-film type, AFFF



19,000 t  
already set in fire  
fighting system

2,100 t/y  
maximum  
production capacity

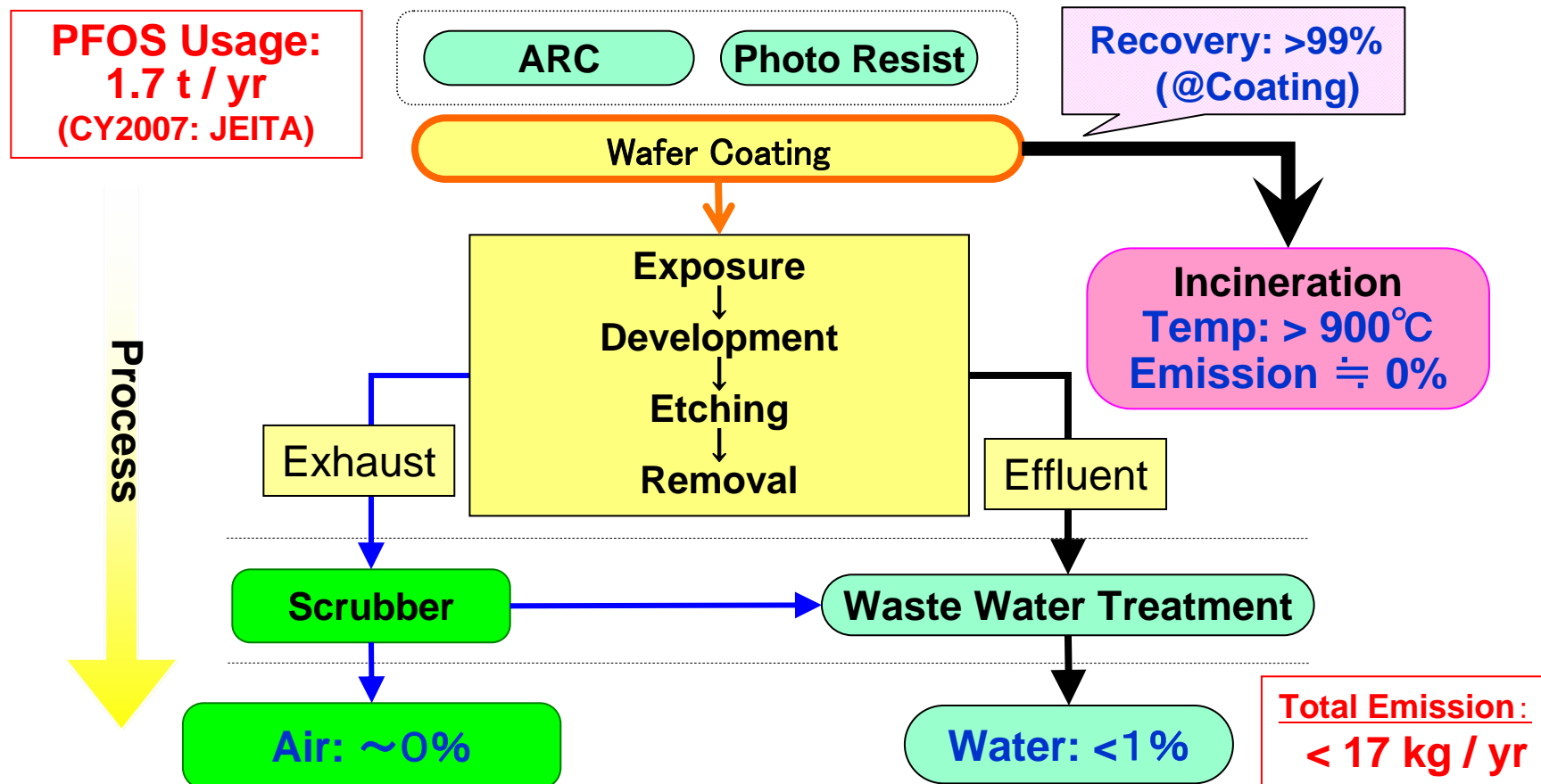


more than 9 years  
(in full production)



Fire fighting system for  
underground parking (400L tank)

- 5. Sound management of acceptable uses -  
**Proper control of PFOS emission  
(example in semiconductor production)**



- More than 99% is recovered and appropriately treated for minimising emissions

- 6. *Summary points for discussion* -

## **Some thoughts among PFOS substitution and alternatives**

- Survey PFOS uses through the supply chain for:
  - Identifying essential uses
  - Drawing users' attention to their PFOS uses
  - Inducing users' efforts for substitution and alternatives
- Understand PFOS advantages for achieving the same level quality by alternatives
- Be aware of time requirement for replacement
- Sound control of PFOS emissions in its uses

# *Thank you*

*Presented by*

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