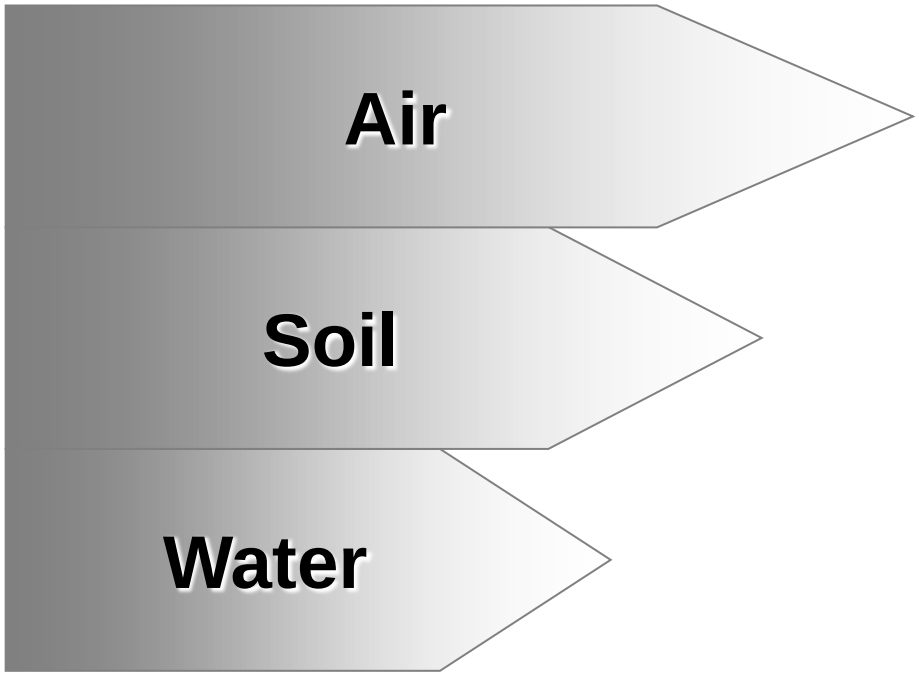
Going beyond present borders in surface tension reduction for Chromium

CASF November 13th 2013, Toronto
Helmut Horsthemke, Enthone

Cr(VI) Emission, areas of concern



- Mist formation during plating due to gassing on anode and cathode - Uncertainty about safe exposure levels
- Risks well manageable and controlled.
- Well established waste water technology in place. Simple and reliable.

Cr(VI) Emission, areas of concern

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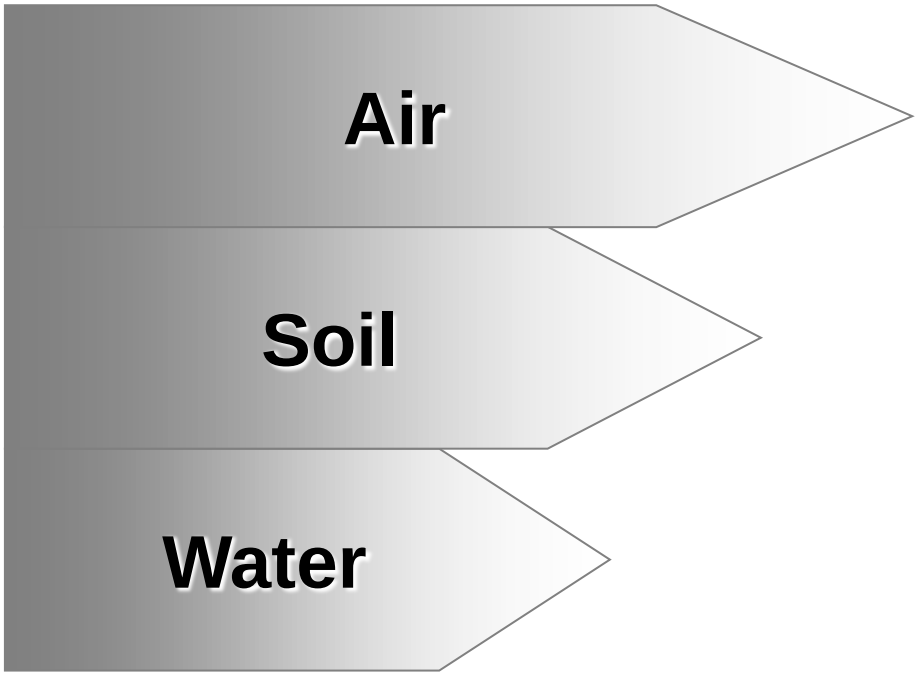


Upcoming tighter regulation
Action required now

Well managed
No present action required

Well managed
No present action required

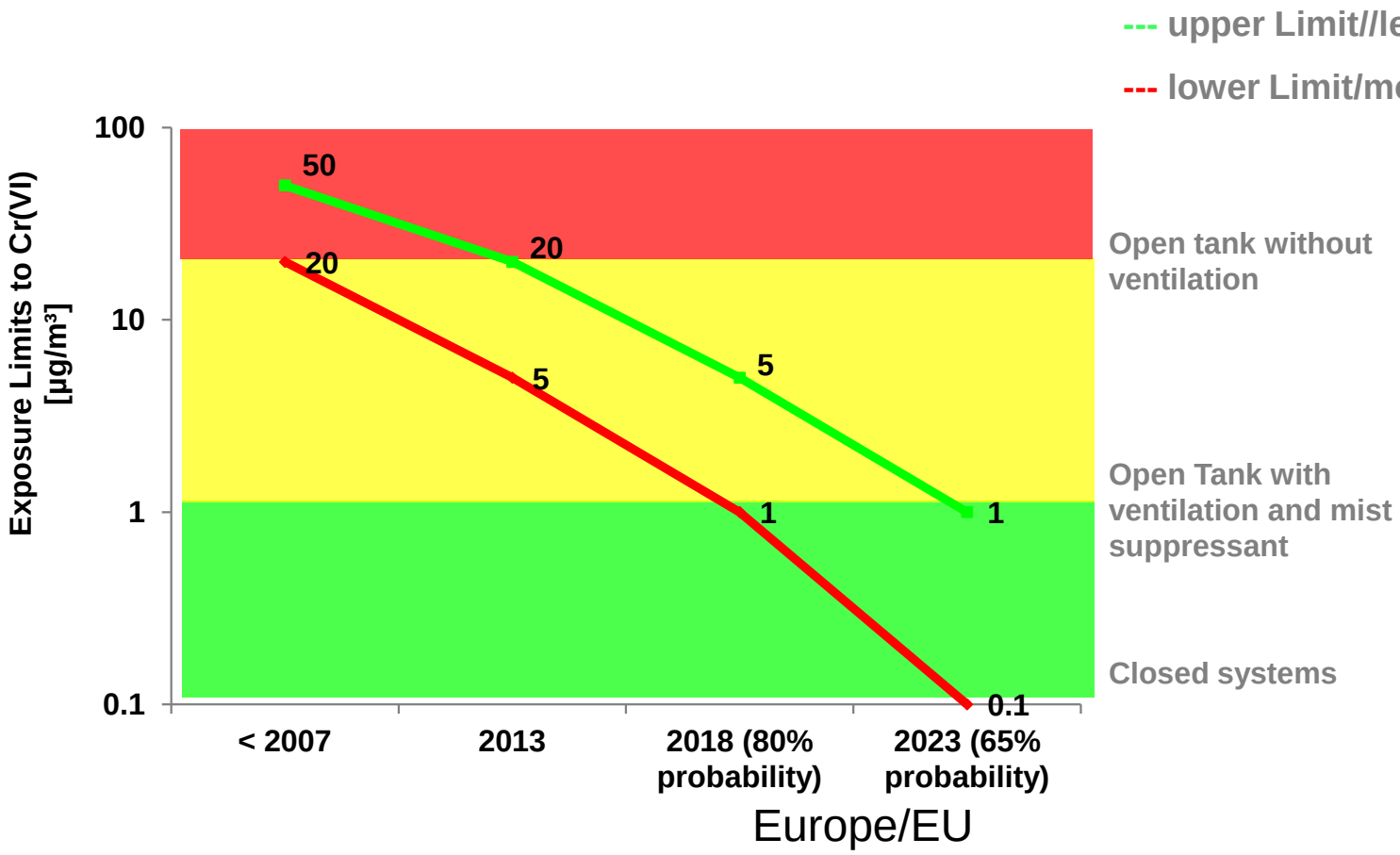
Workplace Safety

- **Canada:** 30 µg Cr(VI) /m³ or < 35 Dyne/cm; PFOS banned since May 2013
- **USA:** Surface tension < 33 Dyne/cm (Tensiometer), ban of PFOS within the next 3 years
- **Europe:** 1µg Cr(VI) /m³ in discussion under REACh for 2018
- **France:** 1µg Cr(VI) /m³ maximum tolerable occupational exposure level after Jan 1st 2014

	New Limits	Previous Limits
Decorative Chromium Plating		
Existing Sources	0.007 mg/dscm	0.010 mg/dscm
New Sources	0.006 mg/dscm	0.010 mg/dscm
Chromic Acid Anodizing		
Existing Sources	0.007 mg/dscm	0.010 mg/dscm
New Sources	0.006 mg/dscm	0.010 mg/dscm
Hard Chromium Plating		
Existing Sources (small)	0.015 mg/dscm	0.030 mg/dscm
New Sources (small)	0.006 mg/dscm	0.015 mg/dscm
Existing Sources (large)	0.011 mg/dscm	0.015 mg/dscm
New Sources (large)	0.006 mg/dscm	0.015 mg/dscm

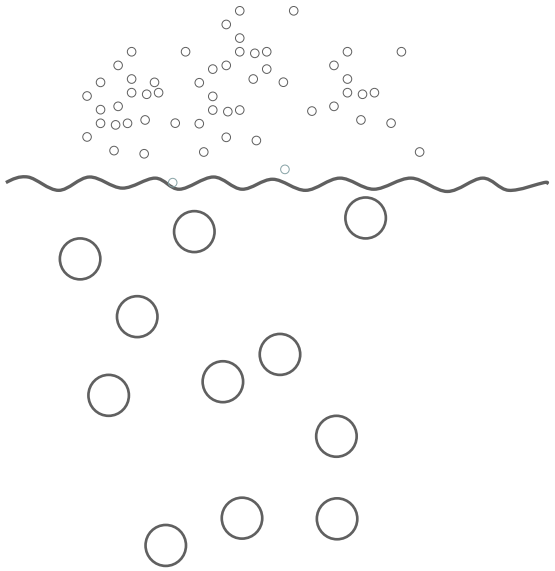
USA and Europe Cr(VI) TOEL's over time

-Tolerable Occupational Exposure Levels-



Airborne emission

- Formation of mist/spay/aerosol is caused by uprising gas bubbles. When bursting at the surface of liquids, small droplets are expelled creating a mist.



Airborne emission

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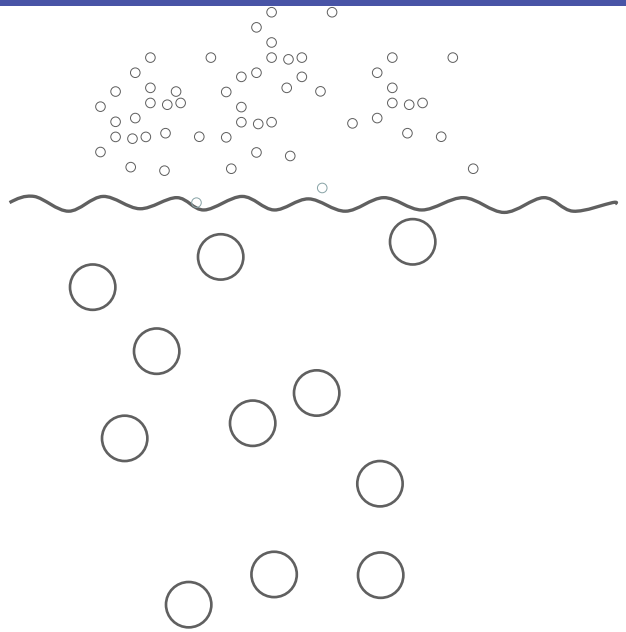
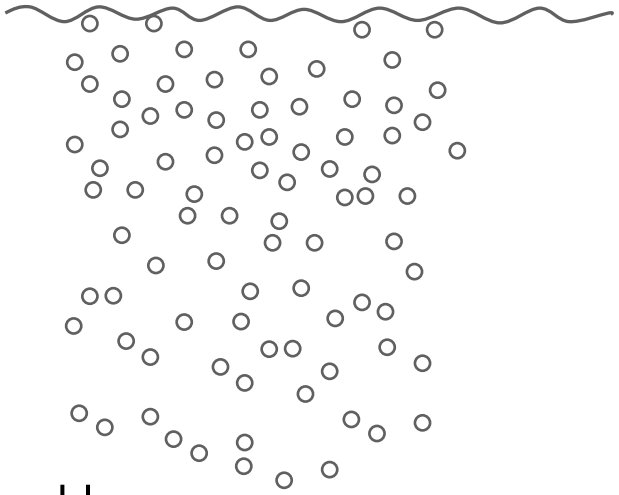


1,7 mm

60 mN/m Cr (VI) solution, no surfactant



<0,2 mm

30 mN/m Cr (VI) solution, 2nd generation PFOS free surfactant

- Bigger diameter bubbles bring more kinetic energy with them to the surface of the solution compared to smaller bubbles.
- Below a certain diameter no mist is formed as not enough kinetic energy is present to eject a droplet.
- At high surface tension the bubble size is greater compared to low surface tension.

Preventing Chrome Mist

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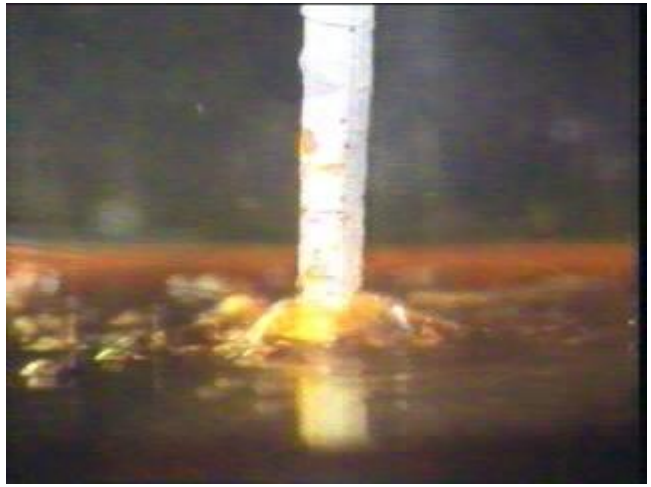
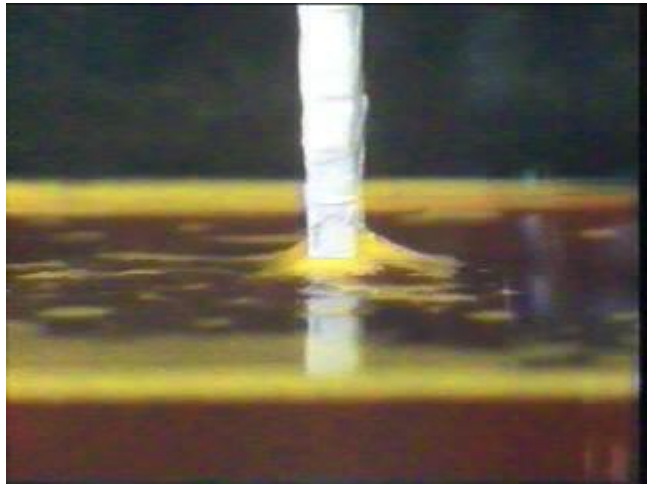
- No surfactant
  Surface tension 60 mN/m (Dyne/cm)
  Upcoming H_2 from cathode and O_2 from anode create spray/mist/aerosol containing Cr(VI)



- Low foaming PFOS surfactant.
  Surface tension 35 mN/m (Dyne/cm)
  Formation of aerosol is prevented by reducing the size of uprising gas bubbles, not by a foam blanket.



Preventing Chrome Mist

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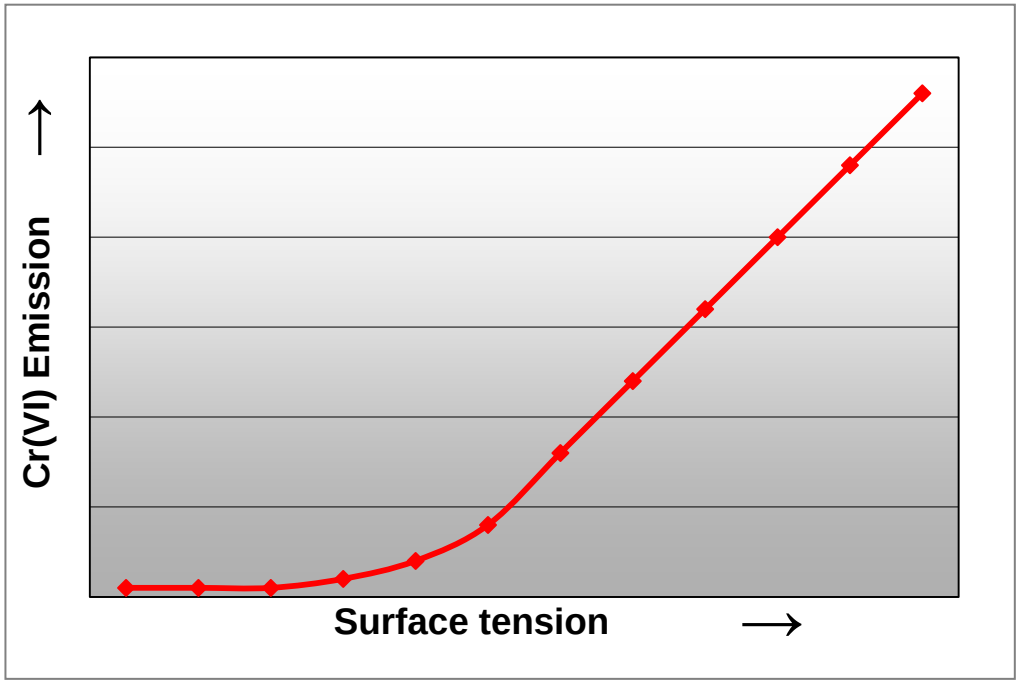
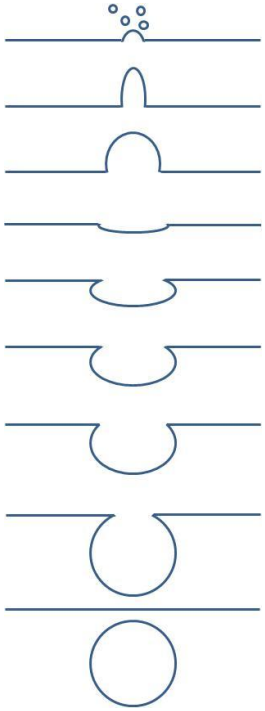
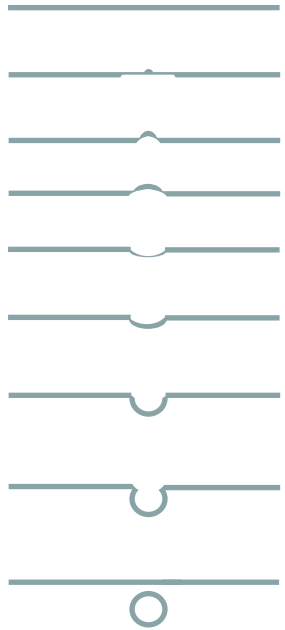




60 mN/m



30 mN/m

- Lower surface tension - Less air borne emission
- Depending on the individual application, mostly excessive foam sets the limit for the minimum possible surface tension to operate the process at.
- Lower Temperatures as with decorative Chrome result in more stable foam
- 1st Generation PFOS replacement products generate more foam than PFOS based low foaming surfactants

Going beyond present borders

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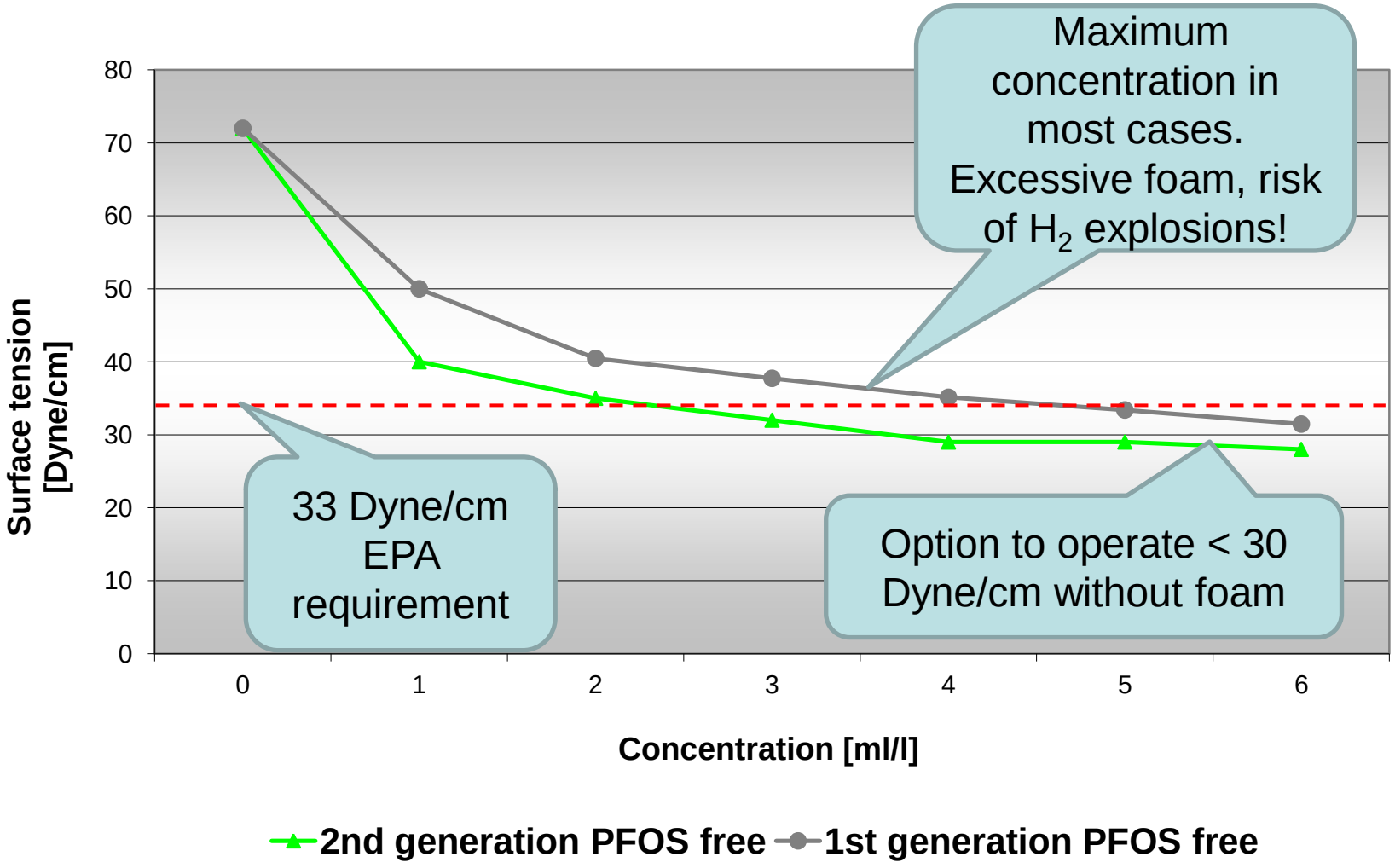

Going beyond present borders

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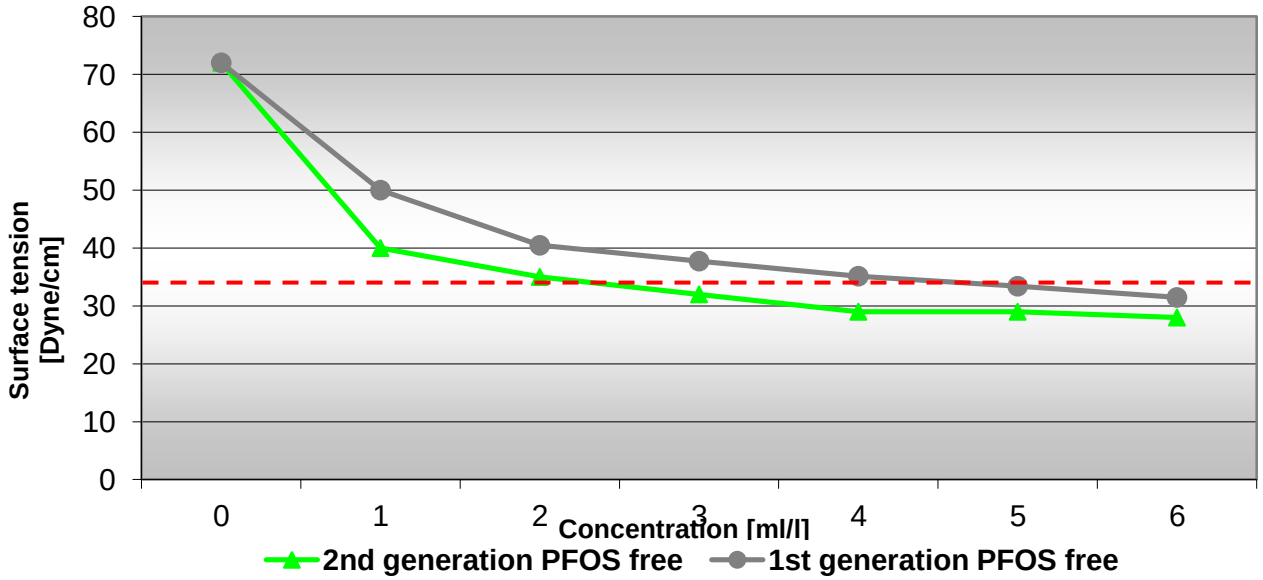
- 2nd Generation PFOS free is suitable to lower the surface tension to any desired level as foam as a limitation does not exist.
- The surface tension can be adjusted to the individual level that is required to meet required emission levels.
- A higher concentration of 2nd Generation PFOS free can be chosen to have a „buffer“ when extended dosing intervals are desired.



Going beyond present borders

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PFOS based

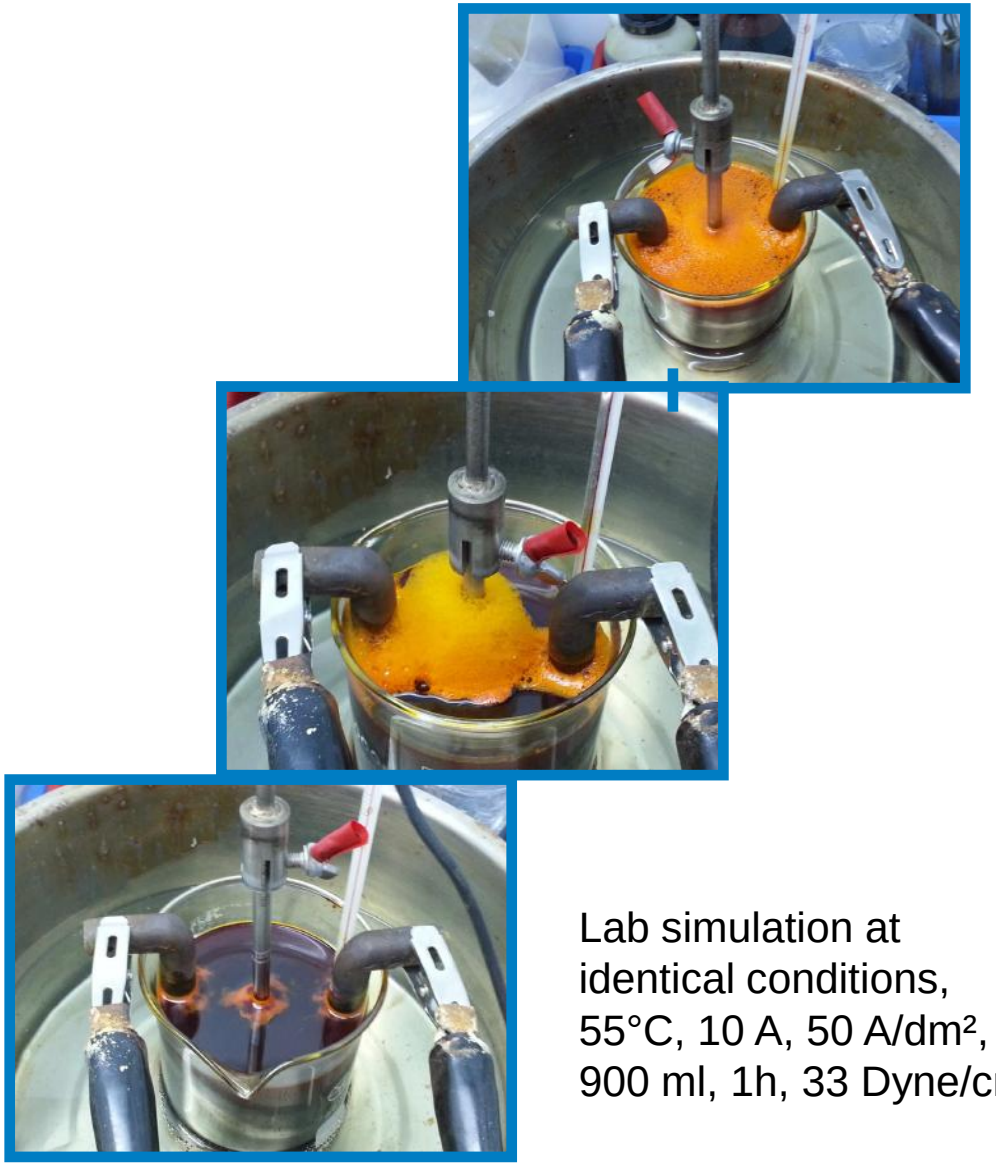
- Foam blanket or low foam option
- wide operation window
- Sensitive to pin hole formation

1st Generation PFOS free

- foaming at higher concentrations and lower temperatures
- Increased risk of H_2 explosions

2nd Generation PFOS free

- Entirely foam free
- No pin hole formation
- Extended dosing intervals
- Option to run < 30 Dyne/cm



Lab simulation at identical conditions, 55°C, 10 A, 50 A/dm², 900 ml, 1h, 33 Dyne/cm

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Objections to Chrome surfactants:

- PFOS restrictions, replacements being inferior
- Excessive foaming
- Pin hole formation in Hard Chrome
- Considered additional Cost
- Difficult to control, narrow surface tension operation window

Objection: Foam

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2nd Generation PFOS-free	1st Generation PFOS-free
Foamless at 30 Dyne/cm	Strong formation of foam at 35 Dyne/cm
No risk of H_2 explosions	Risk of H_2 explosions
Low consumption rate	High drag out rate/consumption
Cooling effect of evaporation remains	High demand for cooling

Objection: pin hole formation

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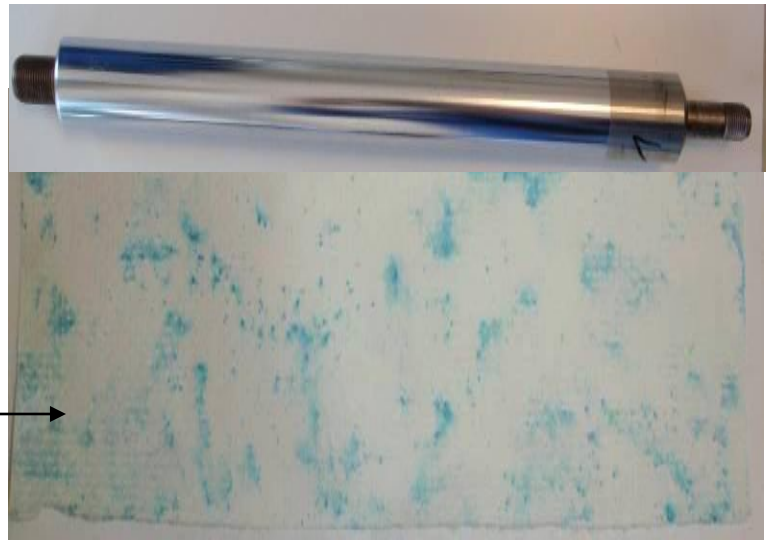
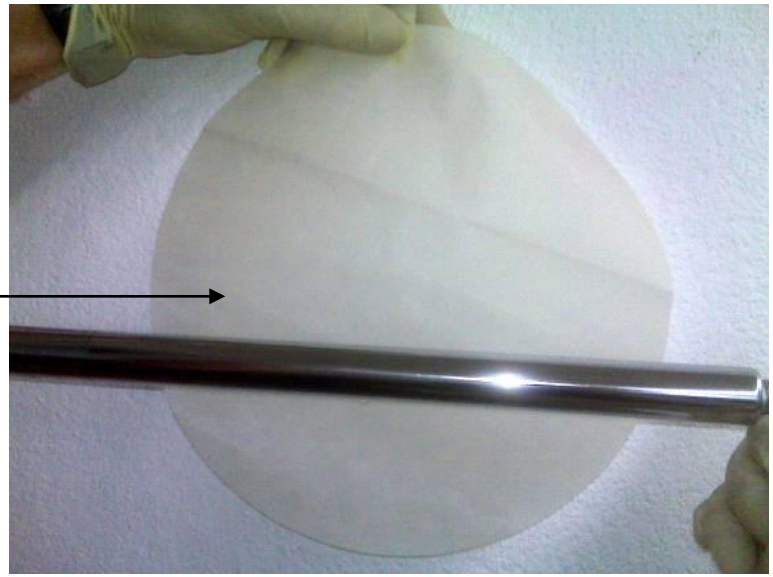
- PFOS-based surfactants face a limited solubility. Precipitation on the substrate surface may result in formation of pores at high levels of metal impurities.



- 2nd Generation PFOS free surfactants provide better solubility preventing formation of pores at high levels of metal contamination in the Chrome solution



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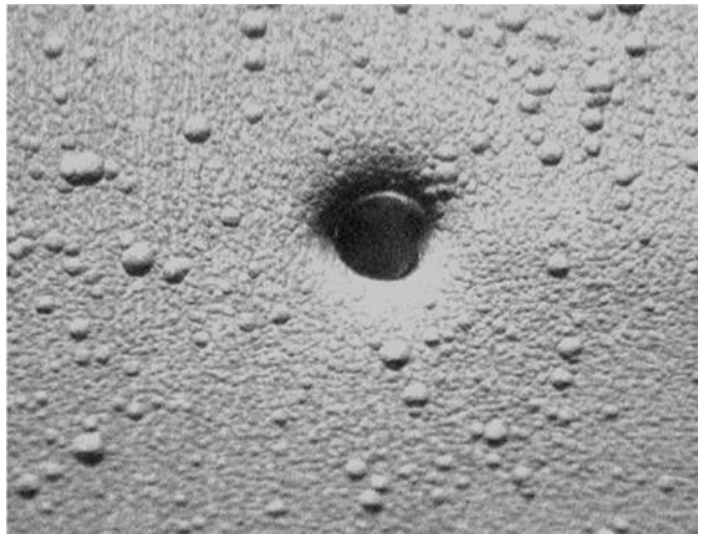

Pin hole formation with high thickness (500 µm; 20 mil), typical defect mode

- 2nd Generation PFOS free surfactants provide better solubility preventing formation of pores at high levels of metal contamination in the Chrome solution

Objection: Cost

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- Surfactants cause cost (about 20% of HC Chemistry, higher % with decorative Chrome due to higher drag out)

- Consider following cost saving aspects:
  - Line remains clean, less maintenance and corrosion on bus bars, anodes
  - No Cr losses to ventilation system, water in scrubber remains clear
  - Reduced drag out rate 100 ml/m² @ 30 Dyne/cm compared to 200 ml/m² @ 60 Dyne/cm
  - Overall consumption of Chrome chemicals will be reduced
  - Ventilation can potentially be reduced resulting in lower heating cost for the building in winter
  - Better working environment

- Overall the surfactant pays of for itself with significant case by case variation

Control methods

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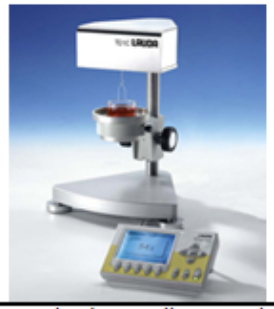
	SITA pro line t15	LAUDA ring-tensiometer TD 1 C	Stalagnometer
			
Principle:	Air is bubbled into the solution through a PTFE capillary. The pressure of the bursting bubble is measured and calculated to surface tension. $\sigma = k\ (P_{max}-P_{min})$	The force required to pull out a platinum-iridium ring from the solution to be tested is measured and translated to surface tension.	Counting of drops of a given volume. Low surface tension results in smaller drops. Result can either be read from a scale or needs to be calculated.
Sample Conditions	Room temperature, solution movement has to be avoided	Room temperature, solution movement has to be avoided	Room temperature, density measurement required
Calibration:	DI water at 20°C	DI water at 20°C	DI water at 20°C
Maintenance:	10,- € to replace PTFE capillary tube occasionally	Platinum-iridium ring replacement 500 €	Cleaning only
Cost of instrument:	6.600 €	8.000 €	120 €
Comment:	Simple and reliable operation. No experience required. Data can be automatically recorded.	Requires some experience to operate. Provides good and reliable data if used properly.	Provides reasonable relative data but poor absolute readings of surface tension. Specific gravity of sample solution impacts on results.
Recommendation:	**Highly recommended**	**Recommended**	**OK to use if relative results are sufficient without precise absolute surface tension readings.**

Control methods

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Reading on SITA instrument[*1]	50,0
ANKOR® DYNE 30 MS content	2,5 mL/L

→ | Surface tension (static) | 33,6 mN/m |
|---|---|

Replenishment recommendation

Targed Surface Tension (static)[*2]	30,0 mN/m
ANKOR® DYNE 30 MS addition	1,2 mL/L

- Simple and robust
- Clean operation
- Reliable reading due to multiple measurements per sample
- Actually measures the function of the surfactant, not just surface tension
- Reasonable investment and low running cost
- Data recording option

Conclusion

- Air borne emission from Cr(VI) solution are concern #1 world wide
- Foam is not essential to eliminate formation of Chrome mist
- Air borne Cr(VI) emissions can be further reduced by overcoming present surface tension limitations
- Historic objections and technical limitations in opposition to use of surfactants have been addressed and overcome
- 2nd Generation PFOSfree surfactants contribute to make Chromium plating more sustainable