Cleaning, Adhesion, & Productivity

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BFK Solutions
Critical Cleaning Consultants, est. 1994

- As the industry leaders, we provide
  - Process improvement, not product sales
  - Experience, expertise, common sense
  - Industry involvement: JS3 (military), IPC, ASTM, U.S. ISO expert, EPA, FDA
- Barbara Kanegsberg, "*The Cleaning Lady*"
  - Biochemist, clinical chemist, manufacturing process
- Ed Kanegsberg, "*The Rocket Scientist*"
  - Physicist, engineer, process evaluation

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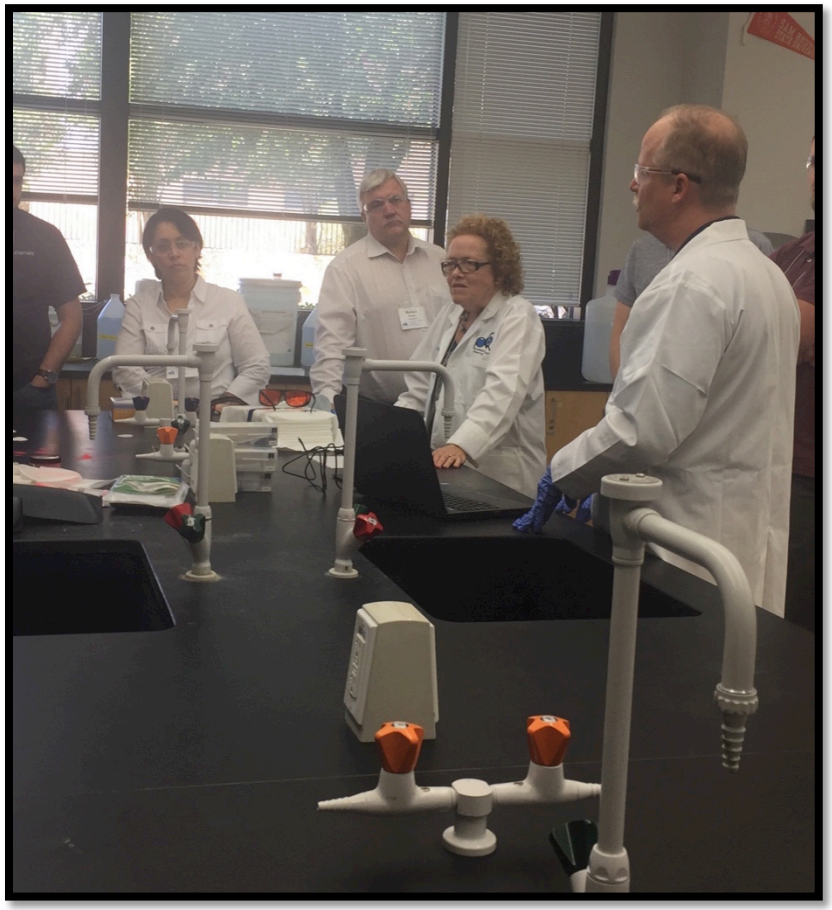
BFK Solutions Educational Resources

- "Clean Source" eNewsletter
  - Free; Sign up!
- Technical column, Products Finishing Magazine
- Product Quality Cleaning Workshops (PQCW)
  - With Dr. Darren Williams, Sam Houston State University
- Editors, 2 volume, "Handbook for Critical Cleaning," CRC Press, 2nd edition, 2011



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Always question authority - including BFK Solutions

- We make the best effort to provide accurate, up-to-date information
- Information, especially quantitative information, is obtained from reliable references
- It's always prudent to reconfirm all technical and regulatory information from the appropriate supplier or regulatory agency
  - SDS (MSDS)
  - Technical data sheet
  - Most recent requirement or regulation
- This presentation contains private and copyrighted material. May be distributed with prior permission of BFK Solutions, LLC

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Overview: Cleaning, Adhesion, and Productivity

- **Why clean before coating**
- How cleaning works
- Cleaning, extraction, separation, detection
- Strategic cleaning

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Why clean?

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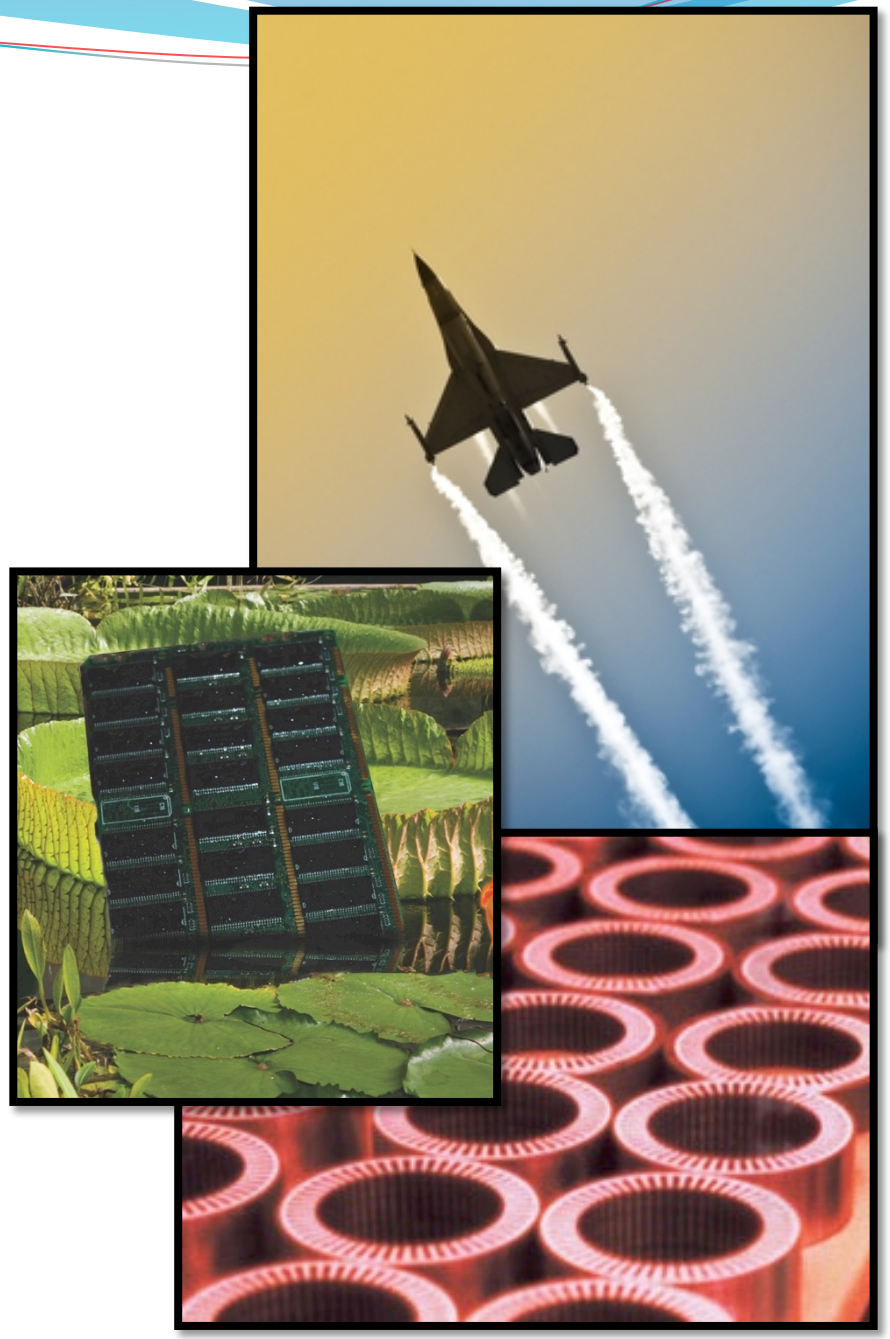
Cleaning is essential

- Electronics assemblies
- Aerospace hardware
- Military weapons
- Implantable medical devices
- Paintings, sculpture
- Computer hardware
- Analytical instruments
- Mixing chambers, product contact



Cleaning is essential

- Optics
- Automotive parts
- Reflectors prior to vapor deposition
- Coffin corners
- Molded plastic parts
- Miniature components
- Nano-components
- Parts made with 3D printing (additive manufacturing)

Begin with the end in mind

- Why are you cleaning?
- What soils are you removing?
- What are the next steps in the process?
- What risks are involved in removing the soil?
- What risks are associated with the residue?

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Product Cleaning

- Soil
  - Matter out of place
    - E.g: burnt on lasagna on a casserole
- Cleaning
  - Removing matter out of place
  - Removing live dirt, dead dirt, any matter out of place
  - Not sterilization
  - Green cleaning – separate issue, cleaning ought to be green
- Most manufactured products have to be cleaned to work

Precision Cleaning

- Precision cleaning
  - Cleaning items that already looks pretty clean
  - Cleaning with a well-defined process
  - Cleaning to a specified process or specified level of residue

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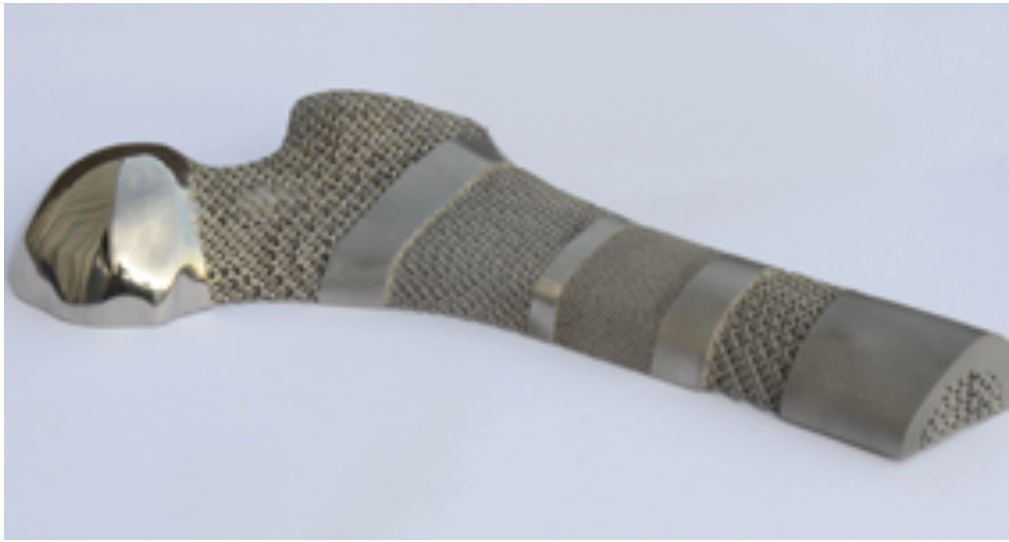
Critical cleaning

- Value-added, “tipping point” cleaning
- Cleaning with an EFFECTIVE, WELL-DEFINED process
- If you don’t do it, product quality suffers
- Any cleaning step is potentially critical cleaning
  - Could be at the beginning of fabrication



Is it soil? .....

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…or is it dirt?

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Soils

Particles (metal fines, chips, skin flakes, polishing grit, 3D powder)
Acids
Water
Solvent
Product Assortment
Residual product/breakdown (in processing equipment)
Deposited cleaning agent residue (including flux residue)
Oils, greases
Lapping, polishing compounds compounds
Metal working fluids
Solder flux (rosin, organic acid, low residue)
Rust-preventative

Nomadic dirt

- Dirt can creep from holes and crevices
- Dirt can
  - Migrate from process equipment
  - Mosey over to process equipment
- A clean surface won't remain clean if there are non-clean surfaces nearby

What happens to coatings if there is inadequate cleaning?

- Poor coating adhesion
- Change in coating chemistry
  - Poor cohesion
  - Changes in appearance (texture, color)
- Contaminants visible under the coating
- Sort of like painting a wall over grease and dirt

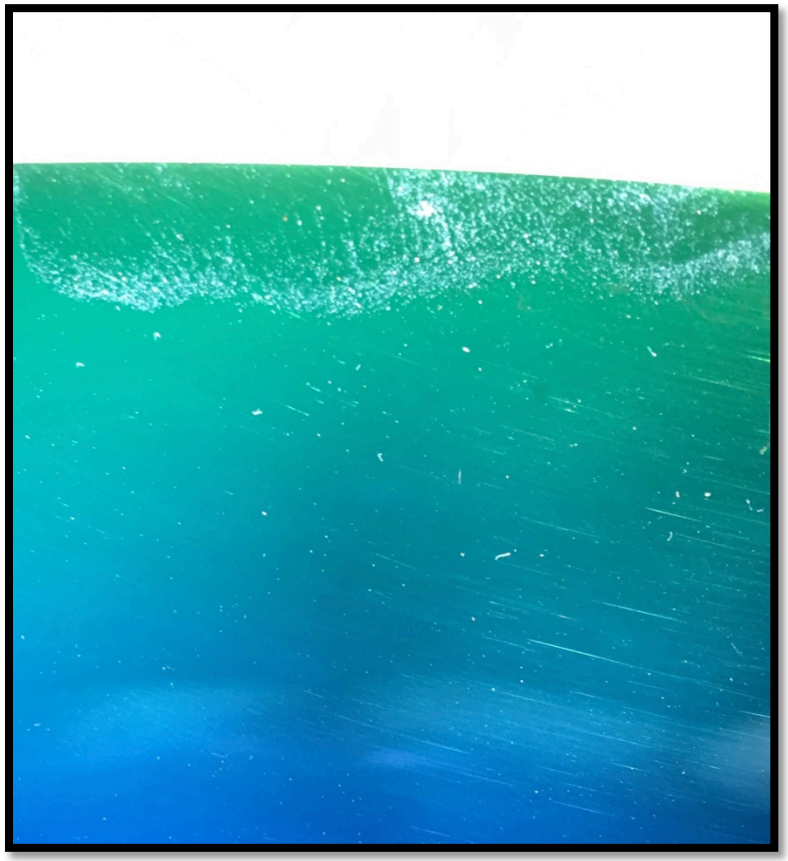

Photo courtesy of Optiforms

Negative impacts of cleaning or coating failure

- Poor product quality
- Delay in market approval
- Costs from delayed shipment
- Hazards for public
- Risks for patients
- Regulatory action
- Legal action

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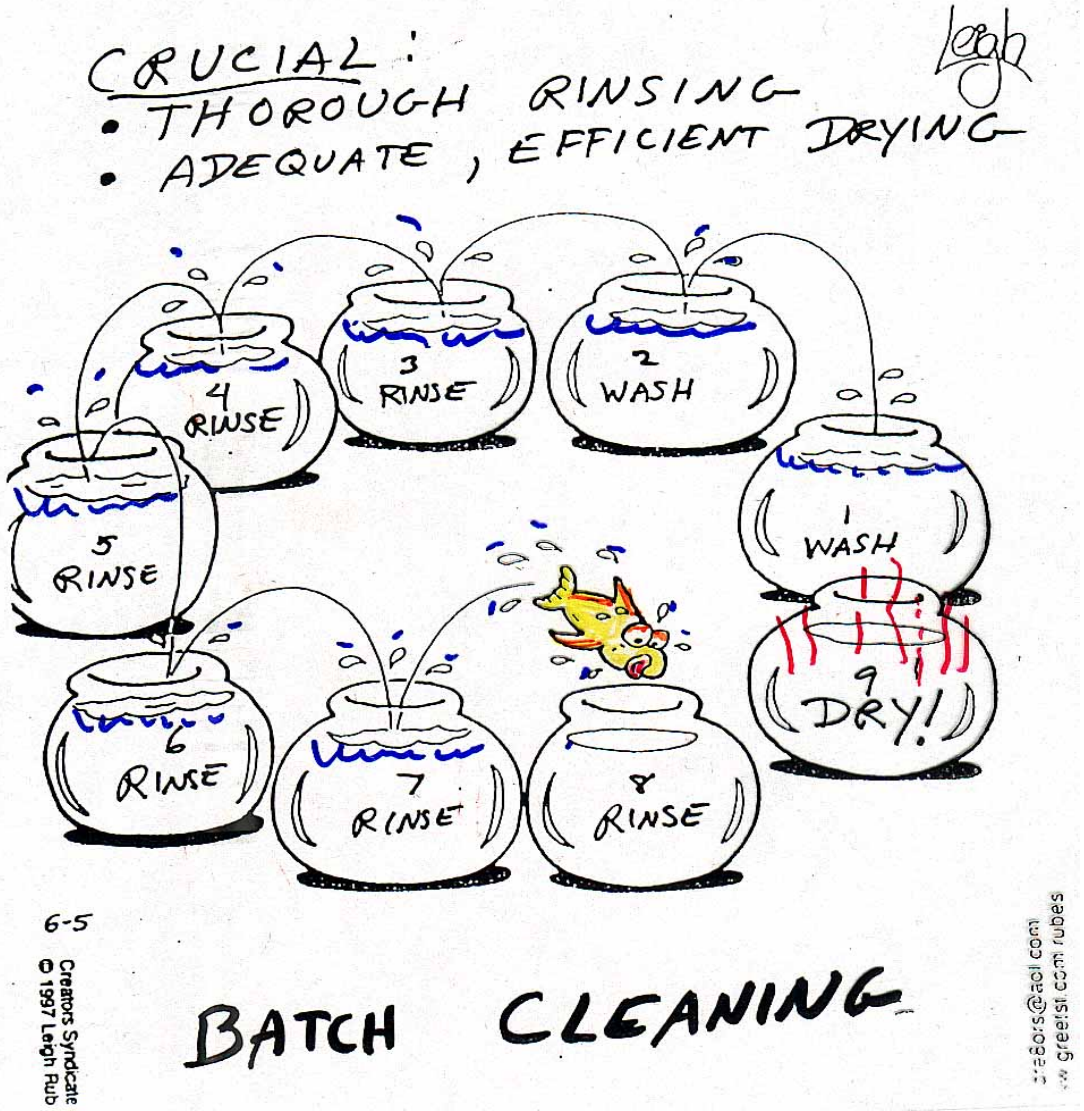
Cleaning is a 'TACTful' Process

- (T) Temperature
  - 10 degree Centigrade increase in temperature doubles reaction rate
    - Rule of thumb
- (A) Action or Force
- (C) Cleaning chemistry
- (T) Time
- Wash, rinse, dry
- Must consider worker safety, chemical emissions

RUBES By Leigh Rubin



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Steps & Functions of Cleaning System:
Think About Cleaning Agent and Cleaning Process Together

- (1) Wash
  - Deliver cleaning agent to surface
  - Provide cleaning action to remove soil without damage to surface
  - Remove soils from proximity of surface (i.e. leave a clean surface)
- (2) Rinse
  - Remove residual cleaning agent
  - Continue cleaning process
  - Vapor degreasing solvent – self-rinse
- (3) Dry
  - Remove water, adsorbed solvent
- Separate, distinguishable operations
  - Allocate $$$ and design time appropriately
- Restore cleaning agent for subsequent operation (Optional, but often desirable)
- All steps: avoid product damage

“I shall endeavour not to bore you. Facts are so much more interesting than theories, don’t you agree?”

The sage words of:

Dr. No

Ian Fleming, James Bond Series

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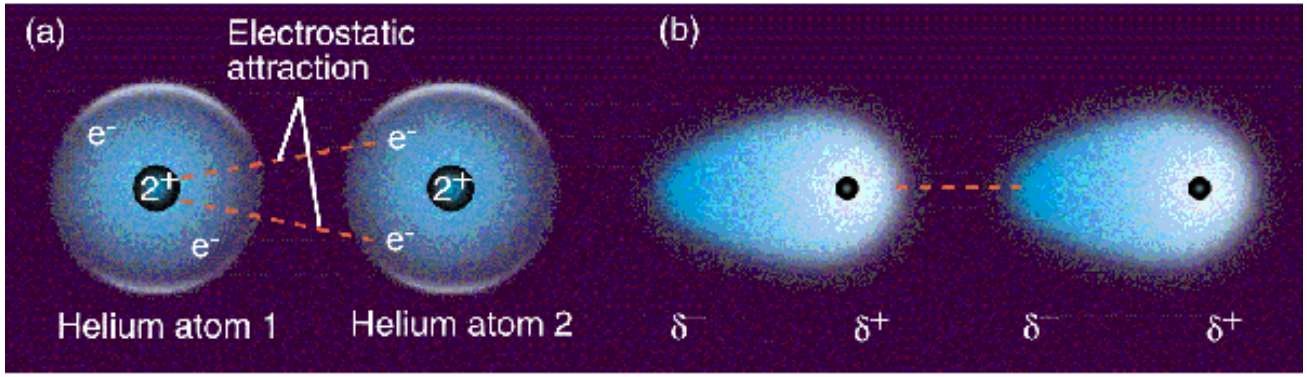
The physics of cleaning

- Soils adhere to surfaces via forces
- Cleaning involves overcoming those forces

Forces

- Polar forces
  - Inter-molecular forces arising from a permanent charge distribution
    - One side of molecule is more positive, other side is negative
  - Polar molecules (dipoles) attract other polar molecules
    - Example: liquid water
- Hydrogen bonding forces
  - Polar force associated with the hydrogen atom (single proton)
- Non-polar (dispersion, Van der Waals, London) forces
  - Weaker inter-molecular forces arising from transient charge distribution---Molecule becomes polar, but not permanently
  - While polar, induces polarity in nearby molecules, causing attractive forces
  - Example: liquid oil, wax

Dispersion forces



Symmetric molecule induces dipole

http://itl.chem.ufl.edu/2045/lectures/lec_g.html

Dispersion forces in nature

Foot of a Tokay Gecko
Photo: David Clements, From Wikipedia

Gecko feet

- Geckos can adhere to a “smooth” dry surface
  - No sticky fluids exuded
  - Thousands/millions of tiny hairs (cilia); each hair has a tiny spatula foot
  - Foot provides surface area (many molecules) for dispersive attraction
  - Microscopic dimension allows foot to fit into small surface irregularities
- Small particles are like gecko feet
- Dried soils are like gecko feet

Why worry if soil sticks?

- Adherent soil can impact coating adhesion
- Contaminated product can contaminate the cleanroom or vacuum chamber
- Adherent soil can impact product performance

What makes soil difficult to remove?

- Manufacturing processes can impede cleaning
  - Soil
  - Force
  - Heat
  - Time
- Product shape and material
- Changes in regulations
  - Environmental, safety

A balancing act

What helps remove soil?

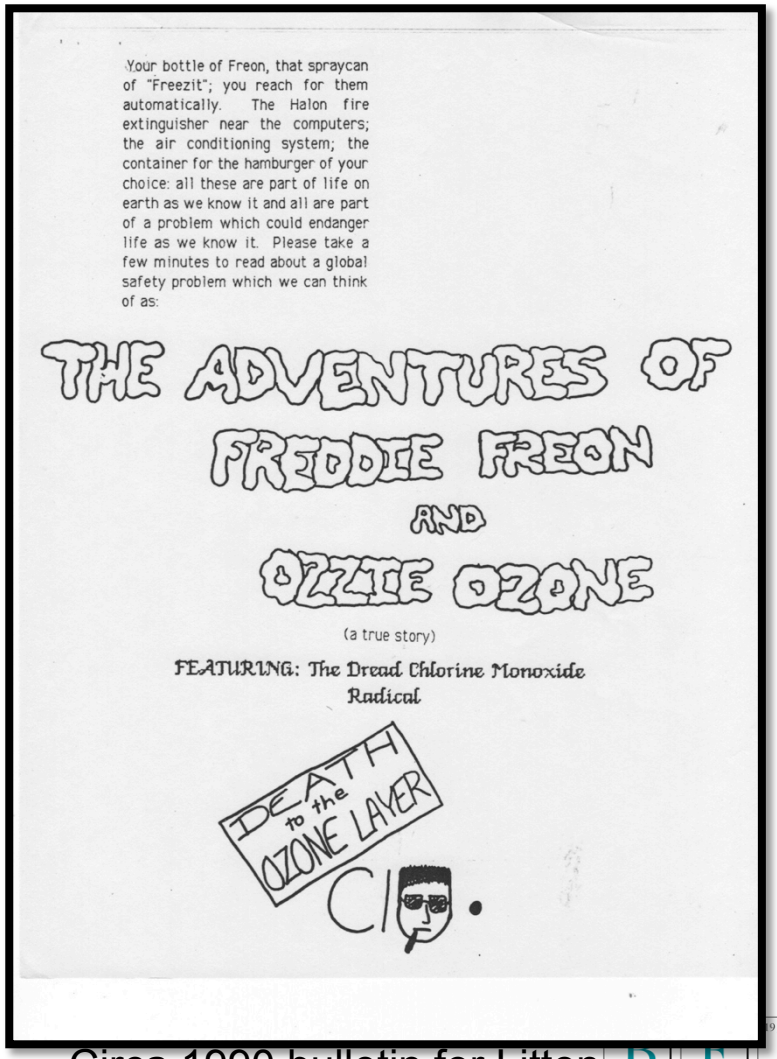
- Forces
- Cleaning chemistry
- Temperature
- Time

What makes soil stick?

- Forces
- Soil chemistry and size
- Temperature
- Time
- Product shape and material
- Changes in regulations
  - Limits available options

Parts have to be pretty clean before plasma cleaning or vapor deposition

- Plasma: chemically reactive
  - Have to be well-defined
- Any vacuum plasma process can include
  - Cleaning
  - Surface modification
  - Residue modification
- Excess soils can
  - Mess up the surface
  - Mess up the coating



Your bottle of Freon, that spraycan of "Freezit"; you reach for them automatically. The Halon fire extinguisher near the computers; the air conditioning system; the container for the hamburger of your choice: all these are part of life on earth as we know it and all are part of a problem which could endanger life as we know it. Please take a few minutes to read about a global safety problem which we can think of as:

THE ADVENTURES OF FREDDIE FREON AND OZZIE OZONE

(a true story)

FEATURING: The Dread Chlorine Monoxide Radical

Circa 1990 bulletin for Litton Industries, created by Barb K.

Key cleaning parameters

- Solvency
  - Match cleaning agent to soil (like dissolves like)
- Wettability, Penetration

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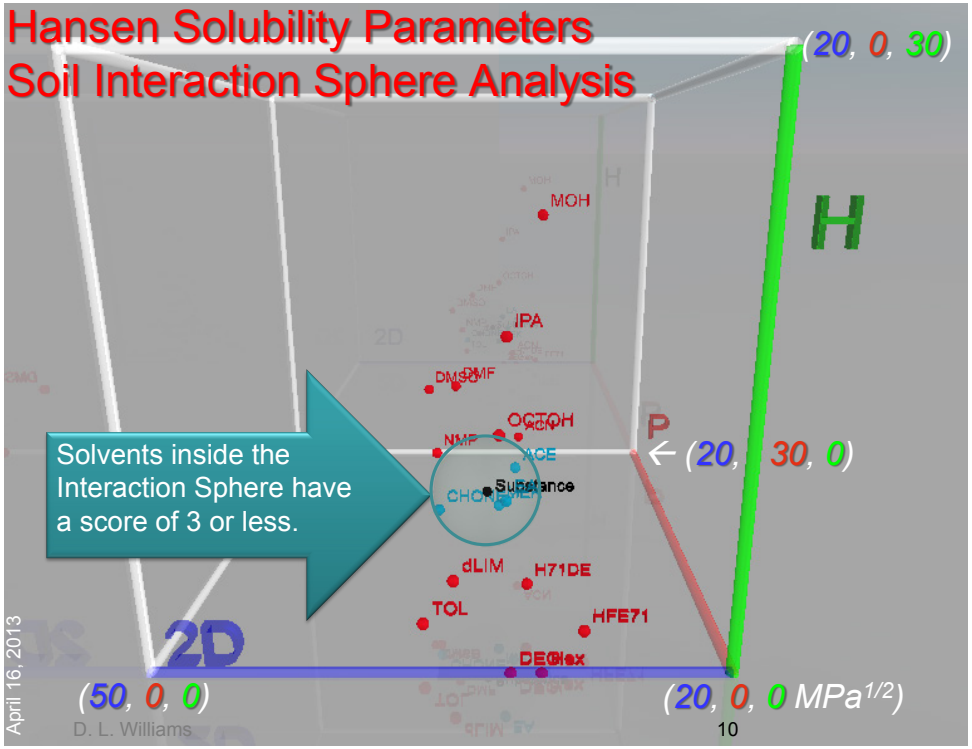
Hansen Solubility Parameters

- Mathematical embodiment of "like dissolves like"
- Involves Dispersion, Polar and Hydrogen bonding forces
- Minimize distance between solute and solvent
  - Radius of soil interaction sphere (R_a)

$$R_a = \sqrt{4(D_{solv} - D_{solute})^2 + (P_{solv} - P_{solute})^2 + (H_{solv} - H_{solute})^2}$$



Courtesy Prof. Darren Williams, Sam Houston State University

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Hansen parameters: Absolute numbers & balance influence solvency

Compound	Non-polar (dispersive)	Polar	Hydrogen bonding
Perchloroethylene	19.0	6.5	2.9
n-propyl bromide	16.0	6.5	4.7
HFC 43-10mee (Vertrel™)	12.9	4.5	5.3
HFE 7100 (Novec™)	13.7	2.3	1.3
Trans-1233zd (Solstice™)	15.5	4.5	2.2
Water	8.6	13.4	25.8
Isopropyl alcohol	15.8	6.1	16.4
Acetone	15.5	10.5	7.0

Hansen solubility parameters – like paint chips

Wetting Index & why it is important

- Penetration/wetting increases with **low** viscosity, low surface tension
- Penetration increases with **high** density (more momentum)
- Wetting index = density x 1000/surface tension x viscosity
  - Teaching tool developed by W. Kenyon
- Why might a high wetting index be desirable?
  - Better penetration close-spaced components
  - Better ”creeping” under thin films
  - More effective removal of particles
  - More efficient extraction

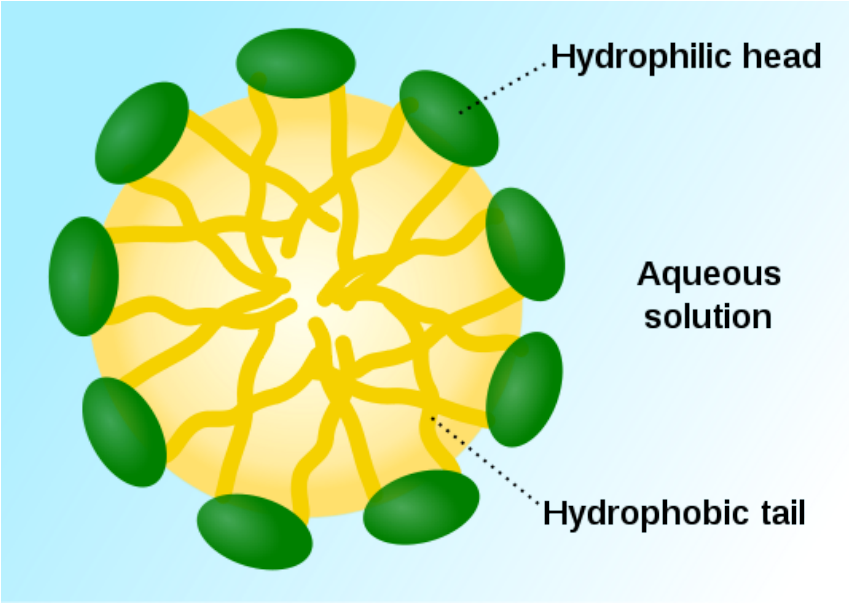
Cleaning Agents	Density g/cm^3 (25 ^{o}C)	Surface Tension Dynes/cm (25 ^{o}C)	Viscosity Centi-poise (25 ^{o}C)	Wetting Index
HFC-43-10	1.58	14.1	0.67	167
HFE 7200 (HFE-569sf2)	1.43	13.6	0.61	172
Trans-1233zd	1.3	13.3	0.489	200
Acetone	0.79 (20 ^{o}C)	23.3 (20 ^{o}C)	0.36 (20 ^{o}C)	94
Isopropyl alcohol	0.78	21.8 (15 ^{o}C)	2.4 (20 ^{o}C)	**15**
d-limonene	0.84	25	1.28	26
H20	1.00	72.8	1.00	**14**
Saponifier solution, 6% ethanolamine-based saponifier	1.00	29.7	1.08	31

Properties of water

- Solvency
  - Good for polar substances, including salts
  - Poor for non-polar substances (e.g. oils)
- High surface tension
  - Low wettability

Aqueous cleaning agents contain chemical additives Compensate for like dissolves like

- Wetting
- Solubilization
- Saponification (base)
- Emulsification
- Sequestration
- Micelle formation (surfactant)



Why be concerned about additives?

- Wide variety of aqueous cleaners
- Changing the aqueous cleaner can affect
  - Cleaning efficacy
  - Residue
- Wide range of rinsability
  - Risks from un-rinsed residues

Aqueous formulations are complex

- Choosing an aqueous formulator is like finding a good chef
  - Many ingredients to choose from
  - Many different “styles”
- You may not need to know the exact recipe, but get to know the chef
  - Do not get all the info and nuances from the SDS

Example: just a *small* change in the cleaning agent

- Manufacturer of commercial & military reflectors
  - Coating in vacuum chamber
- Purchased “household” cleaning chemistry at Costco
- We called the formulators – any changes?
  - Yup!
  - 2013 reformulation to meet CARB VOC restrictions
    - Affects sales of cleaning agents into California
- New product “neat” is 1:7 dilution of old product
- New product is oil splitting
  - Original held oils in suspension
- Asked the formulators: How do we know we have the new product?

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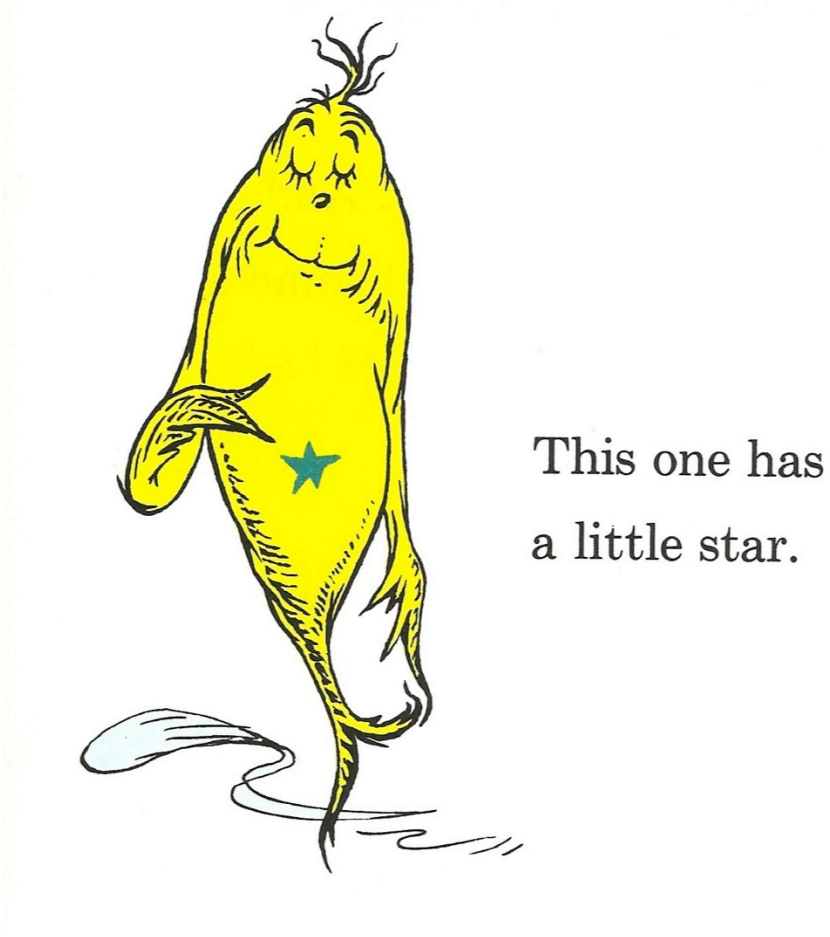
Check the bottles!



- New product - tiny star next to UPC code
- Covered over by store stickers
- Informing the user was left to the distributors

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Next steps after the star

- “Improved” reformulated product unsuitable
- Tested alternative products
- Suggestions
  - Use cleaning agents designed for manufacturing
  - Keep an eye out for changes

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Example: Surface finish, funerary Hardware – it's the water!

- Client processes included plating, vacuum deposition
- Problem: purple & brown coffin corners

Cleaning agent supplier told client to use tap water for rinse

- Problem: Quality and properties depend on source, season
  - Reservoirs (minerals, gases, organics)
  - Wells, aquifiers (minerals)
  - Rain (dissolved gases)
  - May contain additives, e.g. fluorides
  - If filtered, what do filters remove? Particles?, organics?
- Tap water is for drinking, not critical cleaning

Example: Particles in a vacuum – medical detector

- Symptom: Medical test detector imploded during use
  - Operating under reduced pressure
- **Problem: structure complexity**
- Cleaning during assembly difficult
  - Particulate contamination judged responsible for malfunction
    - Detection: visual (in-situ & extracted)
- Approach: instituted sequential ultrasonic cleaning steps
  - several aqueous & solvent products
- Problem resolved
- Better approach: design the product so it can be built

Overview: Cleaning, Adhesion, and Productivity

- Why clean before coating
- How cleaning works
- **Cleaning, extraction, separation, detection**
- Strategic cleaning

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A “who-dun-it”

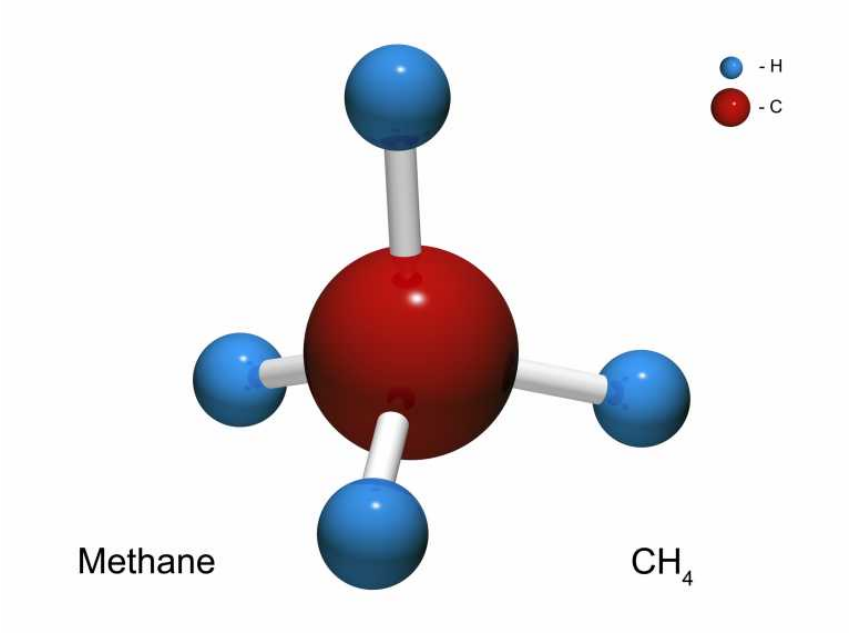
- Adapted from the *Product Quality Cleaning Workshop (PQCW)*
  - Presented with Dr. Darren Williams
  - Sam Houston State University (SHSU), 2018
  - Inspired by SHSU College of Criminal Justice

Cleaning, Extraction, Chromatographic Separation, Detection

- Related activities
- Have distinct purposes
- Understanding the differences important in
  - Developing processes
  - Evaluating standards, guidance documents
  - Working with laboratories
  - Validating/verifying cleaning processes
  - Process control
    - What does the process look like when it's correct
    - What do problems look like?

Why so many steps? Extraction, Chromatographic Separation, Detection

- Identify the contaminant
  - Carbon: 4 covalent bonds
- The are a boatload of organic compounds
  - At least 9 – 10 million identified
- Which organic compound is the culprit?
- Simplify!
  - Make it easy for the lab folks



Summary: Extraction, Chromatographic Separation, Detection

- Goal: Detect
  - What are the problem contaminants?
  - To do that we have to simplify
- Extract
  - Concentrate low levels of contaminants
  - Ferret out contaminants lurking in tight spaces
    - They can “creep” out in a vacuum
- Separate
  - Simplify the problem

This is what your analyst thinks when you send a sample and say: “find the suspect contaminant in this crowd (the fugitive could be hiding) ”

Cleaning (in contrast with extraction)

- Disperse the crowd
- Remove soil from the surface, keep it away from the surface
- Not concerned about destroying the soil
- Don’t want to change the surface or damage the product
- Extraction has commonalities with cleaning

Extraction (in contrast with cleaning)

- Capture the crowd
- Remove soil from surface
  - Involves solvency, wettability
  - May need more than one solvent for mixed soils
- Recover soil for analysis, identification
  - Often, concentrate the soil
- May not want to change or destroy the soil
  - Forensic analysis
- May not care about damaging the surface
  - Unless what you extract from the product interferes with identification
  - Unless this adds to the suspects in the crowd

Chromatography

- We've extracted the contaminants
  - We've extracted the people from the concert
  - They're all at the mall
- Next step: chromatography
  - Separate the people in the crowd
    - At least divide them into smaller, recognizable groups
  - Separate the contaminants

Separation by chromatography

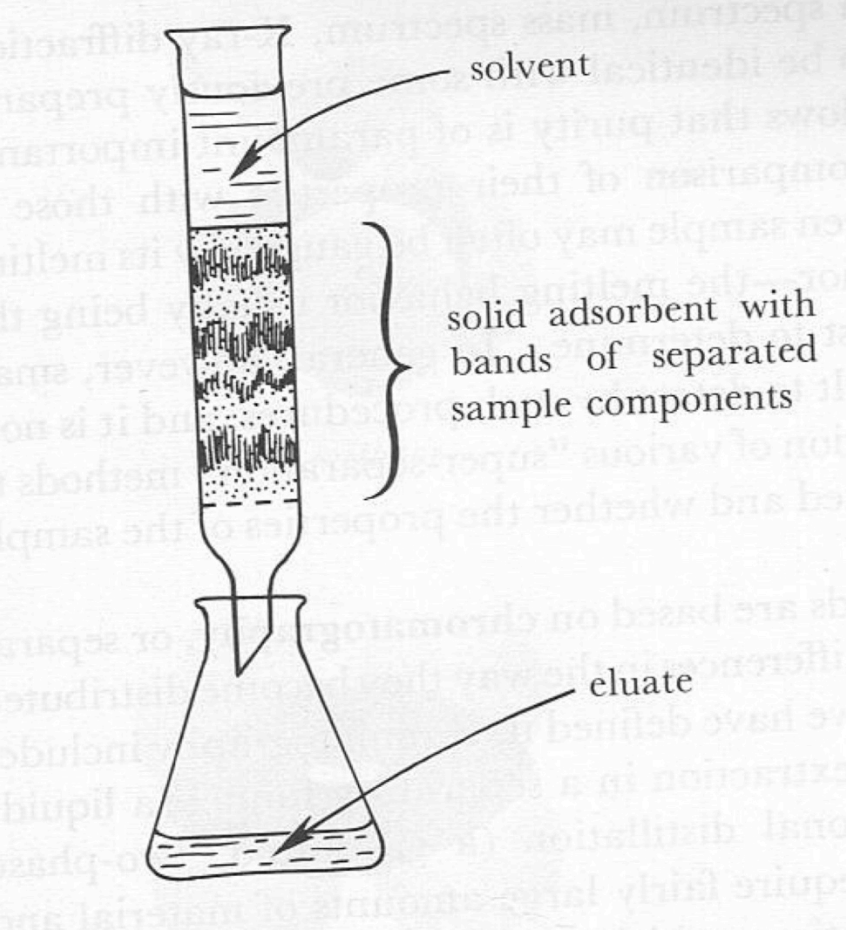
- GC
  - Gas chromatography
- RGA
  - Residual gas analysis
- HPLC
  - High pressure (or high performance) liquid chromatography
    - Or high priced
  - Ion chromatography
    - A type of liquid chromatography
- Sometimes combined with other techniques
  - GC/MS
    - Gas chromatography/ mass spectroscopy

Contemporary gas chromatography – not visually informative

Chromatographic Separation

- Early chromatography separated chemicals in leaves
  - "Chrome" in chromatography referred to color of separated components
  - Currently "chrome" implies identify by separation
- Preparative chromatography
  - "clean" or purify a chemical
- Analytical chromatography
  - Clean a mixture so you can detect contaminants more clearly

Column chromatography



From: Roberts and Caserio, "Basic Principles of Organic Chemistry," W.A.Benjamin, 1964

- Introduce mixture to column
- Stationary phase (sorbent)
- Mobile phase
- Mobile phase passes through the stationary phase
- Result: separate mixture into simpler components
  - Ideally, single molecular species

Mobile phase: separate suspects into groups by attracting them away from the stationary phase

Announce: free ipods!

Announce: New Harleys!

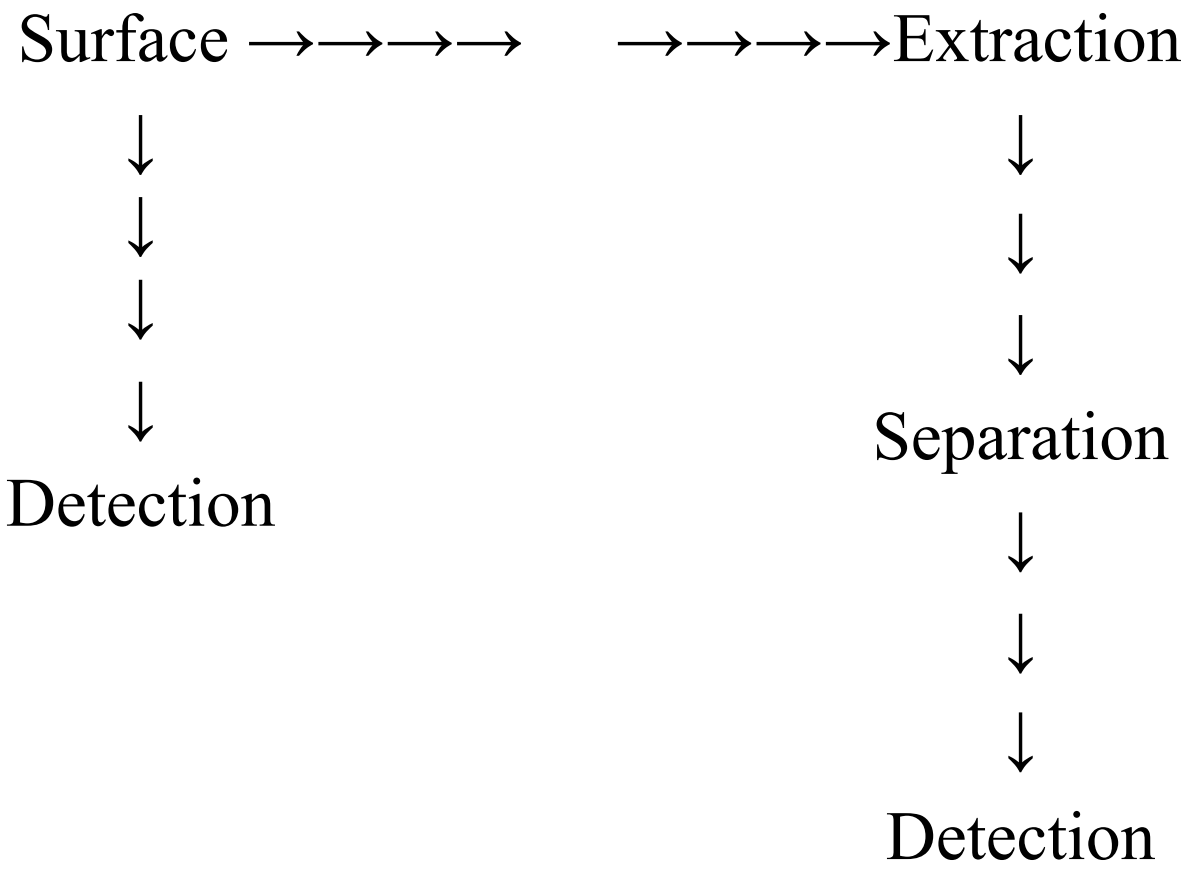
Detection: “See” the people (or groups of people) in the crowd

- Identify the contaminant of interest
- There are different kinds of detectors
  - Specificity: specific molecule, category of “dirt”
  - Sensitivity: how much dirt
- It’s easier to detect purified “dirt”
  - Especially if the dirt is organic
- Even with an extract, you may have to separate parts of that extract
  - Or, can be like trying to identify objects through dense fog
  - Reduces the “fog” so the detector works more reliably

Detection: Profiling

The usual suspects are situational (aerospace, medical, electronic, floor products, has different suspects): even for a given method, use a lab with the correct computer "library"

Sometimes, you can go from surface or extract to detector (not always!)



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- Why clean before coating
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- **Strategic cleaning**

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Options – avoid cleaning

- Don't clean
  - Is cleaning necessary?
- Only work with clean parts
  - Manage supply chain
  - Use disposables
- Keep the part or component clean
  - Before cleaning
  - During cleaning
  - After cleaning
- Redesign the product or component
- Change the soil

Example: Is the fabricator the weak link?

- Poor adhesion of DLC (diamond-like-coating)
- We reviewed supply chain activities
- Requested details about metalworking fluids
- Response: “Sometimes black grease, sometimes yellow grease, sometimes white grease”
  - No SDS provided
- Strongly suspect supplier used grease from dim-sum restaurant

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Don’t clean if you don’t have to …..
but you probably have to

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Example: Flexible, “cell” cleaning versus central system

- Client builds vacuum coating systems & coats product
  - Plasma cleaning in coating chamber
- Also cleans prior to chamber cleaning/deposition
  - Vapor degreasing
  - Aqueous cleaning
    - Large, complex central system – does it all
- Product line has evolved
- Looking at options
  - Modify central system versus smaller, specialized system
  - Modify fixtures to fit standard process baths

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Avoid angst in vacuum applications

- Inappropriate cleaning process
- Change of formulation
  - Soils (e.g. machining fluids)
  - Cleaning agents (“new and improved”)
- Weeping from holes, crevices, welds, etc.
- Porous material--outgassing
- Reliance on plasma to clean

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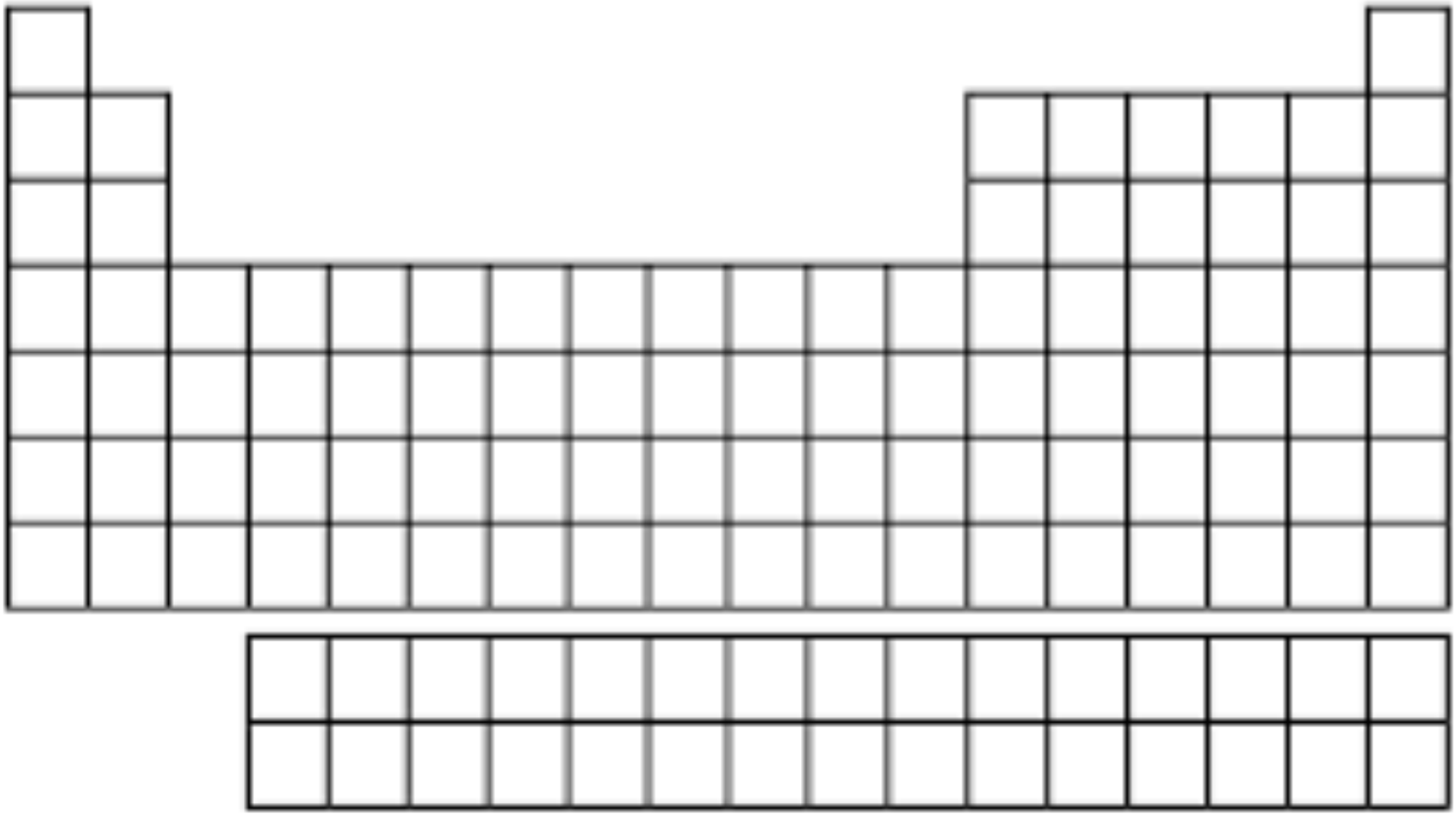
Example: Particles in a medical imaging detector

- Detector made "pinging" noises
  - Associated with particles in a vacuum
- Coped with problem with extensive "break-in" process
  - Operate system under vacuum, at the factory
  - Listened for "pinging" noises
  - Released device after pinging stopped
- Solvent cleaning would have resolved the problem reliably
  - But they didn't use solvent cleaning
  - Why not?

Safety Office derailed critical cleaning processes

- Client had unused degreaser for HCFC 225
  - Unopened drum of HCFC 225
    - It's no longer produced, but the principle holds
- Barb: Why haven't you set up the process?
  - Answer: the Safety Officer won't let us
- Barb: Why?
  - Answer: Safety won't say
- Barb: Can we talk to safety? They can't fire us!
  - Answer: NO! We're afraid of him
- Bottom line: The process was not implemented for 5 years!

Periodic Table of Safe Elements



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TANSTAAFL ("There ain't no such thing as a free lunch") Robert Heinlein, "*The Moon is a Harsh Mistress*"

- Better solvency desired
  - If it dissolves the soil, it MAY damage the product
  - Everyone wants a universal solvent
    - How would you store it?
- Safety, low environmental impact desired
  - If a cleaning agent dissolves the soil
    - it can impact you
      - Our products depend on organic chemicals (metalworking fluids)
      - We're made of organic chemicals
    - It can impact the environment

Questions?

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