Introduction

Methods of precision cleaning for UHV applications: Solvent, Detergent (ex.), Glow discharge (ex.)

Evaluation of cleanliness and quality control (ex.)

Electron stimulated desorption and cleaning

How clean can we clean?

Packaging and storing, effects on cleanliness and secondary electron yield
Some of the relevant contaminants for UHV systems are:

- In general “intermediate vapour-pressure” compounds adsorb and provoke long lasting static outgassing.
- Various hydrocarbons (oils, lubricants and so on from fabrication process) are bad for static and also dynamic vacuum.
- Corrosion inducing elements and compounds (halogens, sulphur…..).
- In some cases silicones (insulating layer of SiO₂ deposits on electrical contacts upon irradiation).
- Surface contaminants generally worsen wettability of the surface and adhesion of further coatings.

NB: Classical cleaning > 1 µg/cm²
    Precision cleaning <1 µg/cm²
Principle:
Solvation of a solute by the solvent which is favoured by Gibbs free energy: entropy driven (diffusion) but controlled by the molecular interaction strength for solute-solute (precipitation) which must not be too strong compared to solute-solvent.

Interactions:
- Ionic (ions in water)
- Hydrogen bonds ($H^+\delta\cdots O^{-}\delta$, $H^+\delta\cdots N^{-}\delta$, …)
- Hydrophilic/phobic: hydrophilic molecules have polar groups and can in general form hydrogen bonds with water molecules
- Hydrophobic effect: solvation of hydrophobic molecules is hindered by entropy since it requires an “ordered” arrangement of water around those molecules

All this was for water…but in most of the other solvents:
- Van der Waals: orientation (polar molecules), induction (polar vs non-polar), dispersion (polar and non-polar).
  “like with like”, interaction of A in medium B is $E_{AA} \sim (n_A^2 - n_B^2)^2$
Degreasing procedures

By immersion:
Dip the piece to be cleaned in the solvent bath (proper temperature and time) with ultrasonic agitation. Final rinsing with pure solvent and drying by evaporation.

Without immersion:
- Heat the bath of solvent to get sufficiently high vapour pressure
- Keep the cold workpiece above the bath to condense the solvent on it
- Collect the condensed liquid with dissolved contamination dropping from the workpiece in a recycling bath
Without immersion:

- ☺ the solvent is continuously distilled and purified
- ☺ ideal for gross degreasing before further steps
- ☹ needs adapted plant to avoid loss of solvent (avoid species harmful for the environment)

☺ both procedures are suitable for parts with complex shape (bellows), porous materials (ceramics, composites...) which cannot be easily rinsed or dried, and cannot sustain aqueous cleaning

☹ “like with like” only, for a given solvent solubility and cleaning efficiency are contaminant dependent

Ex: CO₂ (see later), CCl₂=CCL₂ (not recommended), commercial brands (ex: aliphatic+alcohol+ additives, liquid at RT, P_vap= 6 mbar at 50C, 97%volatile)
CO₂ snow:
- jet spray of liquid CO₂ which condenses in solid clusters: mixture of gas and snow; by landing on the surface it builds a liquid film which dissolves contaminants

- CO₂ is non-polar, dissolves alkanes (but less effective for long chains >20) and silicones; not very effective for molecules with C=O, COOH polar groups, bad for contaminants forming drops on the surface

- to be used by keeping the workpiece warm to avoid condensation of contaminants on its surface (from environment atmosphere)
Supercritical CO$_2$ (SCCO2):
- $T_c$ = 31°C and 72.8 bar: use at 35-80°C and 80-300 bar

Supercritical fluids wet a surface more easily than liquid phase: lower surface tension (1 mJ/m$^2$ for CO$_2$ compared to 32 mJ/m$^2$ for perchlorethylene and 72 mJ/m$^2$ for water), 100 times lower viscosity and similar solubility as liquid phase (solubility increases with pressure)
- can be used with co-solvents or soluble surfactants to dissolve polar molecules and ionic species
Pump (compression) → Heating → Cleaning vessel → Separator by distillation → contaminants → Cooling, condensation → Liquid CO₂
Principle: a detergent can wet any surface (is a surfactant): an amphiphilic molecule with polar head and non-polar tail, soluble in water and organic solvents, can incorporate the hydrophobic material which can thus be dissolved (formation of micelles)
Detergent cleaning procedure

- water and detergent bath
  + T (typically 50°-60°C)
  + ultrasonic agitation
    (or turbulent flow for long pipes which cannot be immersed)
  + rinsing with demineralized or tap water stream or ultrasound
  + rinsing with demineralized water bath (conductivity <5 µS cm⁻¹)
  
NB: the verification of wetting of the surface by the rinsing water is a simple, but effective control

+ Drying in oven 80°-100°C (possible for small parts only and suitable materials) or dry nitrogen (filtered)
Elemental concentration (at.%)%

- %C
- %O
- %Fe
- %Cr
- %Ca
- %Cl
- %N
- %Na
- %Si

Cylinder cleaned without US #1
Cylinder cleaned without US #2
Cylinder cleaned without US #3
Cylinder cleaned without US #4
Cylinder cleaned with US #1
Cylinder cleaned with US #2
Cylinder cleaned with US #3
Cylinder cleaned with US #4
Cylinder cleaned with US #5
Detergent

😊 generally more effective than solvents, used for non-porous materials and parts of simple shape, which can be properly rinsed/dried

😊 pH is not neutral, surface can be oxidized, surface oxides and some alloys (brazing, NEG) can be slightly etched; at best test for your workpiece material

😊 it is difficult to eliminate silicones, since they float on the bath surface and are recollected by the workpiece

NB:
- time and ultrasound power is function of contamination amount, part shape, brittleness, surface roughness, vessel size
- **bath quality must be monitored** (conductivity, pH, concentration of detergent to be effective) as frequently as the use requires it; it is effective to filter and recycle

M.Taborelli, CERN, CAS-2006
Test of cleaning TiZrV NEG with alkaline detergent:

Depletion of vanadium at the surface, presence of silicates, deterioration of activation properties:

XPS composition after thin film deposition and after cleaning

Ex.
Activation temperature (°C) - 1h00

O 1s peak area (A.U.)

NEG cleaned with detergent

NEG as deposited
Uncleanable contaminant: BN

- B segregates to the surface from stainless steel 316LN upon vacuum firing (950°C) and BN precipitates upon cooling (it is introduced in steel to increase hot workability)

- Boron nitride is not removed by usual detergents

- It is not bad for vacuum, but it is insulating, hydrophobic, with low surface energy and adherence to the steel surface (any coating will not adhere and will readily delaminate)

- we found (S. Sgobba et al.) it only in in 316LN having sufficient B (≥ 9 ppm); MnS precipitates could act as possible nucleation sites

- is removed by electropolishing the surface
M. Taborelli, CERN, CAS-2006

The image shows a micrograph with the marking "BN 3" and a binding energy plot with peaks labeled N (316LN) and B (15 ppm B in the bulk). The intensity is measured in a.u. and the binding energy is in eV.
Only detergent and solvent cleaning was discussed here, but also chemical etching, electropolishing, passivation.......are widely used
A difficult case: extruded copper pipes

Copper pipes for a UHV chamber designed to receive NEG surface coating showed **peel off of the coating and metallic particle residues**

❖ Amiss extrusion tool did not enable draining of the copper shavings, which remained instead incrusted on the tube’s surface.
Mechanical removal of most of the Cu particles (Cloth and hot high pressure water jet) and chemical etching of the internal surface with ammonium persulphate (about 60µm) + chromic acid passivation and rinsing.
After degreasing: Glow discharge cleaning

In DC or RF (reQUIRES more complex setup), see A. Mathewson and F. Dylla

$+ 300 \ldots 1000 \text{ V}_{\text{DC}}$

Mechanism: sputter cleaning of the chamber walls

Gas:
- Ar, some implantation of Ar in the wall (eliminate by baking at 350°C in StSt)
- Ar+$5-10\% \text{ O}_2$, more effective to eliminate carbon surface contamination by oxidation (forms volatile CO, CO$_2$ which are pumped)
- He, H$_2$, mainly for fusion reactor walls, not usual UHV systems

On StSt, Al, Cu, Ti and... Be.

Problem: possible coating of insulators with sputtered metal

M. Taborelli, CERN, CAS-2006
Auger spectra before/after GD on 316LN

Before GD

Ar+10%O₂ GD

Ar GD

Air exposure after GD

Pure Ar

A. Mathewson, Vacuum 24, 505, 1974

C decrease

1.6x10¹⁹ ions/cm²

7.8x10¹⁶ ions/cm²

1x10¹⁸ ions/cm²
Ion stimulated desorption (by N$_2^+$, 2KeV): Ar desorption after Ar GD

A.Mathewson, CERN-ISR-VA/76-41 and il Vuoto vol XVII 1987, p102

M.Taborelli, CERN, CAS-2006
Special case: Be cleaning with O$_2$ glow discharge
(S.Calatroni, CERN)

Beryllium is difficult to handle because of toxicity of its oxide (not safe to put it in a detergent cleaning bath!).

At sufficiently low kinetic energy (below ~400eV) the sputtering coefficient of O on C is higher than on Be due to chemical reaction; even better ratio for BeO

Test made on small sample: The amount of C on the surface decreases after plasma cleaning. no Be is found on the stainless steel strip used to hold the sample in place.
metallic impurity on the Be

from sputtering

Cu

Co

O

C

6x10^{17} \text{ ions.cm}^{-2}

decrease

Intensity [a.u.]

Binding energy [eV]
Quality control and qualification of cleaning procedures

Significant number of samples contaminated in a standardized way with representative contaminants, oils, mixtures.....

Clean the samples with the procedure under evaluation

Analysis of sample cleanliness

Compare to your application-dependent acceptance levels

Reject or accept procedure
Sample analysis: XPS

- surface analysis technique for surface sensitivity. XPS is simple for interpretation, sensitive and able to identify most contaminants (does not distinguish silicones and silicates).

- At CERN, the acceptance level for contamination is set to 40 at% of C on StSt (45° emission; XPS parameters must be kept constant for comparisons); based on experience of performance (and also realistically achievable results); corresponds to 0.5-0.8 nm coverage.

- Criteria from static/dynamic outgassing can be equally valid.

- For equal absolute amount of C on the surface, the measured at%C is material dependent as the probing depth (ex, 44% on copper, 29 at%C on Al, 30 at%C on Be, 36 at%C on Ti).

- CERN standard cleaning procedure gives 25 ±5 at% C on 10 copper samples cleaned nominally in the same way in the same run; scattering is larger between different runs.
Cleaning of standard contaminated copper samples: air exposure \leq 30 minutes

Stainless steel 316LN

Binding energy [eV]

Intensity [a.u.]
<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auger spectroscopy (AES)</td>
<td>modifies C content, see later</td>
</tr>
<tr>
<td>Static SIMS</td>
<td>good (silicones), but difficult to quantify in general, highly sensitive</td>
</tr>
<tr>
<td>FTIR</td>
<td>good (silicones) through elution</td>
</tr>
<tr>
<td>ESD</td>
<td>see later</td>
</tr>
<tr>
<td>Total. Refl. X-Ray Fluoresc.</td>
<td>needs mirror-like sample</td>
</tr>
<tr>
<td>UV-vis spectr, Ellipsometry</td>
<td>through elution, hard to identify species</td>
</tr>
<tr>
<td>OSEE, Surface potential diff.</td>
<td>no identification of species, substrate dependent</td>
</tr>
<tr>
<td>Gravimetry</td>
<td>low sensitivity (we need $\sim 10^{-7}$ g/cm$^2$)</td>
</tr>
<tr>
<td>Outgassing rate</td>
<td>only partial identification of contaminants, special sample shape</td>
</tr>
<tr>
<td>Water contact angle</td>
<td>no identification</td>
</tr>
<tr>
<td>Radioactive tracer</td>
<td>on selected contamination only</td>
</tr>
</tbody>
</table>
**Why should we pay attention with electron beams (as AES) for cleanliness characterization?**

Typical density for the e-beam: $10^{-7}$A on 100x100µm$^2$ gives in 10 s a dose of $6 \times 10^{16}$ electrons/cm$^2$.

Important electron stimulated desorption of C related species!

Use unfocused technique as XPS (about 10-100 times less damages) with higher signal-to-backg. or scan the beam (J.Cazeau, Appl.Surf.Sci. 20, 1985, 457).
Cleaning and dynamic vacuum: Electron Stimulated Desorption test of detergents and solvents on 316LN

Desorption induced by 500eV electrons after 150°C bake and after 300°C bake

All the detergents (colour lines) tested so far are better than the solvents (possible residues left....)

Typical $\eta$ (150°C)

- $H_2$: 0.1
- $CO$: 0.02
- $CO_2$: 0.03
- $CH_4$: 0.004

Less than 35 at% C in AES

Chiggiato, Benvenuti et al, Vacuum 53, 317 (1999)
-Contaminating hydrocarbons have low surface energy (~25 mJ/m² for alkanes, 72 mJ/m² for water, 1850 mJ/m² for Cu, 100-1000 mJ/m² for most oxides) and can adsorb easily on metallic surfaces and oxides.

-In general they do not react chemically with the substrate (at RT) and therefore form a loosely bound layer preventing good adhesion of thin film coatings.

Detection of silicones by FTIR

- **Elution** of contaminant from the “cleaned” part (tube, valve, ..) with a defined quantity of hexane per surface area
- Deposition of a drop of solution on a ZnS window (transparent to IR)
- Measurement of transmittance after evaporation of the hexane

Sensitivity depends on the area used for the elution (various drops can be cumulated if necessary to increase concentration)

**Problem:** Uncertainty on the effectiveness of elution

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**S.Ilie, C.Petitjean, C.Dias-Soares**

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**M.Taborelli, CERN, CAS-2006**
How clean can we clean?

Air exposure provokes hydrocarbons re-adsorption on sputter cleaned copper surface (C_xH_y have low surface energy)

Trials of cleaning by keeping the sample in the rinsing water up to Insertion in XPS does not improve the situation.
Effect of storage in different packaging after cleaning

Storage of cleaned OFE copper

- Al foil
- Air (open glass box)
- PE (CERN store)
- PE pure (Newform)
- PE+Al foil

C concentration [at%]

- 6 months
- 1 month
- as cleaned
Effect on secondary electron yield storage

Evolution of copper SEY as a function of storage

- Alu foil
- Air
- PE
- PE pure
- PE+Al foil

B.Henrist, N.Hilleret,

M.Taborelli, CERN, CAS-2006
Influence of re-adsorbed contamination on SEY of copper
Check on your cleaning procedure with the own cleaning plant on your own materials
Design cleanable parts (shape, roughness,...)

Avoid undesirable compounds (halogens, silicones, Zn, Cd, BN...) in the fabrication process: even for the best cleaning procedure you will find them once at the end!

Avoid packaging in polymers in contact with the sample unless the polymer has been previously qualified.

All this will save time.
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