Basics of plasma treatment

TIGRES
Plasma for perfect adhesion

Introduction

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TIGRES

Plasma for perfect adhesion

Introduction

Peter van Steenacker

Electronics engineer

Sales Manager since 1998 for plasma systems. Extensive experience with plasma nozzles (APPJ), DBD-Plasma and vacuum plasma.

Extensive experience in lecturing regarding plasma treatment, with presentations, seminars, webinars and training.

Head of PlasmaXperience, the platform from TIGRES for plasma know-how

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TIGRES
Plasma for perfect adhesion

TIGRES GmbH

TIGRES GmbH has been established in 1993 as an independend, family owned technology based company

Targets:

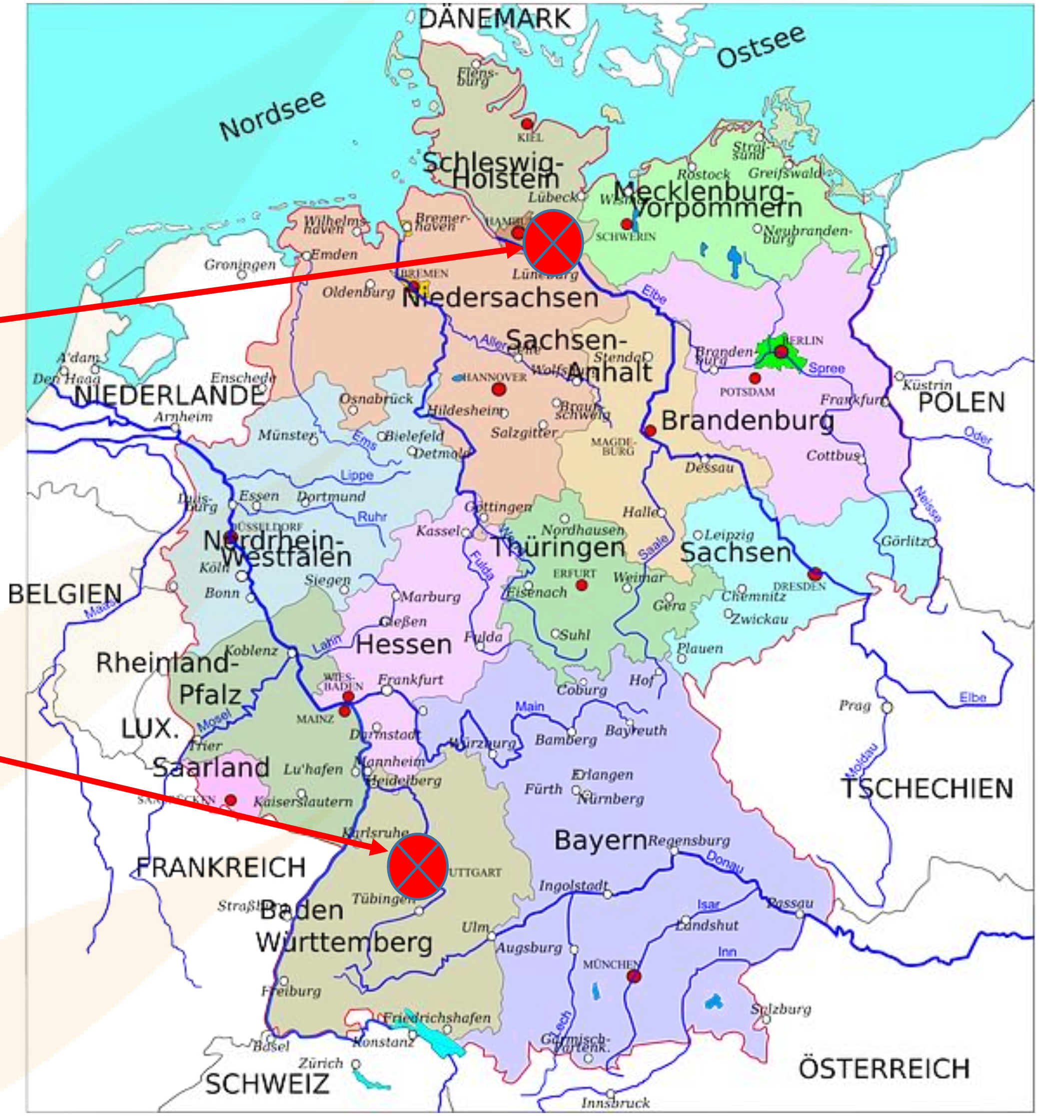
- ✓ Development
- ✓ Production
- ✓ Sales

of atmospheric plasma (AP) units

- ➢ AP Plasma devices for narrow and wide plasma application
- ➢ AP Plasma in different power categories
- ➢ AP Plasma with different temperatures
- ➢ Generators

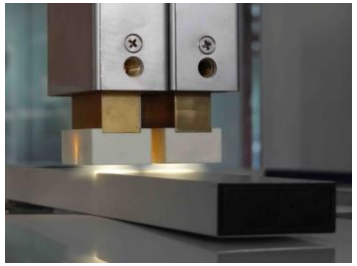
TIGRES GmbH Germany

- Appr. 25 Empolyees
- Main office and production in Marschacht (near Hamburg)
- Sales office near Stuttgart
- Appr. 14 sales agents world wide



Picture from OpenClipart-Vectors auf Pixabay

Plasma for cleaning, adhesion and coating

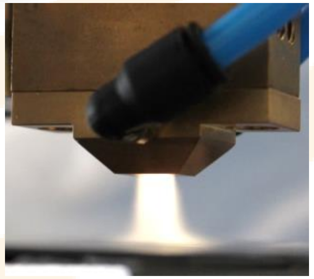


Preparation

„Cleaning“ , partial heating, drying, ionisation, oxidation, reduction

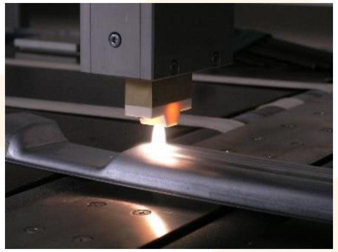
Activation

Improvment of adhesion and wettability



Coating

Plasma polymerisation, thin layers

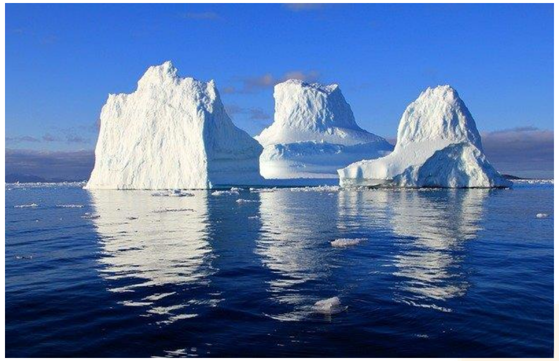


Deburring

Removal of burrs and sharp edges

What is Plasma?

Solid → Melting → **Liquid** → Vaporization → **Gas** → Ionization → **Plasma**



Freezing ← Condensation ← Deionization/Recombination

Energy → Energy → Energy

Plasma is an ionised gas.
More than 99 % of all visible mater in the universe is in the plasma state (Wikipedia).

Plasma for pretreatment

1. Atmospheric plasma

2. Vacuum plasma

Corona "plasma" (DBD)

(gr./lat. for "Crown")

1. T-Jet

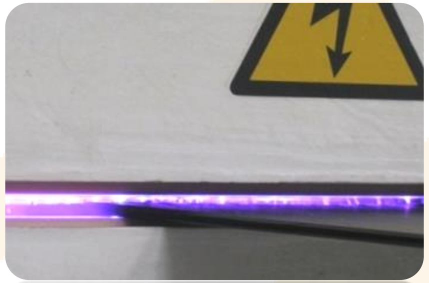
Electrical discharge, laminar air flow,

high voltage up to appr. 15 kV.

2. DBD

Dielectric Barrier Discharge,

High voltage up to appr. 100 kV



3. Free radiating discharge

High voltage up to appr. 100 kV and more

https://commons.wikimedia.org/wiki/File:Plasma_wheel_2_med_DSIR2018.jpg

„Potential free“ Plasma (gr. for “moldable”, “Jelly”)

1. Nozzle plasma
   I. CAT
   II. T-Spot
   III. MEF

Atmospheric Plasma,
vortex air flow,
practical potential free,
if handled correctly!

2. Vacuum plasma

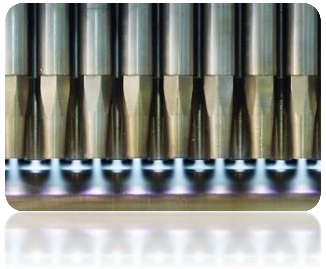
Picture: Plasmatechnology

Potential free

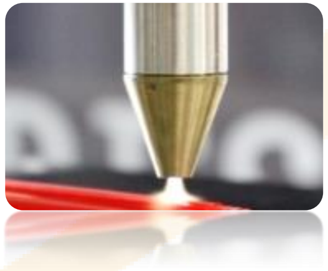
Atmospheric plasma

Forms:

MEF



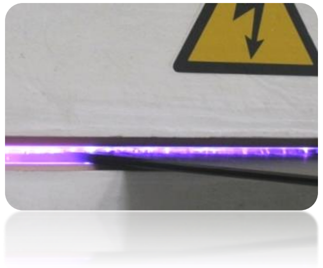
T-Spot



CAT

T-Jet

DBD



Nozzle plasma (Plasma Jet)
(almost potential free)

Dielectric barrier discharge DBD/Corona
(high voltage potential)

Atmospheric plasma

The surface

Dust, dirt, oil etc. >1µm

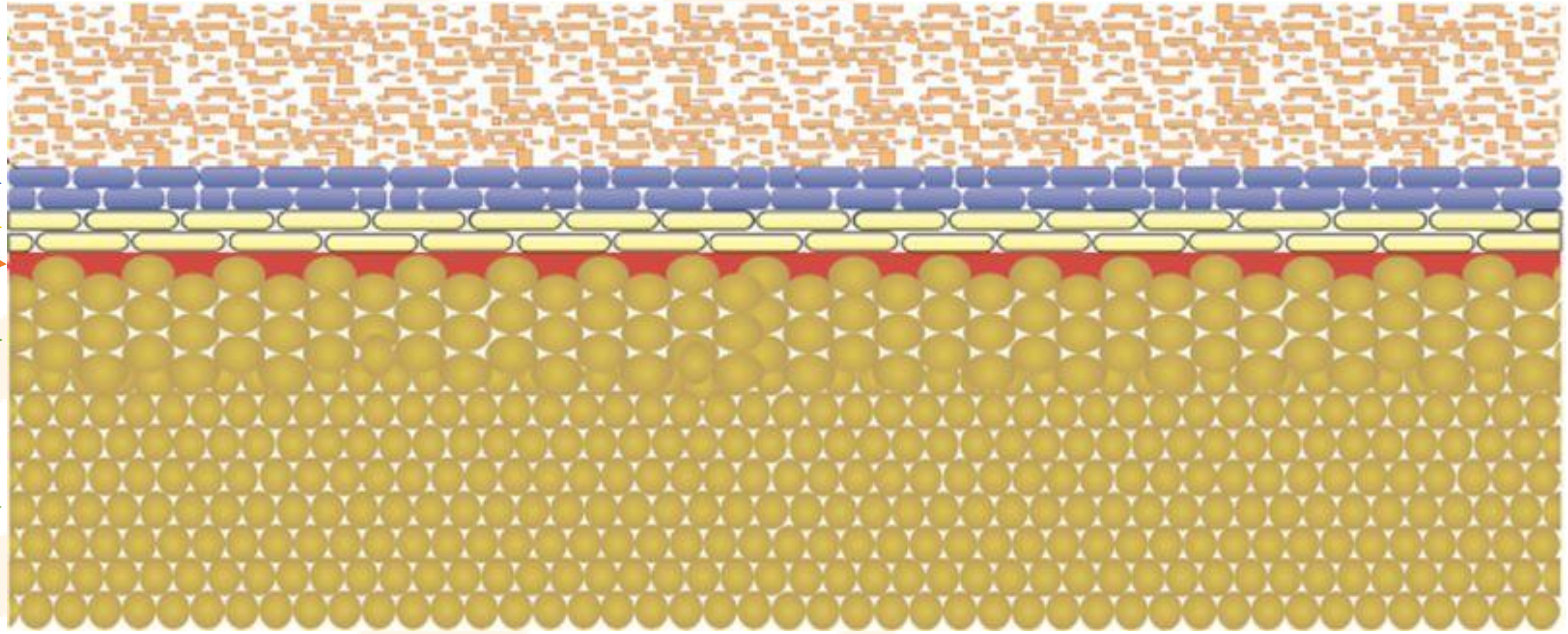
Gases, water 5-10 nm

Oxides, additives 5-10 nm

Boundary surface

High density layer >1 µm

Undisturbed region



Picture: Dipl. Ing. (FH) Simone Fischer

The perfect surface

Dust free

Fat free

Dry

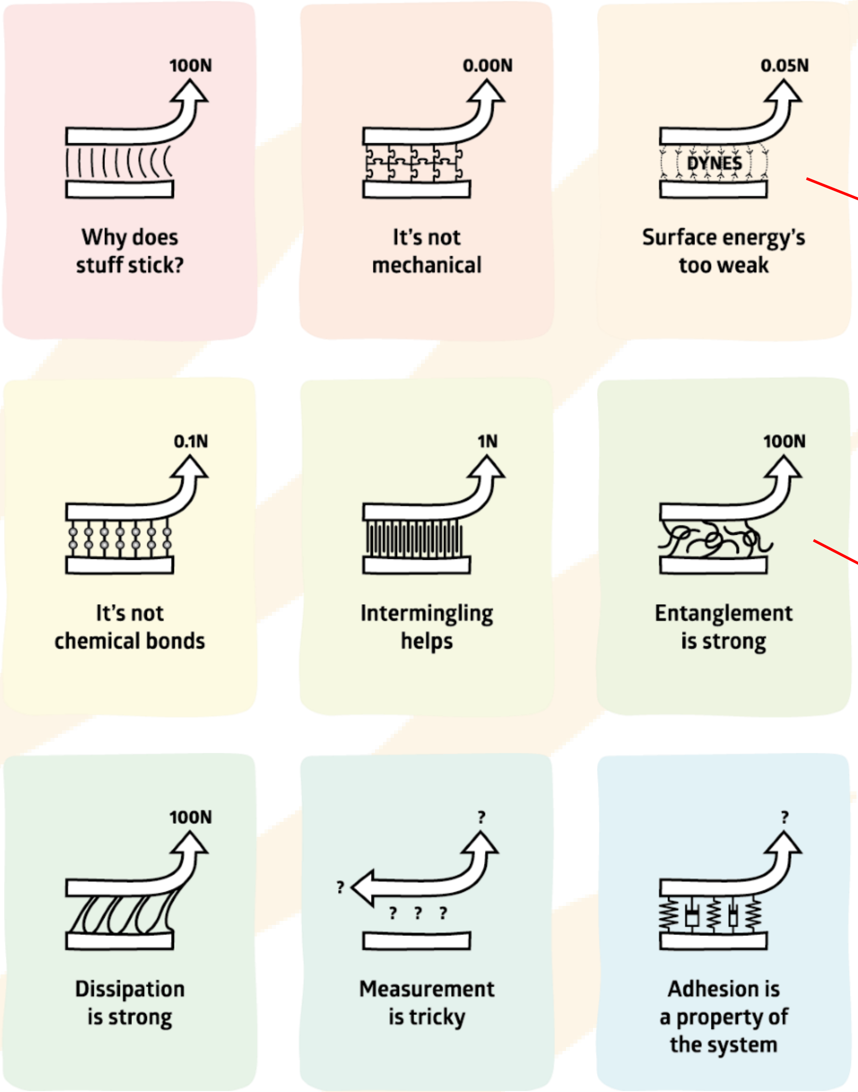
Adhesion theory

Effects multiply each other

1. Primary valency bonds
2. Secondary valency bonds
    1. Van der Waals interactions
    2. Dipol interactions
    3. Induction forces
    4. Dispersion forces
    5. Hydrogen bonds
3. Mechanical clamping
    1. Change of surface from semi-crystalline to amorph, (enables Polymer-Polymer-Interdiffusion)
    2. Electron/ion bombardment
4. Diffusion
    1. PVC with diffusion adhesives
    2. PS with Cyanacrylat
    3. PMMA with UV adhesives
5. Electrostatic forces

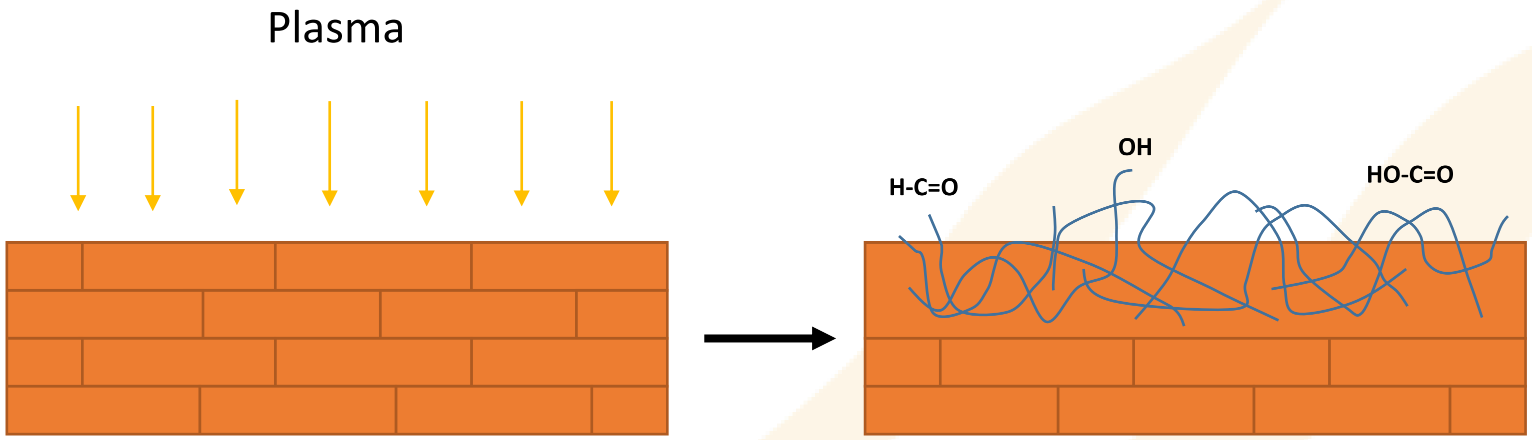
Adhesion: Why does stuff stick?

Prof. Steven Abbott
PhD in Chemistry
https://www.stevenabbott.co.uk/about-prof-steven-abbott.php



https://www.stevenabbott.co.uk/practical-adhesion/

Influence of plasma on crystallinity



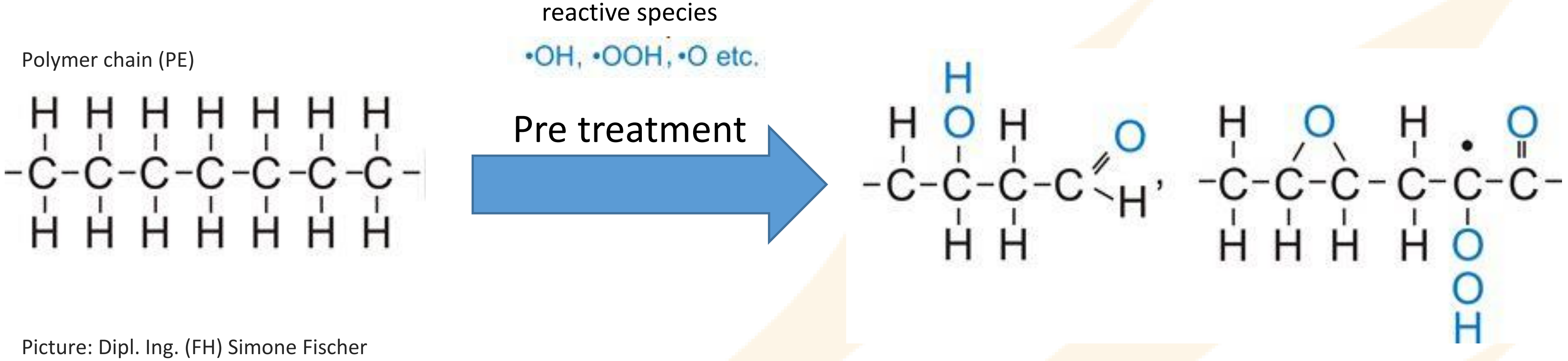
Crystallin/partly crystallin surface

Amorphous surface

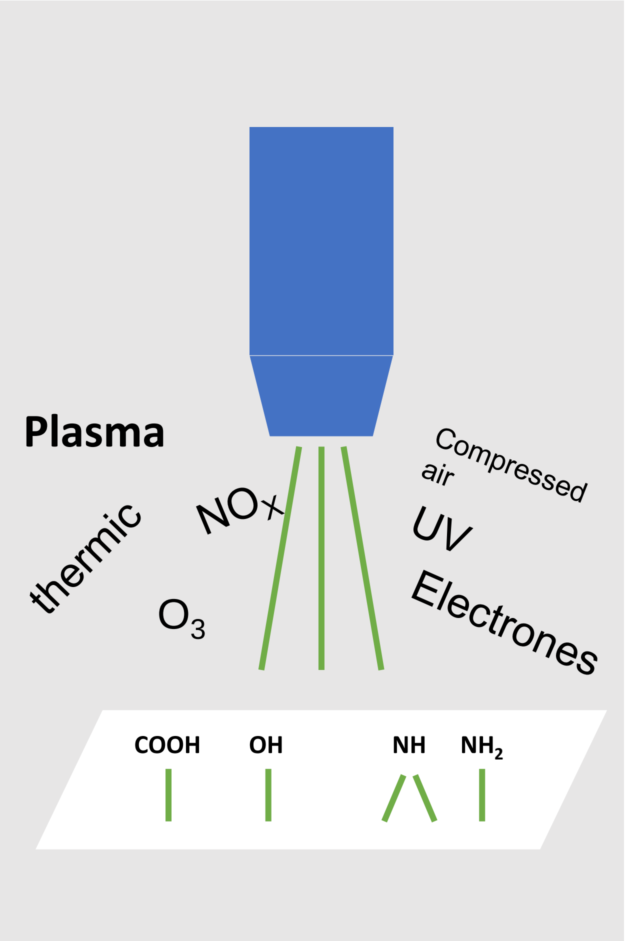
Effect of plasma treatment:
Surface gets more amorphous
Enables intermingling/Entanglement

[Source: https://www.stevenabbott.co.uk/practical-adhesion/entanglement.php](https://www.stevenabbott.co.uk/practical-adhesion/entanglement.php)

Reactions on the surface



Picture: Dipl. Ing. (FH) Simone Fischer



- ➢ Radicals and photons, created by the plasma, break the polymer chains
- ➢ Oxygen and nitrogene is bounded to the polymer chain

⇨ Increase of surface energy of the Polymer

Effect of surface treatment on wettabilty

Influence of surface treatment on the wettablity of polymers

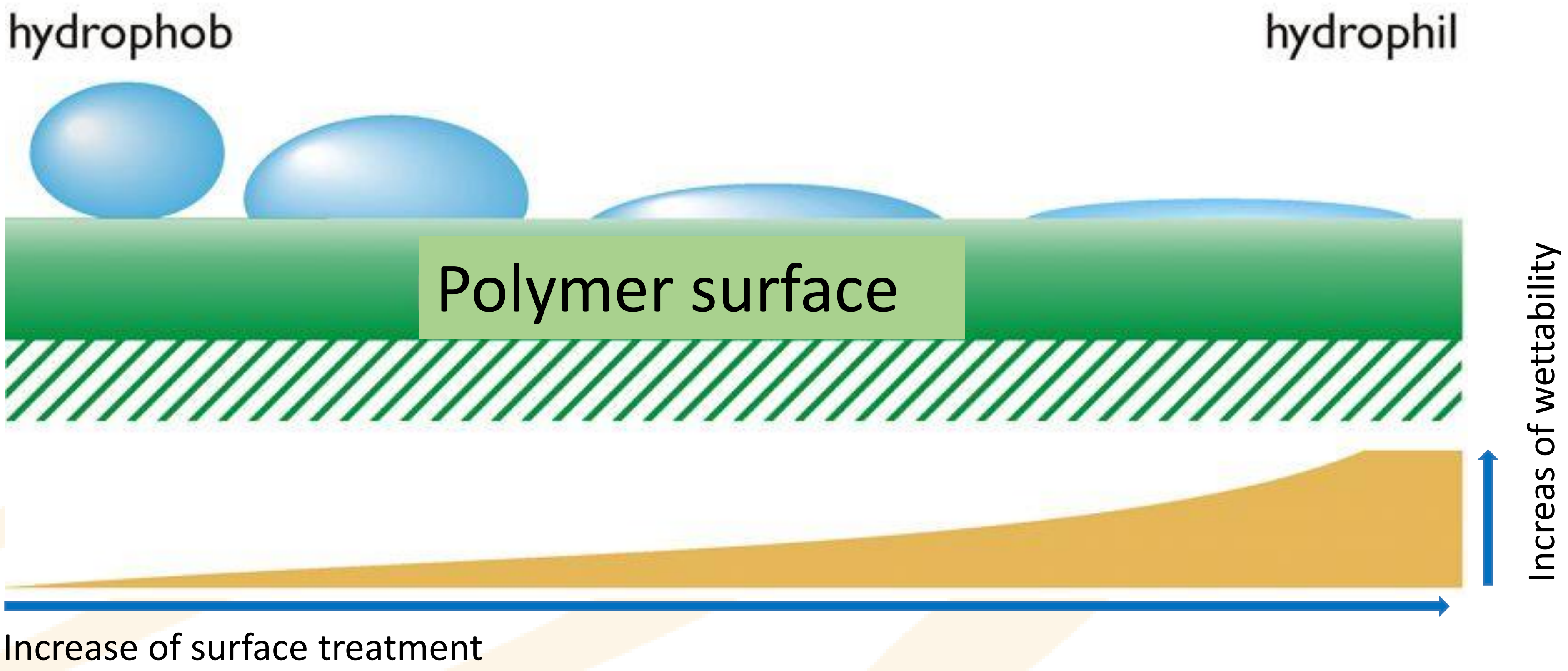
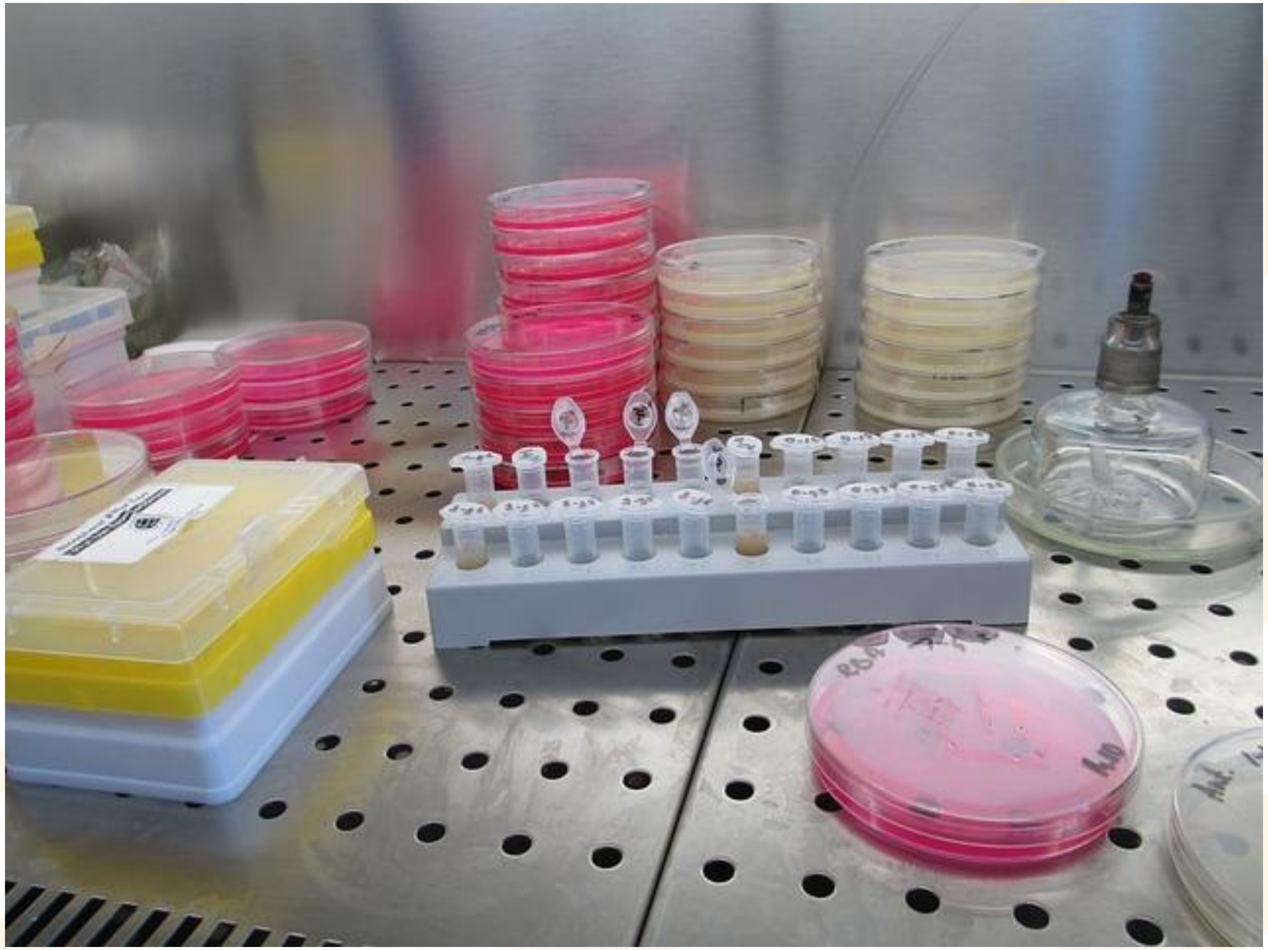


Bild: Dipl. Ing. (FH) Simone Fischer

Application Wettability

Goal: Enabling wettability of cell culture products



Required surface energy: > 72 mN/m

Surface energy and material

Typical surface energy of polymers:		Typical specified surface energy for:	
PTFE	< 18-19 mN/m	UV-Ink	Appr. 48 – 56 mN/m
Silicone	< 20 mN/m	Water based ink	Appr. 50 – 56 mN/m
PP	Appr. 29-31 mN/m	Coatings	Appr. 46 – 52 mN/m
PE	Appr. 30-32 mN/m	UV-glue	Appr. 44 – 50 mN/m
PS	Appr. 34-38 mN/m	Water based glue	Appr. 48 – 56 mN/m
PC	Appr. 35-44 mN/m	Solvent based glue	Appr. 38 mN/m
PUR	Appr. 43-47 mN/m		

Application Wettability

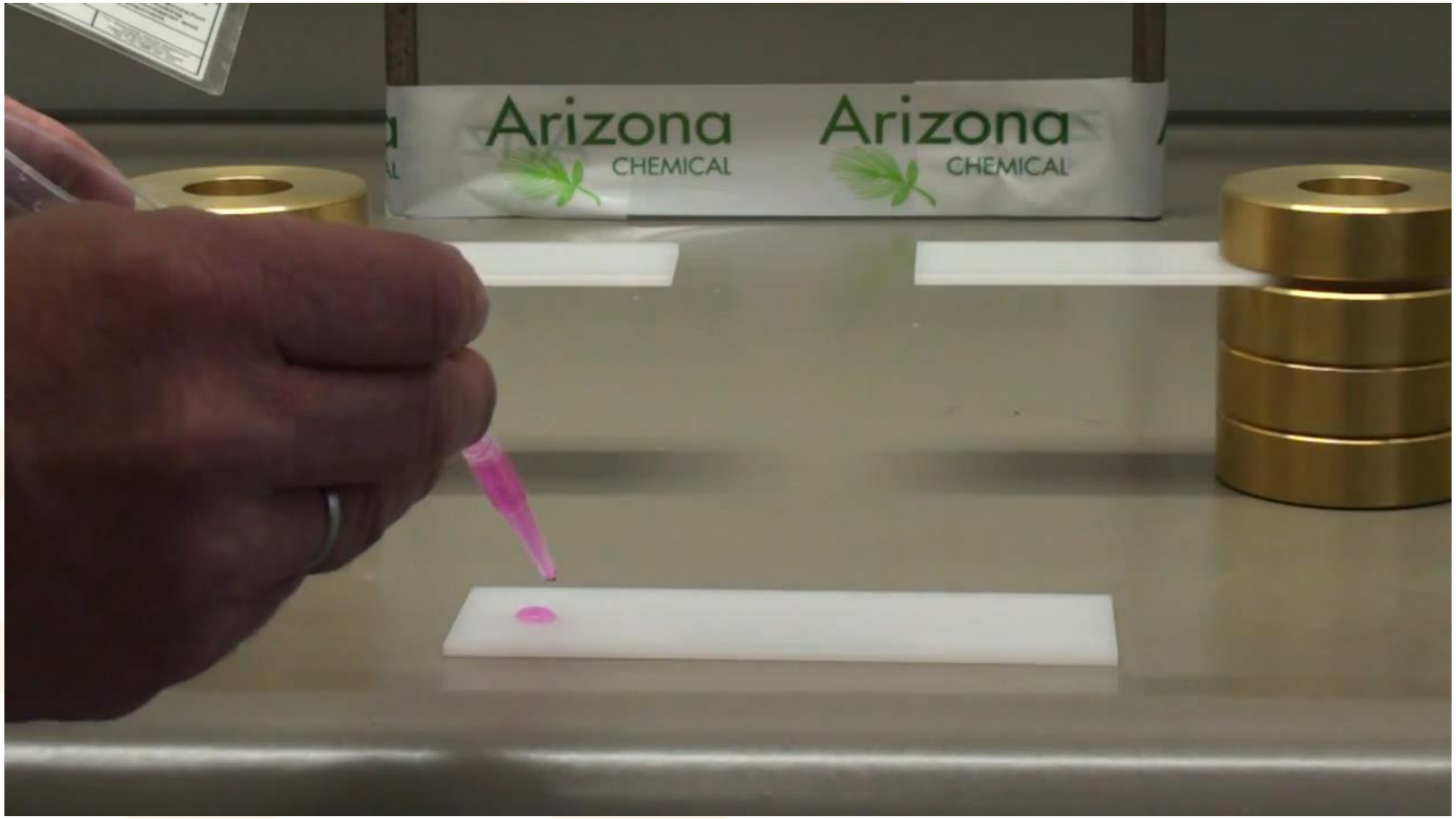
Goal:
Good readability of inkjet print
(and adhesion)

Requirement:
Good wettability

Wettability myths

Prof. Steven Abbott
PhD in Chemistry
https://www.stevenabbott.co.uk/about-prof-steven-abbott.php

HDPE and water



Video: Red Herring, **https://www.youtube.com/watch?v=XXIGb6XFELY**

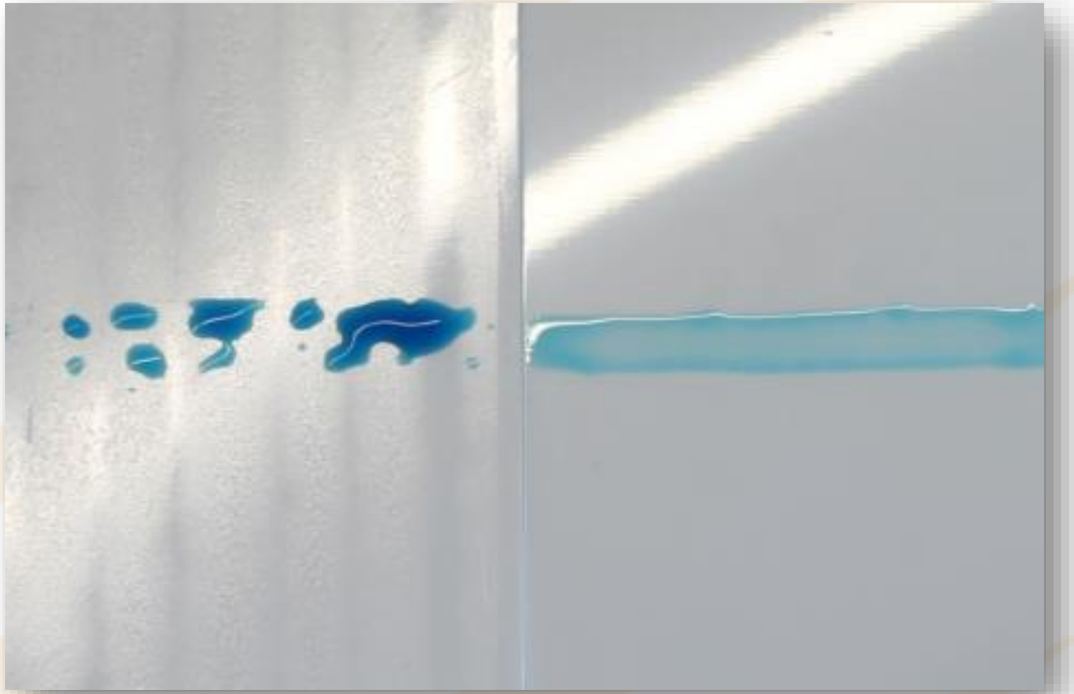
Test inks for measurement of surface energy

Definition:

- ➢ Measurement is done in mN/m. In the past it was also refered to as „Dyne“
- ➢ ISO 8296: The film of the test ink has to have a sharp edge for 2-3 sek. or more
- ➢ ISO 8296 is defined for PE film
- ➢ Lifetime is 3 months according to the ISO 8296. More details in separat test ink slides.
- ➢ Test ink shop

Wettability of surface

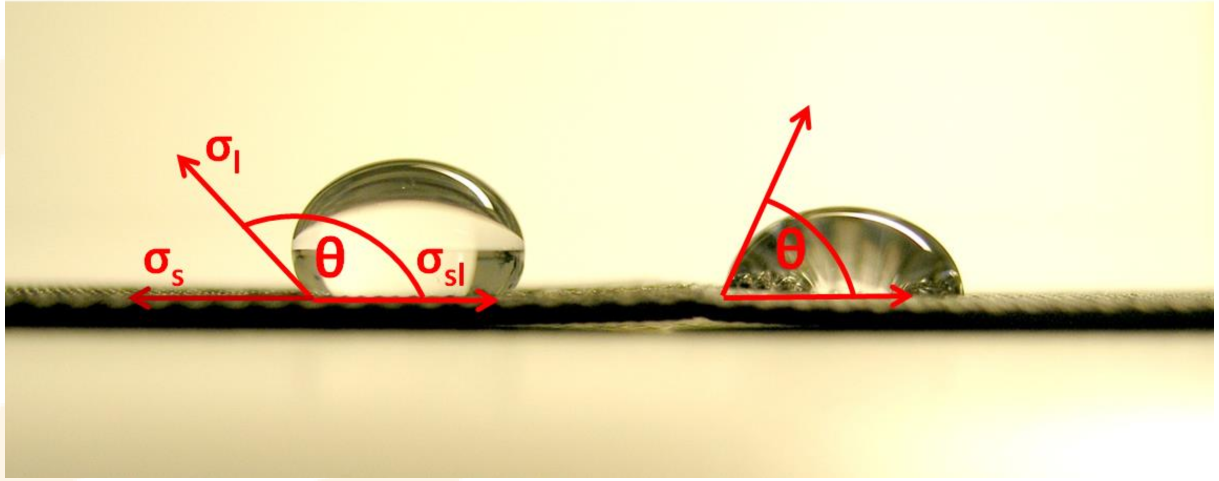
Low surface energy
Test ink stay for less than 2-3 sek.



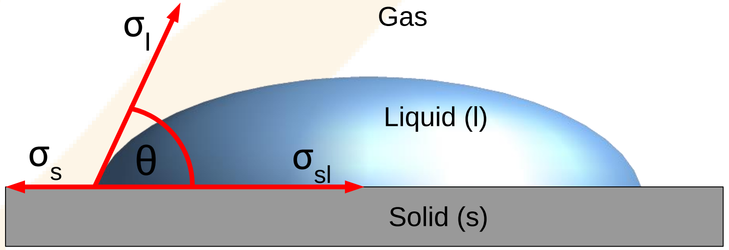
High surface energy
Test ink stay for 2-3 sek. or longer

Measurement of surface energy

- The contact angle can be measured very exactly with a contact angle meter
- It is possible to measure polar and disperse parts
- The polar part shows the polar interaction of dipols in the surface (oxygen)



Picture: Krüss, www.mobile-surface-analyzer.com



Young's equitation: $\cos \theta = (\sigma_s - \sigma_{sl}) / \sigma_l$

Simplification : $\sigma_s - \sigma_{sl} = \sigma_c$ = "critical surface energy"

σ_l : surface free tension of the liquid

σ_s : surface free energy of the solid

σ_{ls} : interfacial free energy solid/liquid

θ : contact angle

What wettability really measures...

Adhesion is influenced by:	Measurable by test ink:
ADHESION:	
Primary valency bonds	No
Secondary valency bonds	**Yes**
Electrostatic forces	No
Diffusion	No
Mechanical clamping	No
COHESION:	
Orientation of boundary layer	No
Strength and deformability of adherent layer	No
TESTING TECHNIQUE:	
Tension distribution in sample	No

Conclusion wettability:

A good wettability is often required, but not a sufficiend necessity for good adhesion

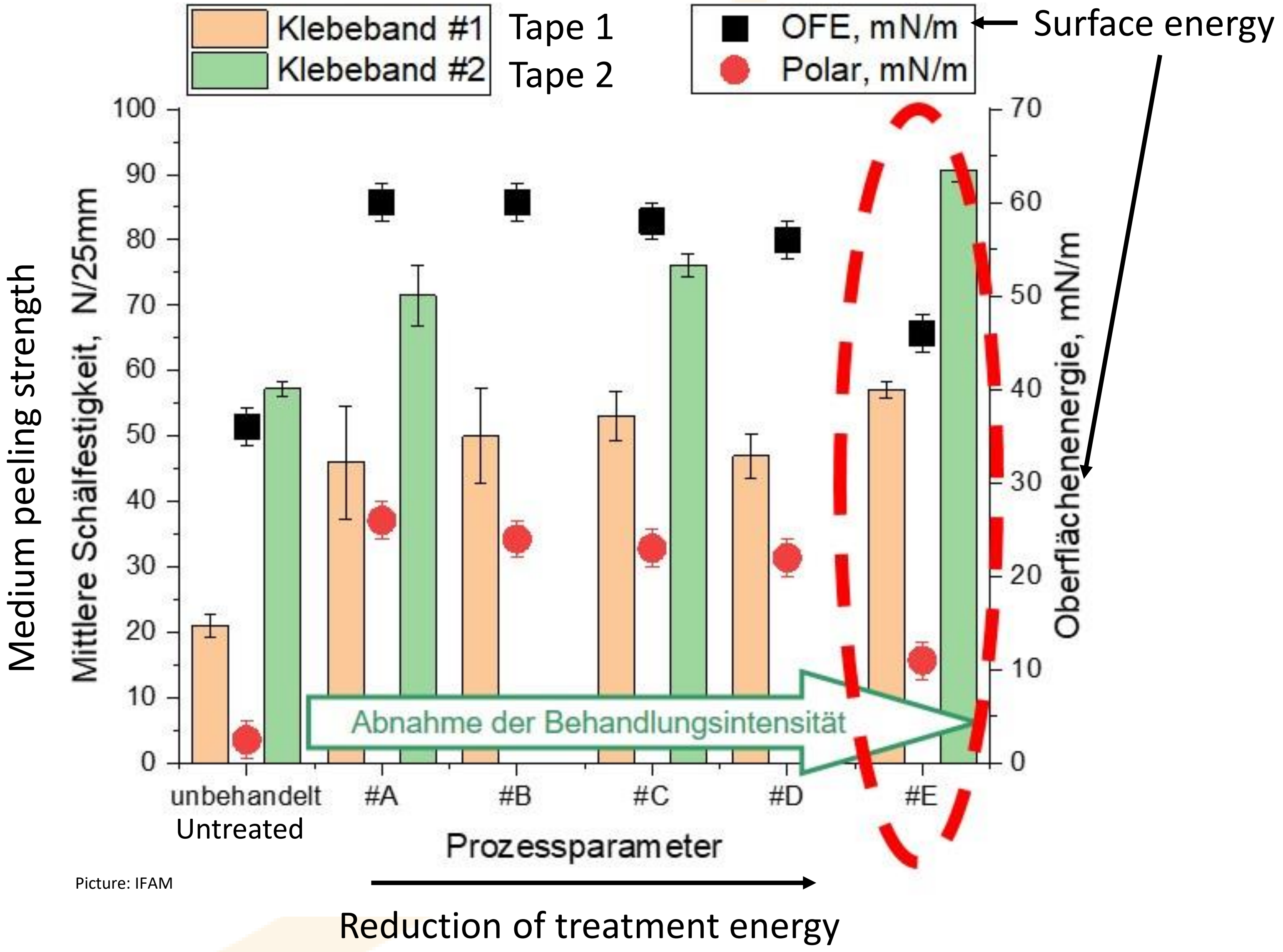
What wettability (doesn´t) show

Read more (german only): https://www.plastverarbeiter.de/106103/wie-lange-sind-plasmaaktivierte-polymeroberflaechen-offen/

„However, within the scope of the tests carried out, no, often postulated, simple correlation between the surface energy and adhesion of the adhesives or strength of the resulting adhesive bonds could be determined.“

PDF of Fraunhofer IFAM: https://www.ifam.fraunhofer.de/content/dam/ifam/de/documents/Klebtechnik_Oberflaechen/PLATO/plastverarbeiter-2020-beitrag-fraunhofer-ifam.PDF

Material: Varnish



Picture: IFAM

Insufficient treatment

Problem:

After treatment, wettability is high, but sufficient adhesion has not been achieved yet

Example:

PP has to be glued

50 W/m²/min of plasma energy is applied (DBD)

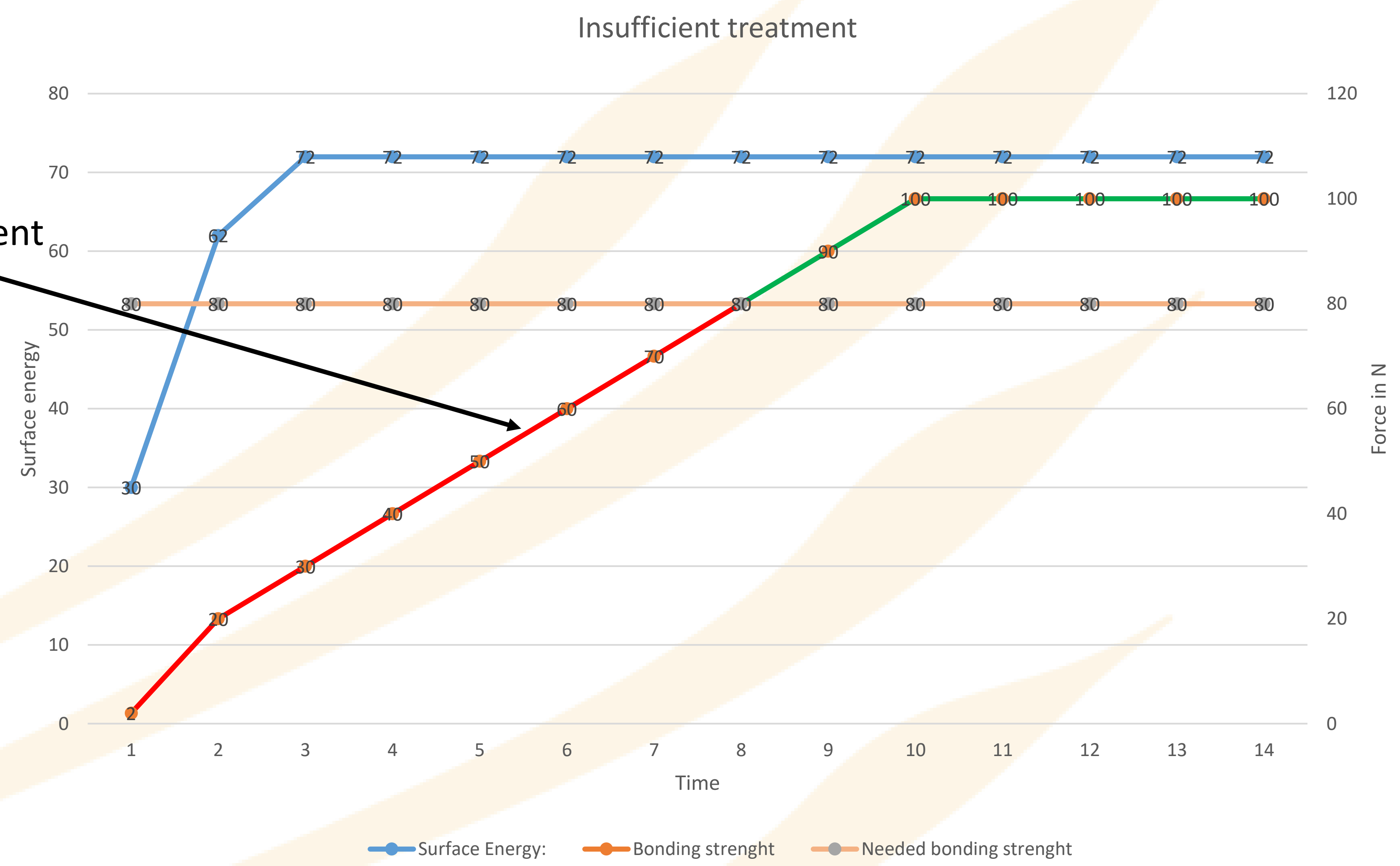
High wettability (>72 mN/m), but no sufficient adhesion

400 W/m²/min of plasma energy is applied (DBD)

High wettability (>72 mN/m), sufficient adhesion

Insufficient treatment

Insufficiend treatment



Over treatment

Problem:

After treatment, adhesion is weak, although a very high surface energy has been achieved

Example:

PVC film has to be glued

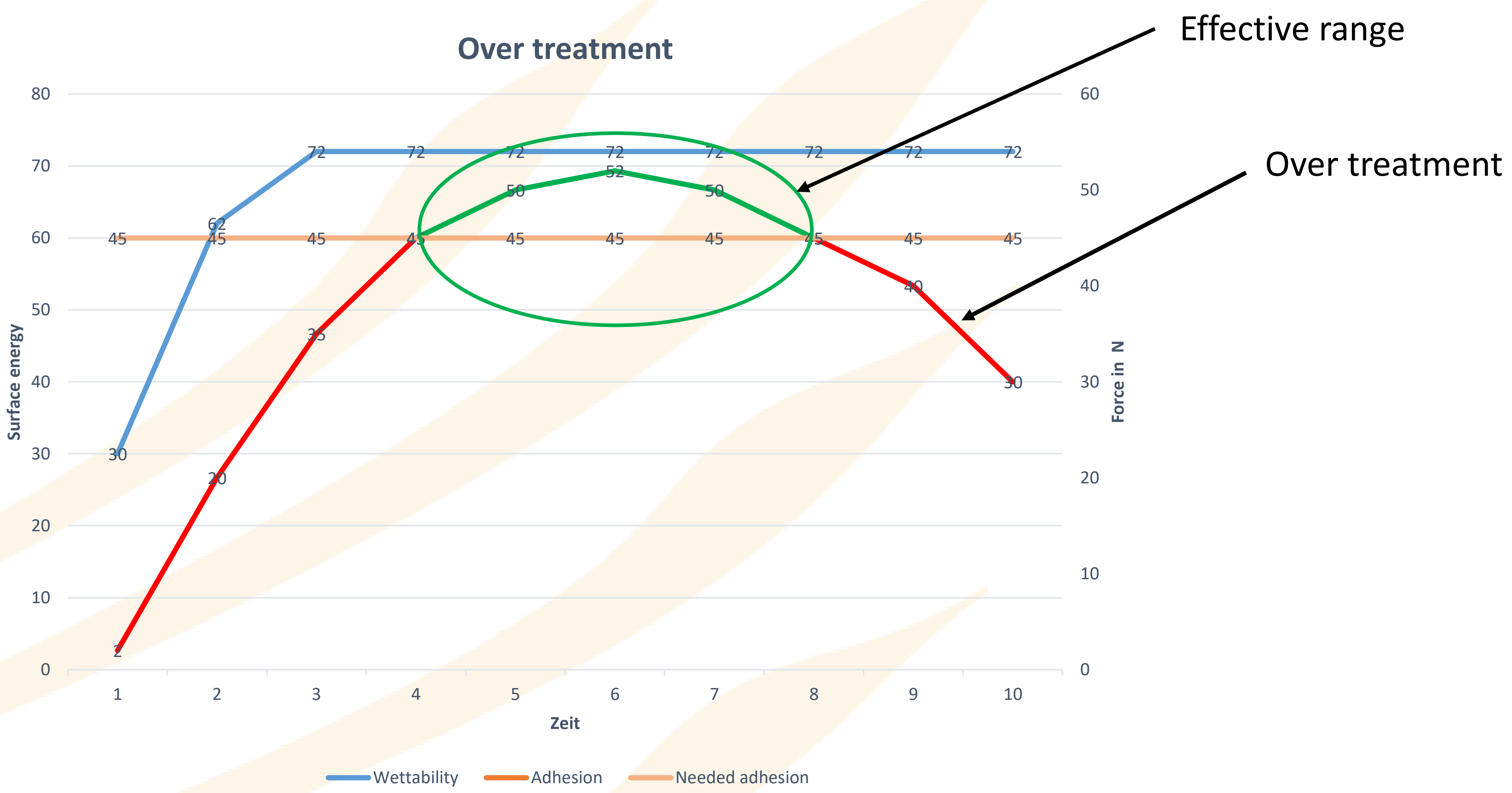
10 W/m²/min of plasma energy is applied (DBD)

High wettability (>72 mN/m), but no sufficient adhesion

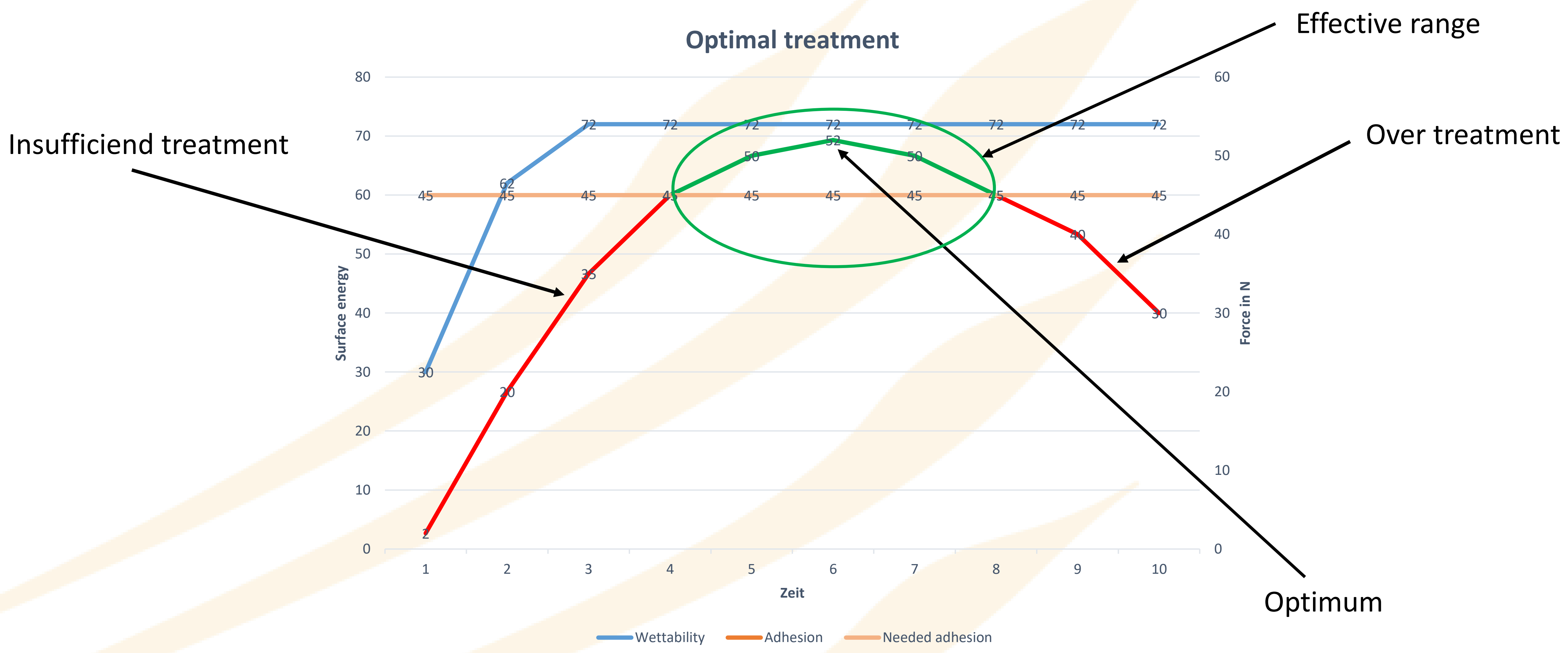
2 W/m²/min of plasma energy is applied (DBD)

High wettability (>72 mN/m), sufficient adhesion

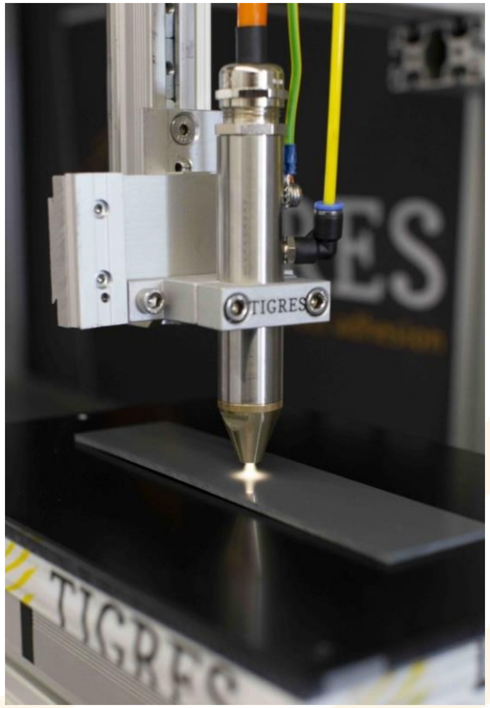
Over treatment



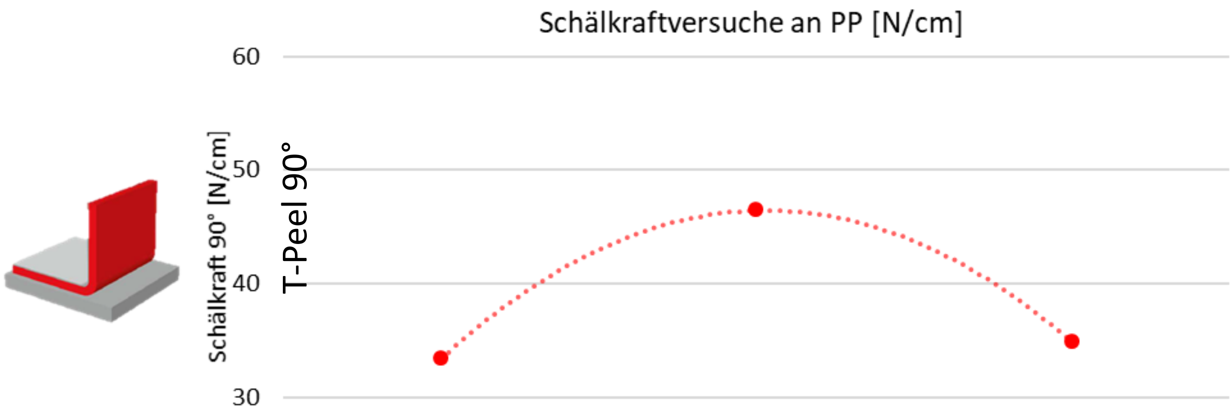
Optimising plasma: Finding the perfect plasma dose



Effect of plasma dose on adhesion



Peel test on PP (N/cm)



Power setting:

Leistungseinstellung [W]	250	375	500
● Schälkraft [N/cm]	33,4	46,4	34,8

Peeling power (N/cm)

Speed: 20 m/min
Tape: tesa ACX^{Plus}

Over treatment

What happens when you over treat?

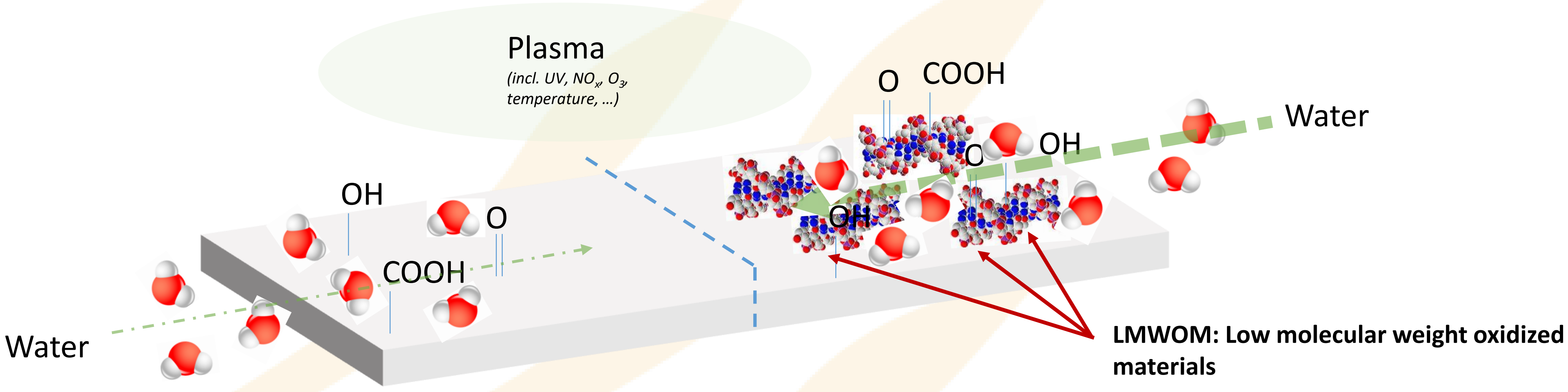


Bild: tesa SE

State 1:

Activation & Hydrophilisation

State 2:

Over treatment creates Polymer-Debris

Over treatment leads to high surface tension, but creates also:

- water solvent debris (→ allows moist to penetrate in boundry layer – leads to weak boundry layer
- Degradation of surface

Overtreatment: Example tesa-tape

Used materials: PP GF30 and tesa ACX® 7076

Used plasma technic: T-Jet Corona

Type of break:
(A) Adhesive break
(M) Mixed break
(C) Cohesive break

Number of treatments	Cleaning	T-Peel [N/cm] after 3d/RT	Surface energy [mN/m]	T-Peel [N/cm] after 240h 40° C/100% rel. H - immediatelly	T-Peel [N/cm] after 240h 40° C/100% rel. H - reconditioned
1 x	tesa cleaner	40,9 (C)	44	32,1 (M)	39,4 (C)
3 x	tesa cleaner	42,2 (C)	48	8,9 (A)	19,5 (A)

Picture: tesa SE

Tapes are very sensitive to overtreatment!

Finding the perfect plasma dose

TIGRES
Plasma for perfect adhesion

How to optimise plasma treatment?

Possibilities to influence the plasma dose:

☹ **Adjust distance of nozzle to surface**

Cons:

1. Normaly very smal process window of a few mm
2. Unpractical for different power levels with fixed nozzles

😐 **Change of treatment speed of nozzles or material**

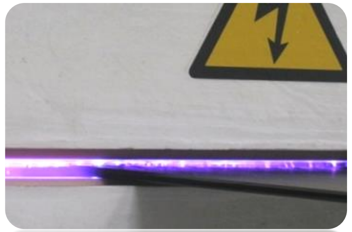
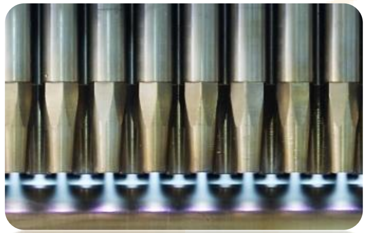
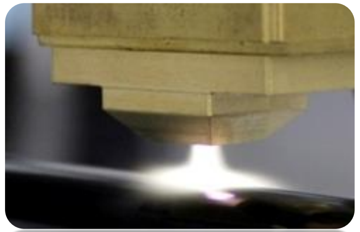
Cons:

1. Only possible, if process speed can be achieved (f.e. to fast or to slow)
2. Difficult in some productions (f. e. extrusion)

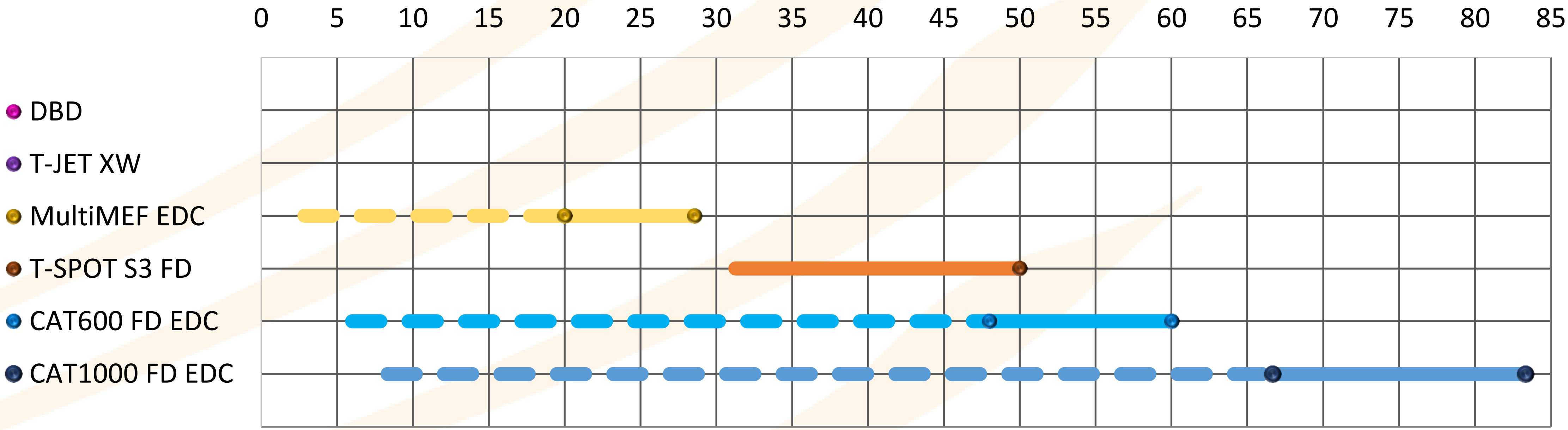
☺ **Power adjustment via generator**

Advantage: Can be adjusted directly in generator according to the need, if process windows is suitable.
Can be adjusted on the fly, online. Also also via I/O and BUS.

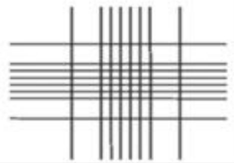
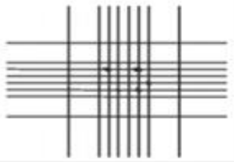
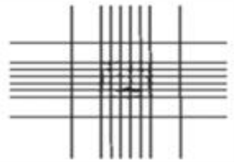
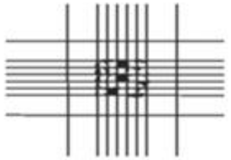
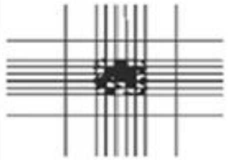
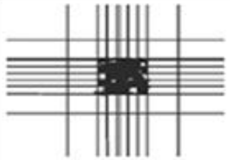
Plasma tools, power ratio

DBD	T-JET	MultiMEF	T-SPOT	CAT
				
1 W / 1 mm	600 W / 70 mm	200 W / 7 mm	250 – 500 W / 10 mm	600 o. 1000 W / 12 mm
1 W/mm	8,5 W/mm	28,6 W/mm	25 – 50 W/mm	50 o. 83 W/mm

Powersetting approx. (W/mm)



The correct plasma dose determines the success of the adhesion!

Cross-cut	According to DIN EN ISO 2409
	0: The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
	1: Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5 % is affected.
	2: The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5 %, but not greater than 15 % is affected.
	3: The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15 % but not greater than 35 % is affected.
	4: The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 65 % is affected.
	5: Any degree of flaking that cannot even be classified by classification 4.

Picture: Thierry Präzisionslackiertechnik GmbH Cross hatch cutter

Conclusion

- ✓ A good wettability is often required, but not a sufficiend necessity for good adhesion
- ✓ For optimal test results, a test series with different power settings is useful to find the optimal plasma dose
- ✓ Power adjusable plasma generators enable an optimal plasma dose

<u>Proof of adhesion of application is necessary!</u>

Questions so far?

The surface: Contamination

Typical contamination of the surface:

- Oil
- Grease
- Additives
- Finger prints
- Slip additives
- Release agents
- Oxydes
- Dust

Cleaning with plasma

Oxidation processes:

-Oxidation of <u>organic</u> material into vapour, CO_2 and organic particles

$(-CH_2 - CH_2-)_n + 3nO_2 \rightarrow 2nCO_2 + 2nH_2O$

Kinetic energy:

-Acceleraction of particles (+100 eV) removes particles

?

True, but partial

Thermal/kinetic energy:

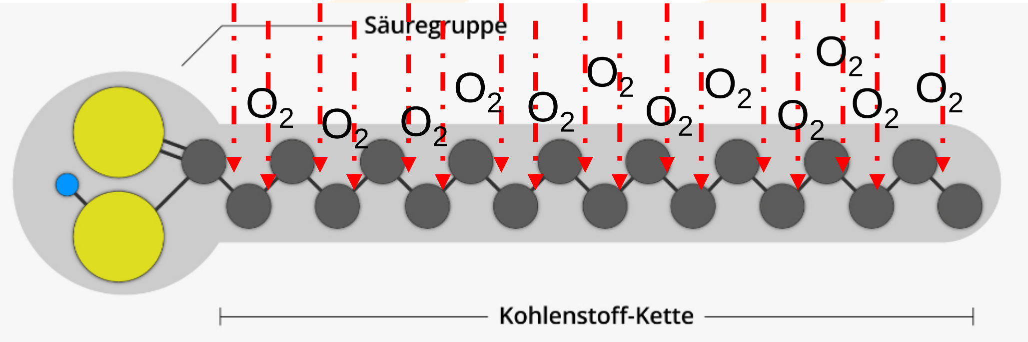
-High plasma temperature and air pressure has cleaning effects

Effect of plasma on contamination

Cleaning Contamination: [g/m²]	Fine cleaning Contamination: [mg/m² - µg/m²]	Ultra-fine cleaning Contamination: [ng/m² - Molekules]

1 g/m²≈ 1 µ Layer thickness
> 6.600 Layers of molecules!

Molecule fragmentation with plasma



→ $xCO_2 + yH_2O$

Size comparison for a carbon single bond: 0,15 nm

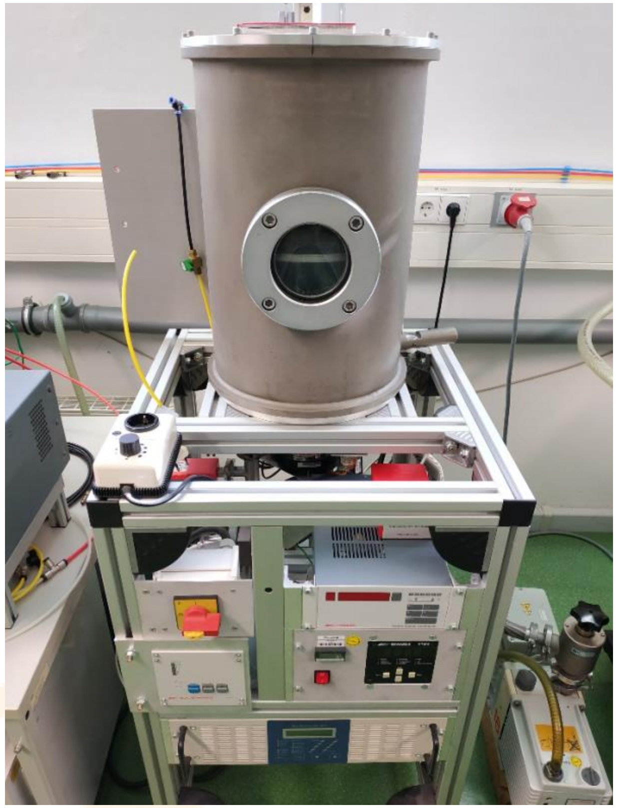
Pictures: tesa SE

Cleaning possible, but entire removal of contamination with atmospheric plasma unlikly

The surface: Cleaning with plasma

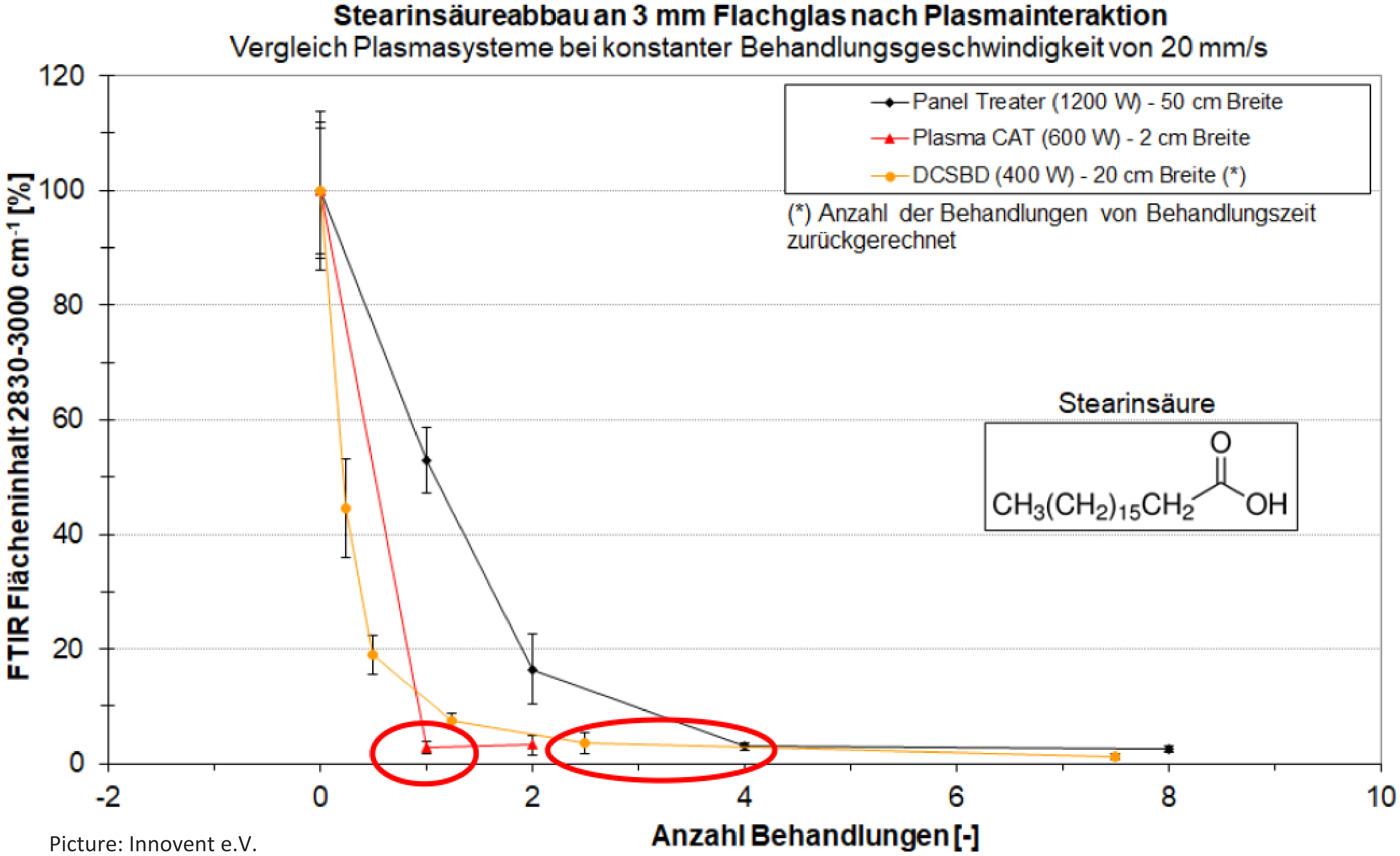
FTIR Spektroskopie

Contamination stearic acid app. 100 nm



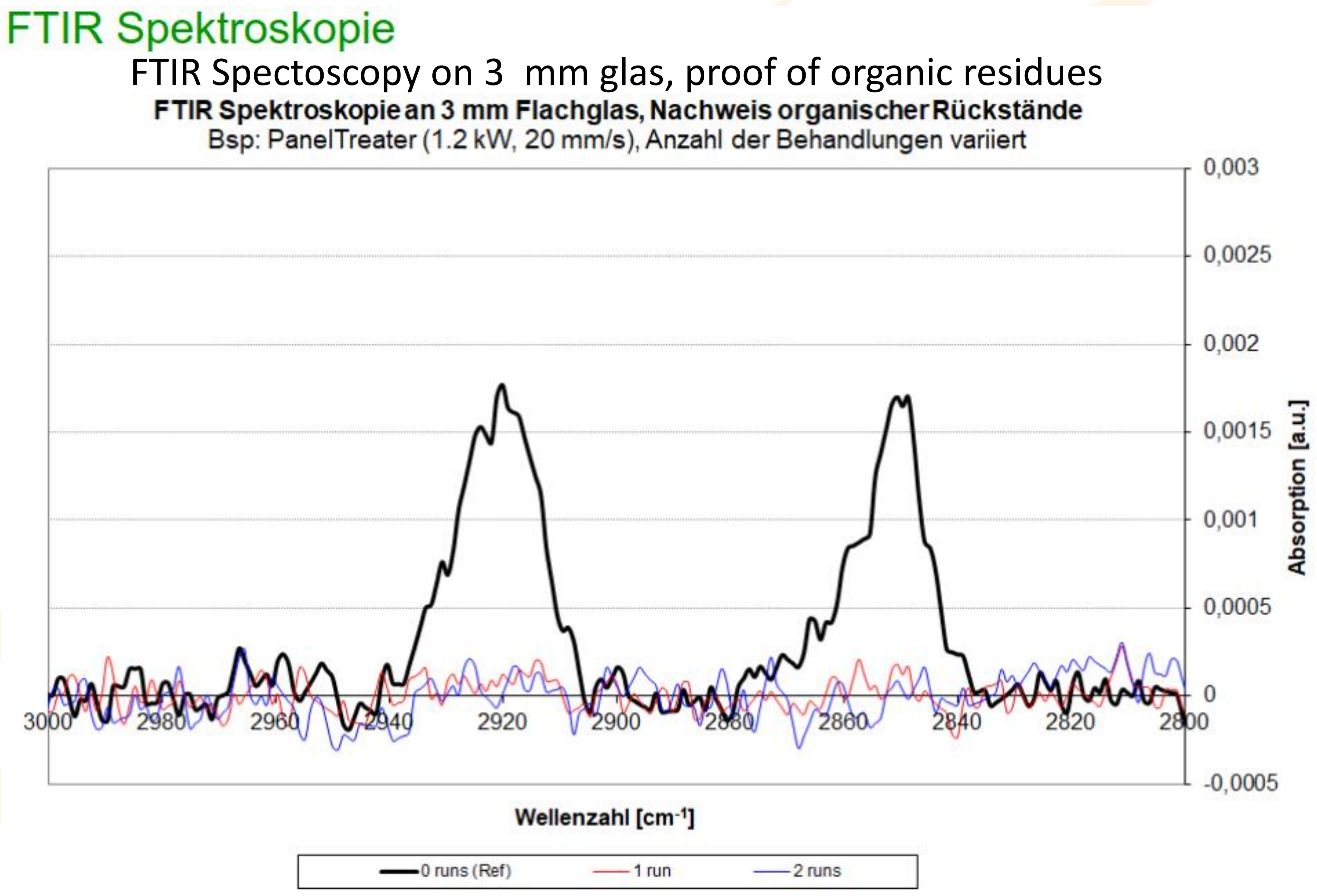
Picture: Innovent e.V., Dr. Oliver Beier

Reduction of stearic acid on 3 mm glas after plasma at 20 mm/s



Picture: Innovent e.V.

The surface: Cleaning with plasma

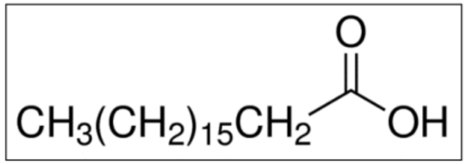


FTIR Spectoscopy on 3 mm glas, proof of organic residues

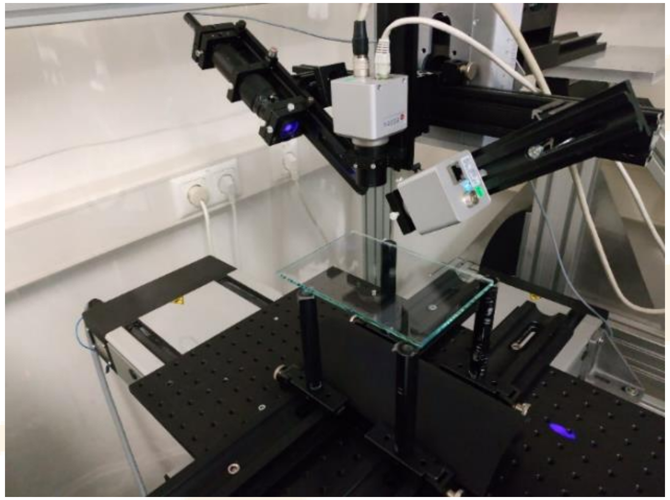
Picture: Innovent e.V.

The surface: Cleaning vs. plasma treatment

Cleaning of von Stearic acid



Laser scanning



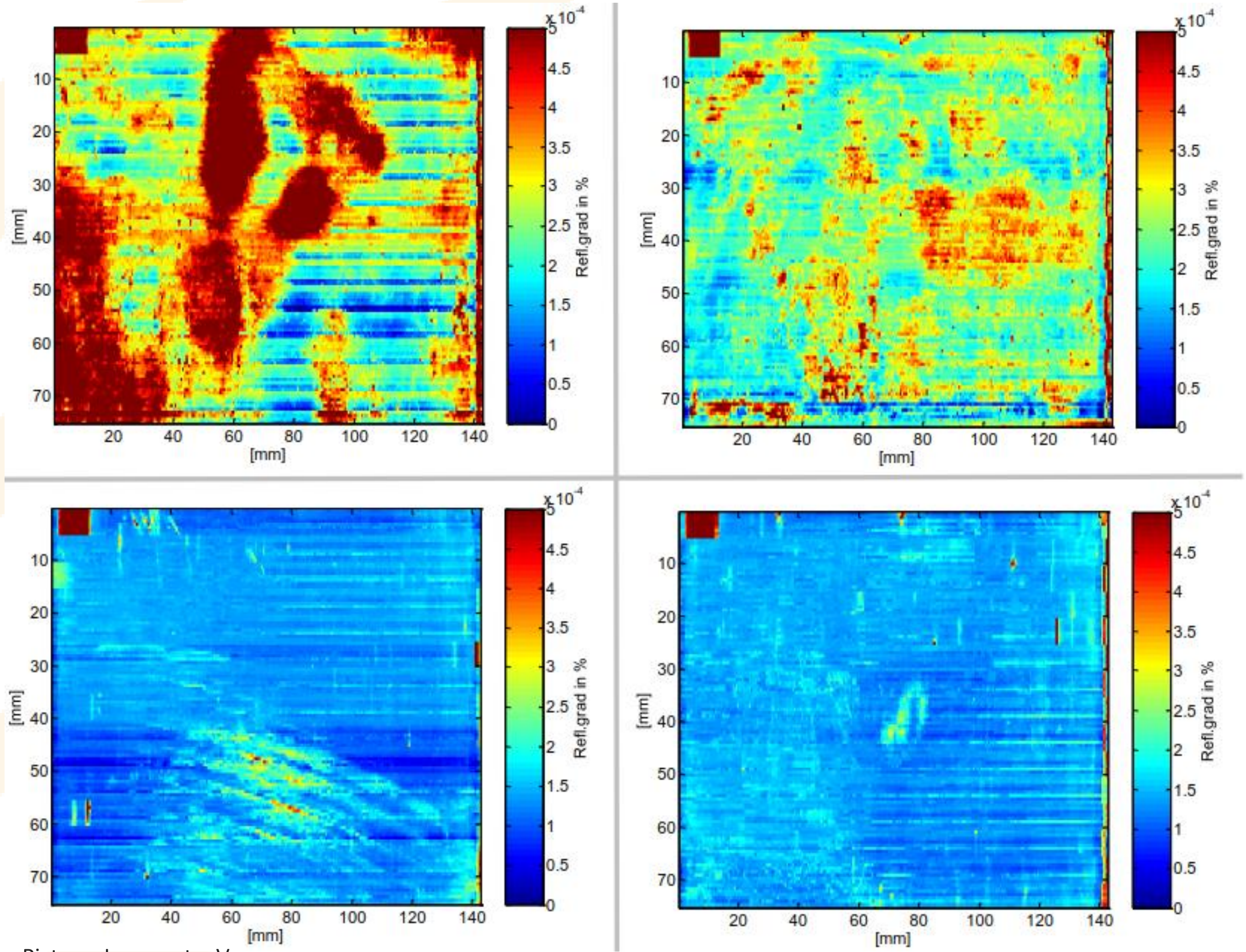
Pictures: Innovent e.V.

Before plasma

After Plasma (400 W, 10 sek)

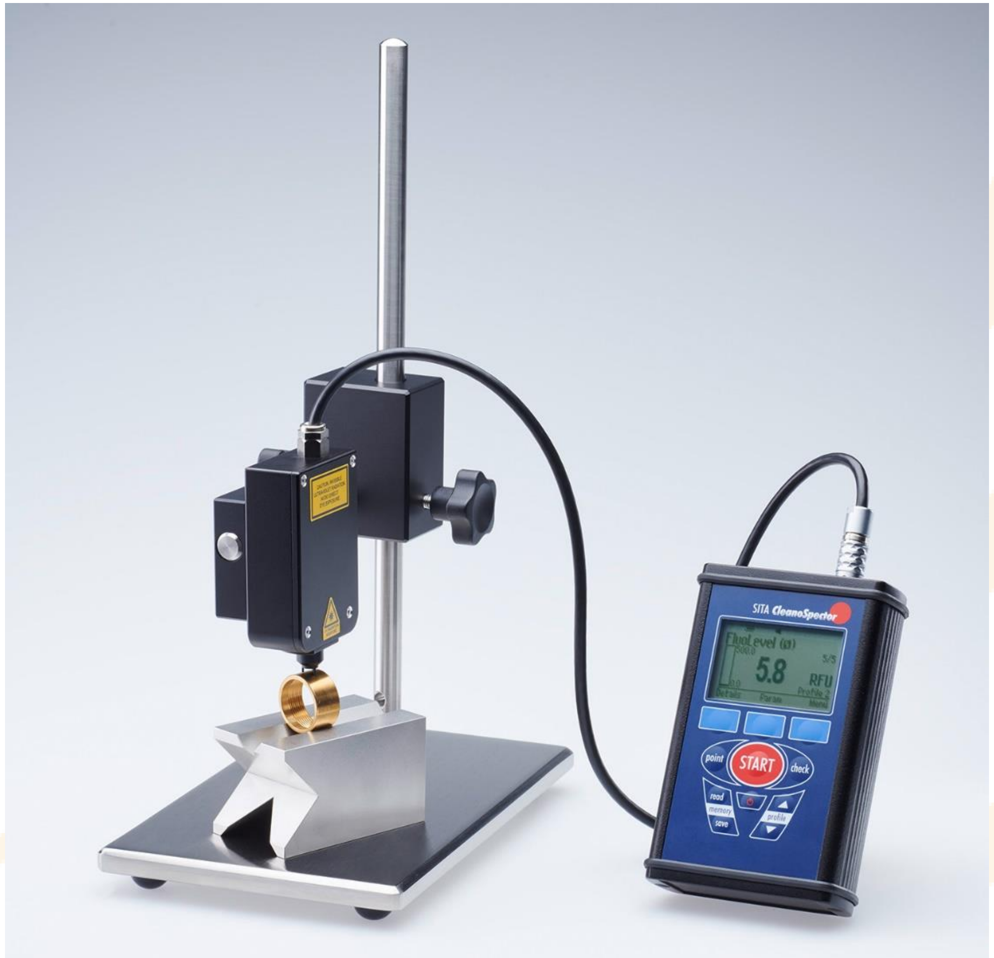
Float glas uncleaned

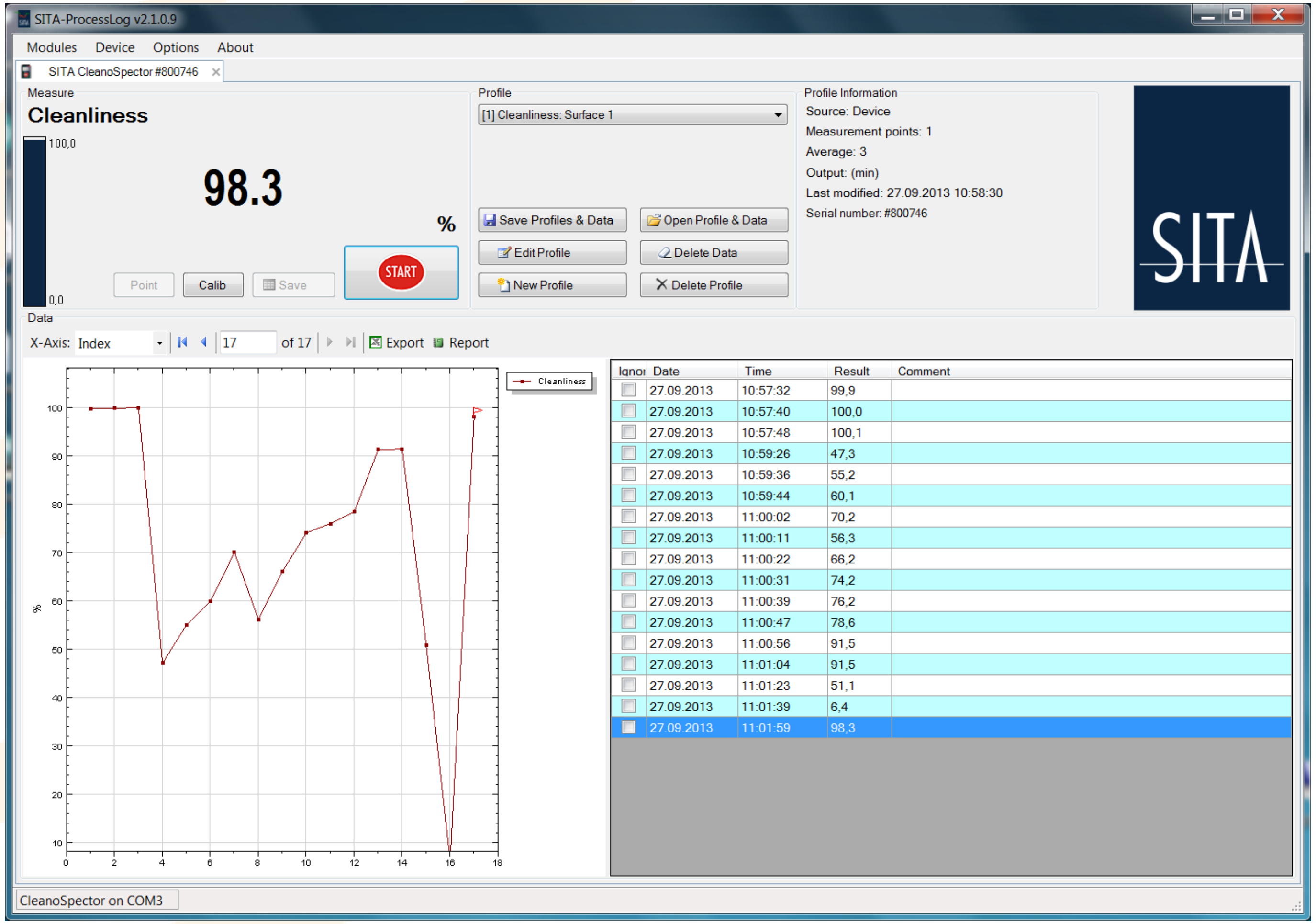
Float glas cleaned



Picture: Innovent e.V.

The surface: Measurement of organic contamination





Picture: https://www.sita-process.com/produkte/fluoreszenzmesstechnik/sita-cleanospector/

The surface: Cleaned vs. contaminated

Polypropylen cleaned	Polypropylen contaminated

Plasma & bonding with tape ACX^{plus} 7812

Break: cohesive	Break: adhesive

Pictures: tesa SE

Can surface energy predict bonding?

The surface: Cleaned vs. contaminated

Condition	**Surface energy** [mN/m]	**Bonding f. T-Peel 90°** [N/cm]	**Break type**
Polypropylen cleaned [with Isopropanol]	30	12	A[100%]
Polypropylen cleaned & plasma treated	→ 44	→ **78**	K[100%]
Polypropylen contaminated [Silikone system PDMS – 1h block storage 40°C]	< 30	5	A[100%]
Polypropylen contaminated & Plasma treated	→ > 48	→ 9	A[100%]
Plasma: TIGRES T-SPOT S2: v = 40 m/min, d = 5 mm, PWR = 60 % r = 6 mm Break type: Adhesion break [A], Mixed break [M], cohesion break [K] Measurement: T-Peel 90°, 300 mm/min, Delay 3d			

Adhesion force doesn´t correlate with surface energy!

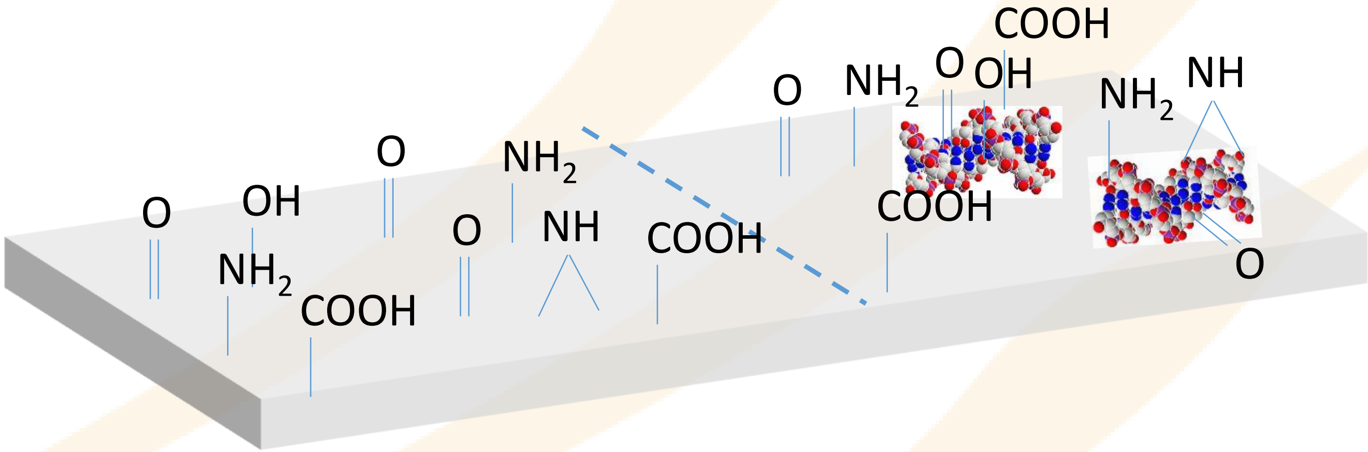
Contaminations can not be safely identified with surface energy values!

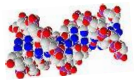
Bilder: tesa SE

The surface: Cleaned vs. contaminated

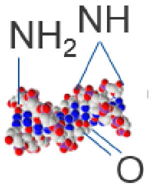
Surface free of contamination

Surface with contamination





= Contamination, org. molecule



Pictures: tesa SE

Clean surfaces are functionalised with plasma

Also Contaminations are functionalisied and show high surface energies.

This doesn´t show a good adhesion or cleaning of the contaminated surface.

Surface analytics

If plasma does not clean the surface fully, why is it used?

The surface: Cleaned vs. contaminated

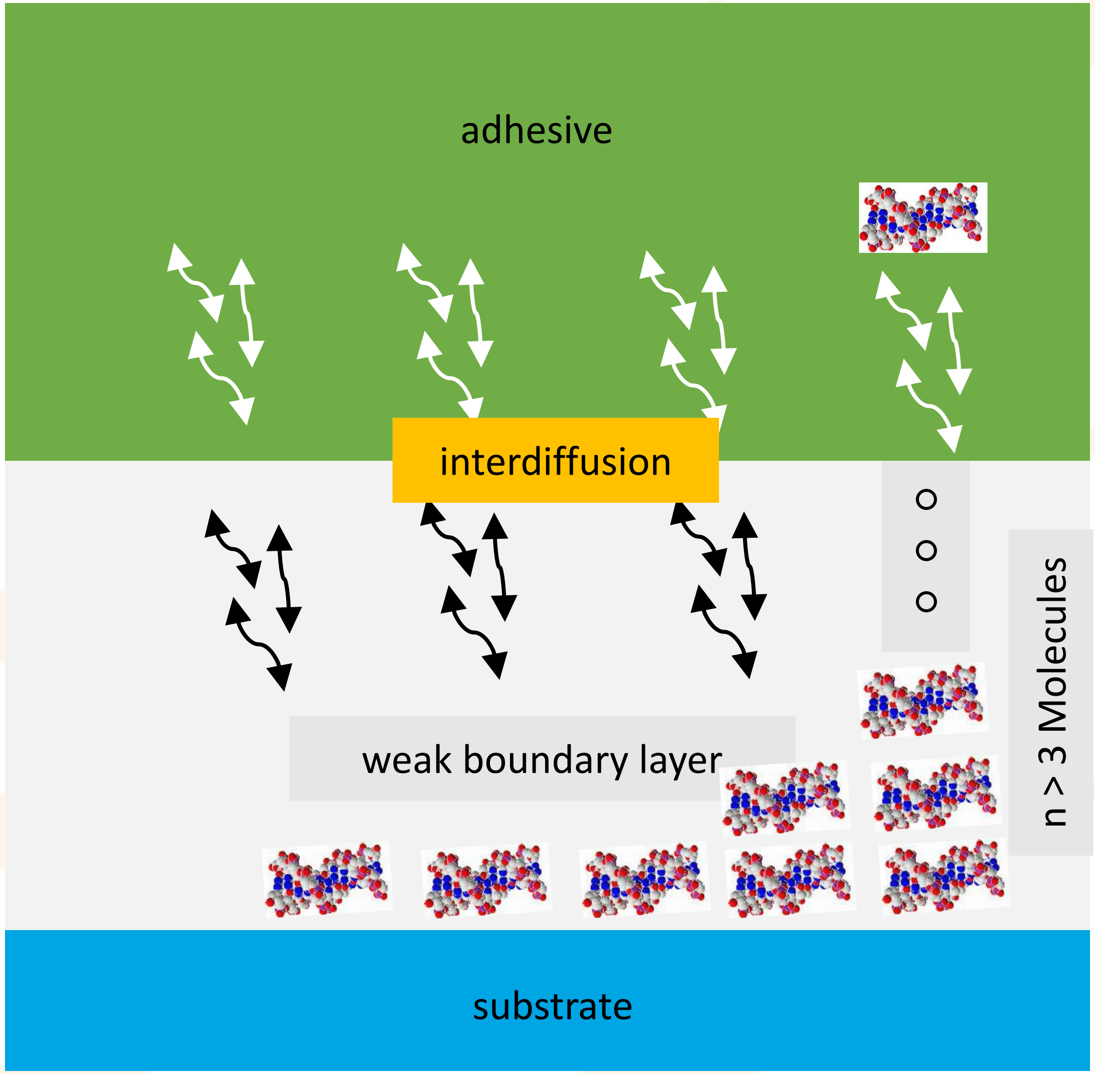
Condition	**Surface energy** [mN/m]	**Adhesion T-Peel 90°** [N/cm]	**Break type**
Polypropylen cleaned [with Isopropanol]	30	12	A[100%]
Polypropylen cleaned & plasma treated	44	**78**	K[100%]
Polypropylen contaminated [Silikone system PDMS – 1h block storage 40°C]	< 30	→ 5	A[100%]
Polypropylen contaminated & Plasma treated	> 48	→ 9	A[100%]

Plasma: TIGRES T-SPOT S2: v = 40 m/min, d = 5 mm, PWR = 60 % r = 6 mm
Break type: Adhesion break [A], Mixed break [M], cohesion break [K]
Measurement: T-Peel 90°, 300 mm/min, Delay 3d

Pictures: tesa SE

Why the does plasma often work on contaminations?

Diffusion in the Bulk of the adhesive/ink/paint is neccessary!



Pictures: tesa SE

Interdiffusion depends strongly of the contamination and the type of glue/media

Where does plasma help on contamination?

- Liquid systems als glue, inks, paint etc. can be able to absorb activated organic material
- ☹ Solid systems like tapes have only very limited capacity to absorb contamination

Conclusion cleaning with plasma: Yes, but...

1. Cleaning:
   - Yes, but: Removal/Hydrophilizising of <u>thin</u> layers of organic components (<u>*Fine*</u> cleaning, especially in vacuum plasma). Test of application is necessary!

2. Electrostatic neutralizing:
   - Plastcis don´t attract dust – side effect of plasma treatment

Conclusion plasma for cleaning:
If plasma works it is:

1. Simple and easy to use
2. Cost effective
3. Reproduceable
4. More environment friendly

Lifetime of treatment

The lifetime of the treatment can vary a lot, between minutes (silicone) and years (PS)

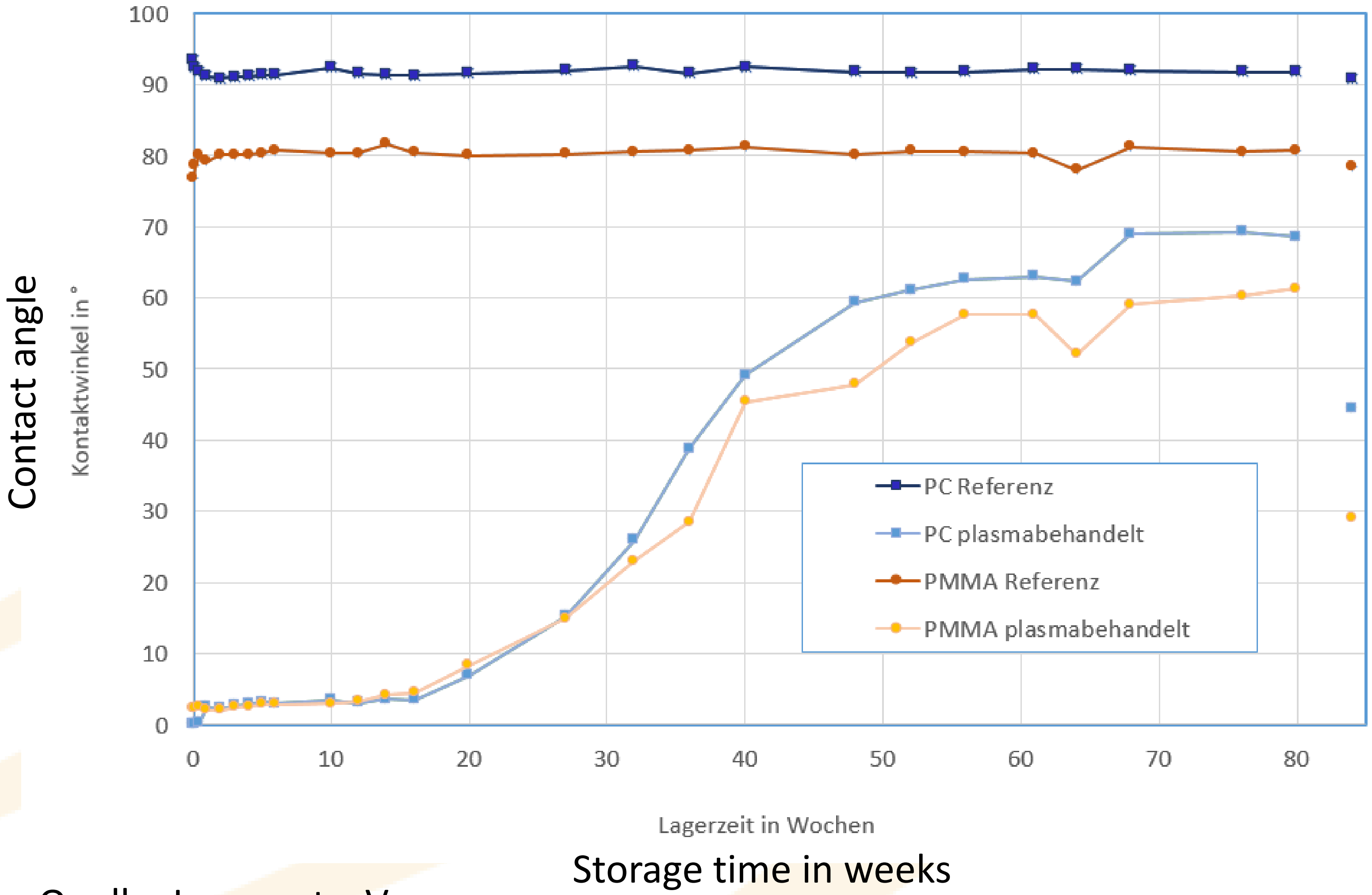
Mostly days to weeks.

Influences:

- Material
- Treatment method
  - Plasma versus Flame
  - Electrons, ions and photons etc.
- Additives (slip agents, antistatics etc.)
- Age of polymer when treated (f.e. PE film)
- Humidity
- Temperature
- Etc.
- Storage: In aluminum foil

If possible, the application should be done directly after the treatment

Lifetime of treatment in reality



Quelle: Innovent e.V.

Not all Plasmas are the same

Different types of plasma can have different effects

Differences can be:

- Atmospheric or vacuum plasma
- Material of electrodes
- Frequency of plasma
- Temperature of plasmas
- Treatment in primary or secondary plasma
- Created radicals
- Created reaction produtcs (O^3, NOx etc.)
- UV-Proportions
- Exposure time: Treatment processes need time. F.e. 2 x 500 W can be better than 1 x 1.000 W. The plasma dose can therefore, with same end results, be different
- Etc.

Overview procedure on material – adhesion and wettability

Improvement of Adhesion/oxydation							Key:	
Method:	**DBD**	**T-Jet**	**CAT**	**T-Spot**	**MEF**	**O³**	good	mostly satisfying results
Treating gas	Air	Air	Air	Air	Air	Air	average	results on average
Material:							poor	mostly poor results
PE	good	good	good	good	good	good		Material, with mostly only one technic working well
PEX	poor	average	good	good	good			
PP	good	good	good	good	good	good		
PC	good	good	good	good	good	good		
PMMA	good	good	good	good	good	good		
PEEK	poor	poor	average	average	average			
PET	good	good	good	good	good	gut		
PS	good	good	good	good	good	good		
POM	poor	poor						
ABS	good	good	good	good	good	good		
ABS/PC	good	good	good	good	good	good		
PA	average	average	good	good	good			
PA 6.6	average	average	good	good	good			
SAN			good	good	good			
PVC	average	average	good	good	good			
Fluor polymers:								
FEP	average	average	poor	poor	poor			
PVDF								
ETFE	average		average	average	average			
PFA	average		poor	poor	poor			
PTFE	average		poor	poor	poor			
Elastomere:								
Silicone	average	average	average	average	average			
TPE	poor	average	poor	poor	poor			
TPU			poor	poor	poor			
EPDM	good	average	good	good	good			
PUR	good	good	good	good	good			
Rubber	average	average	average	average	average			
gummi elasticum	average		average	average	average			
Others:								
UV-Coating	good	good	good	good	good			
Powder-Coating	good	good	good	good	good		Wax and PE-particles can disturb adhesion	

Overview procedure on material – cleaning and reduction

Cleaning/Oxidation:				
Method:	**DBD**	**CAT**	**T-Spot**	**MEF**
Treating gas	Air	Air	Air	Air
Metals:				
Stainless steel	good	good	good	good
Aluminum	good	good	good	good
Copper	average	average	average	average
Silver				

Reduction:				
Method:	**DBD**	**CAT**	**T-Spot**	**MEF**
Treating gas	Forming gas	Forming gas	Forming gas	Forming gas
Metals:				
Aluminum	poor	poor	poor	poor
Copper	average	average	average	average
Silver	average	average	average	average

Key:	
good	mostly satisfying results
average	results on average
poor	mostly poor results
	Material, with mostly only one technic working well

Forming gas = N + appr. 2-3 % H

Testing TIGRES Plasma: On site, with test equipment, in the lab

Testing at your production facility:
We support you with process consulting and in the testing with plasma systems at your production facility.

Rental systems:

More than 20 rental systems are available for testing. Training included.

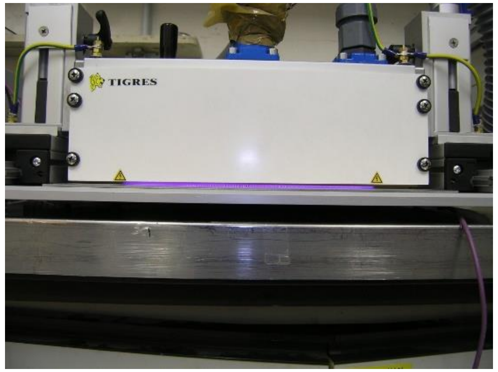
T-SPOT

CAT

MEF

T-JET

DBD



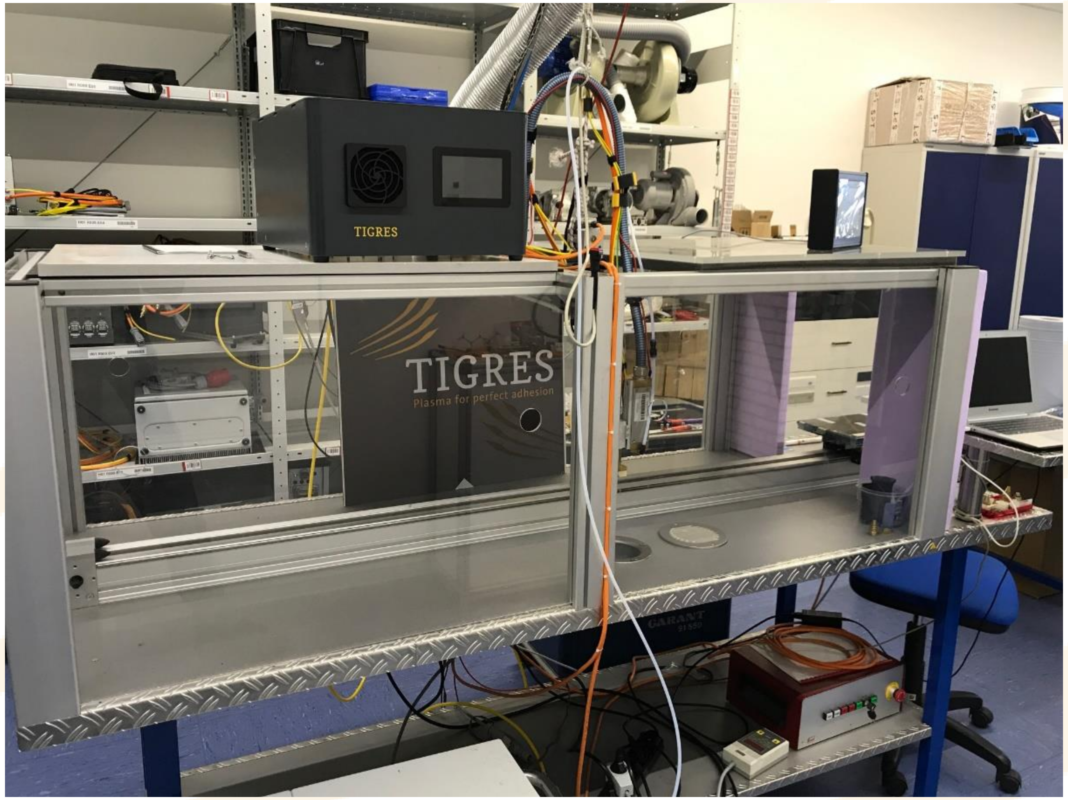
Testing TIGRES Plasma: In the lab

Processing of your samples:

Processing and analysing of samples for or with you, with verification and documentation of the results.

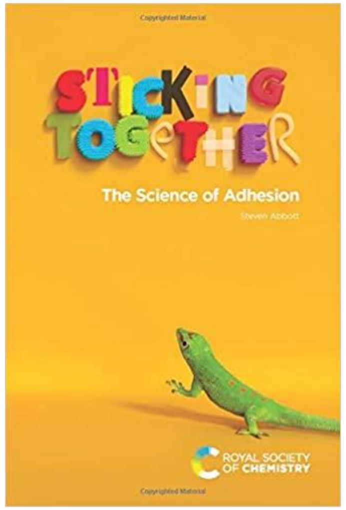
Practical training how to use plasma equipment for:

Activation, Cleaning, Deburring and plasma coating



TIGRES: Literature

For beginners: „Sticking together, the science of adhesion“, in english by Prof. Steven Abbot, PhD in Chemistry:



https://amzn.to/3ppgWRE

All the books in englisch by Steven Abbot:

https://www.stevenabbott.co.uk/books.php/

TIGRES: Next webinars

Next webinar:

7.7.21, 16:00 CEST, in englisch

Plasma treatment for perfect printing:

Digital printing

Inkjet printing

Tampon printing

Silk screen printing

Etc.

Limited amount of participants!

Register for webinar:

https://www.tigres-plasma.de/en/webinars

TIGRES: Linkedin

Please connect with TIGRES to stay in contact and get information about webinars, seminars, shows and plasma related content:

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TIGRES GmbH

https://www.linkedin.com/company/tigresgmbh

Thank you for your attention!

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