Use of Atmospheric Plasma Technology in Manufacturing and Application of Adhesive Tapes

tesa SE

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Agenda

- Introduction
  - Motivation
  - Plasma fundamentals
- Technology overview
  - Atmospheric plasma technologies (focus tesa)
- Examples
  - Applications at tesa
  - Aspects of surface analysis
  - Plasma enhanced deposition
- Plasma activation in customer applications
  - Plasma activation
  - Example from automotive industry
- Wrap-up

Company Profile

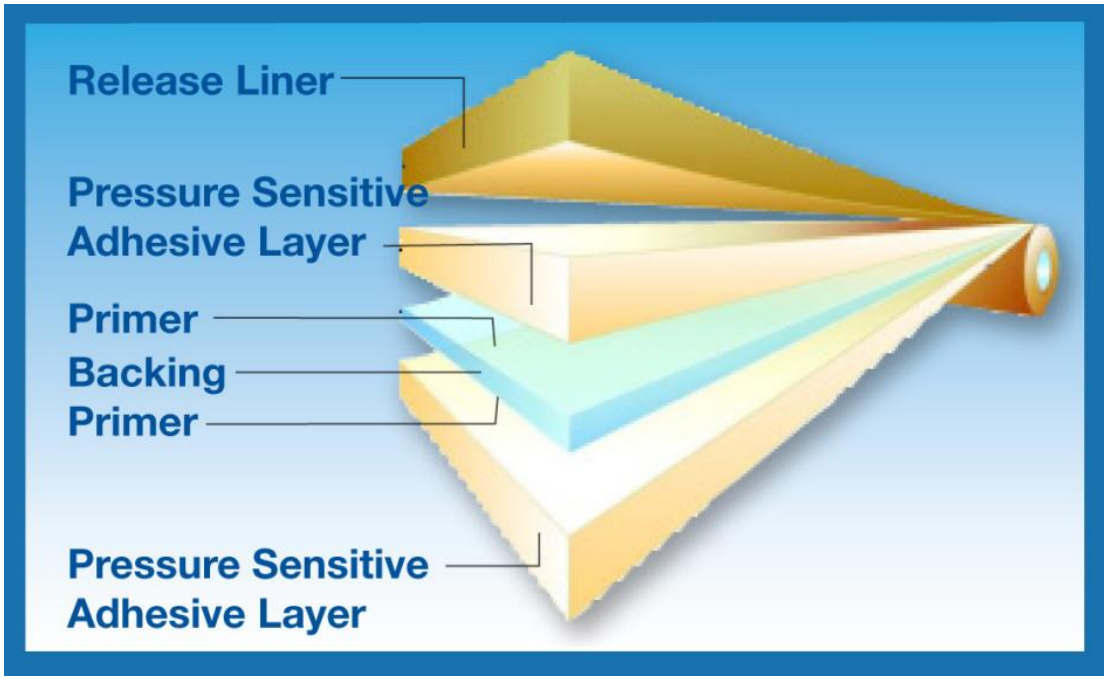
tesa SE:

- One of the world's leading producers of **self-adhesive solutions** for **industry, trades, and consumers**
- **125 years of experience** in
  - Coating technology
  - Development of adhesive masses and innovative product solutions

tesa is the **global market leader** in many application fields

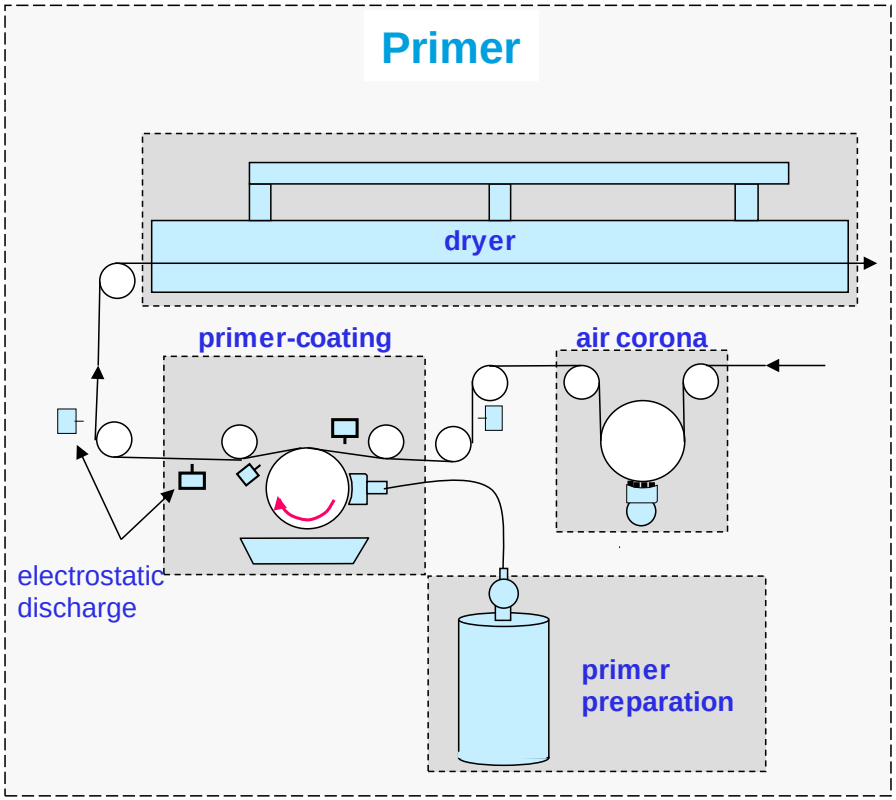
tesa Tapes – General Structure

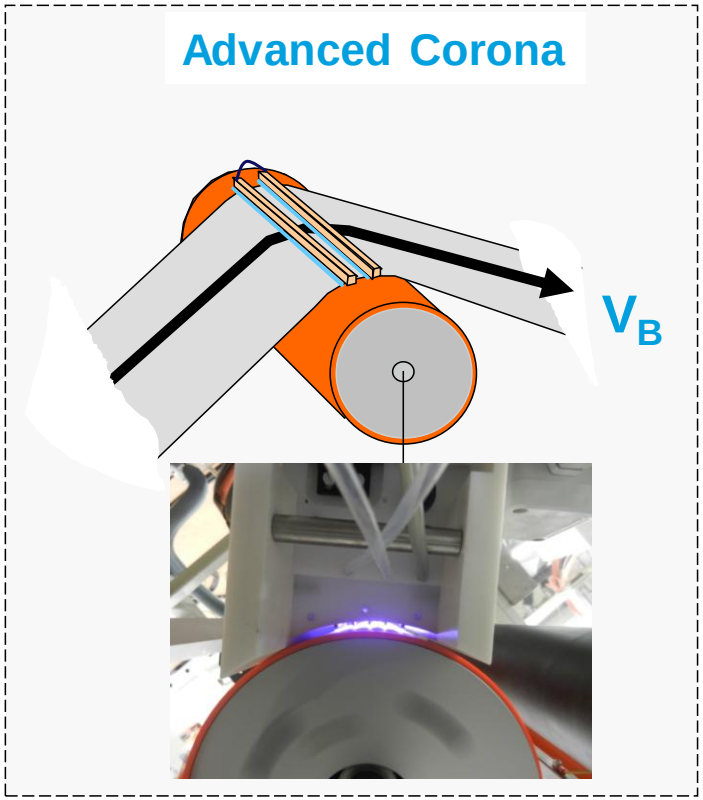
- tesa tapes are multilayer products
  - layers have to adhere to each other,
    therefore in many cases adhesion promotors (primer) necessary



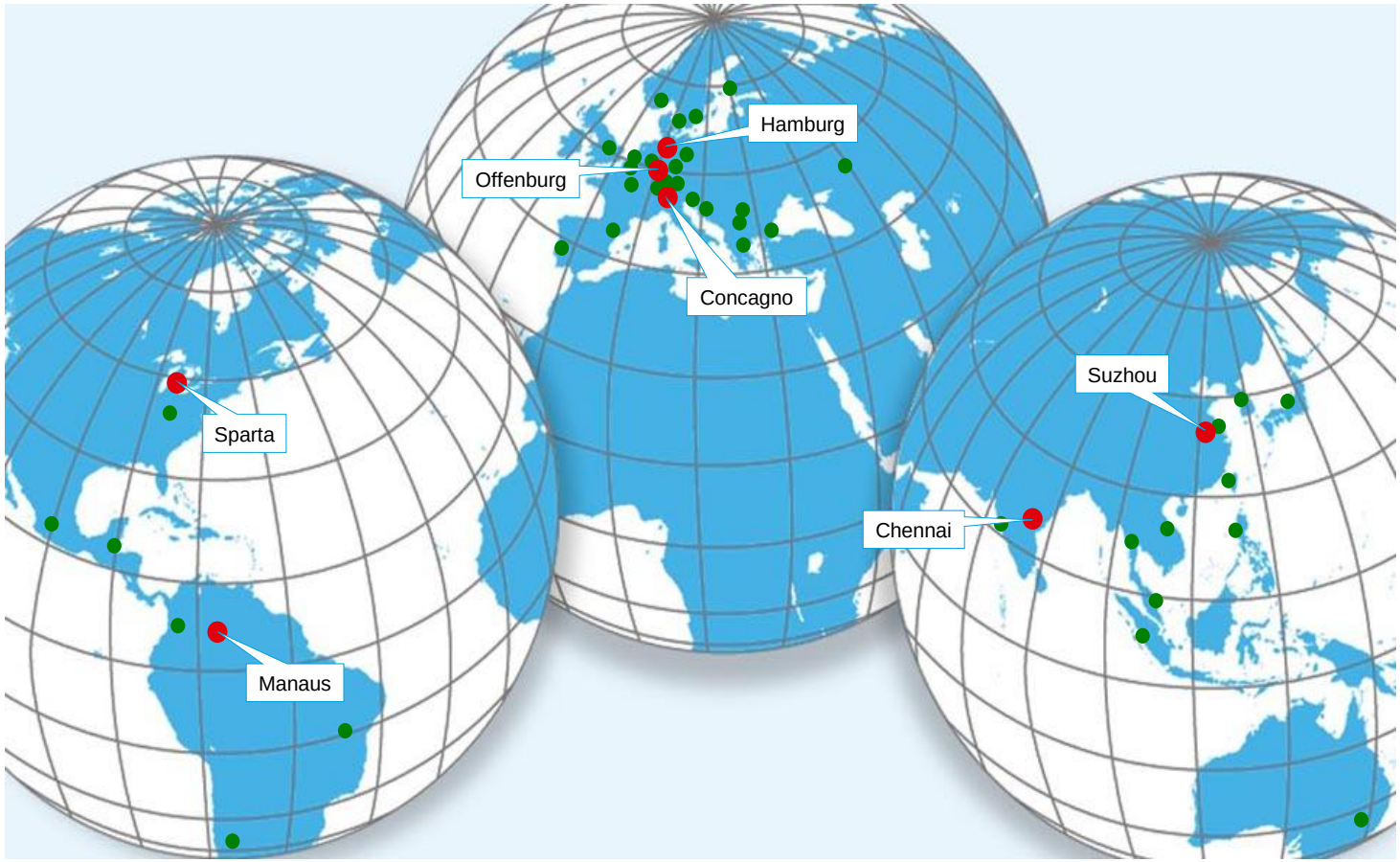
Motivation for use of plasma treatment

- Pre-treatment of web materials for increase of adhesion between layers
  - advancing from chemical primers towards innovative plasma treatments





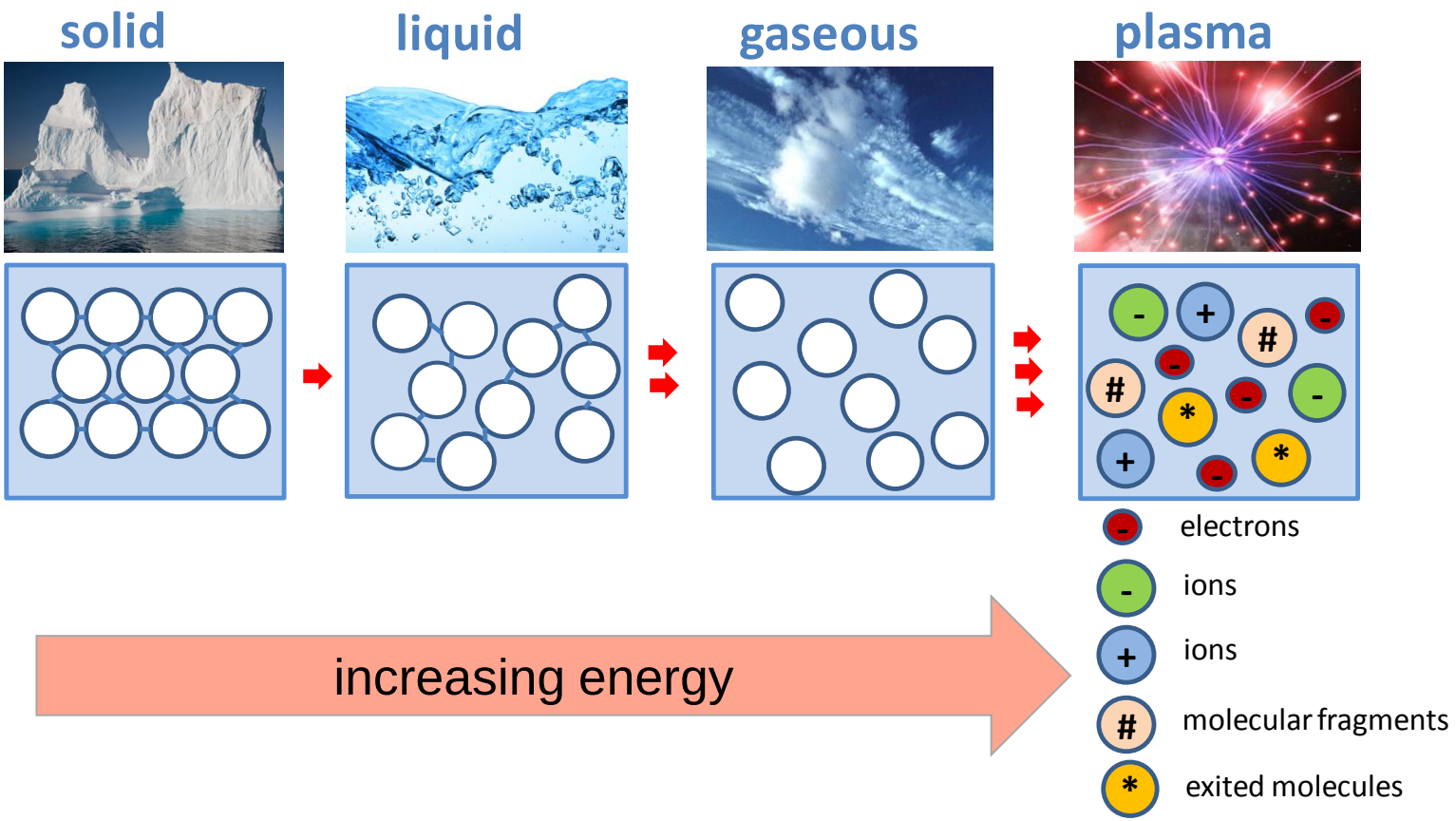
Where to Use Plasma: tesa´s Production Sites



- World-wide access to advanced plasma technologies necessary

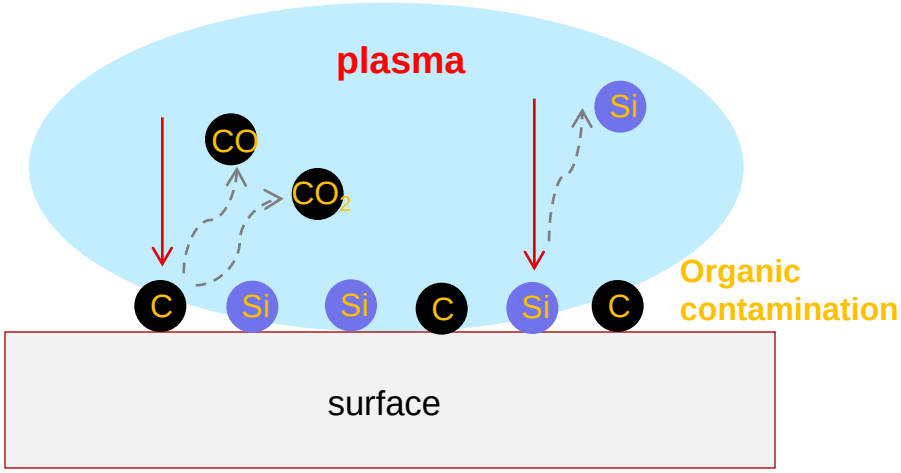
Plasma Fundamentals

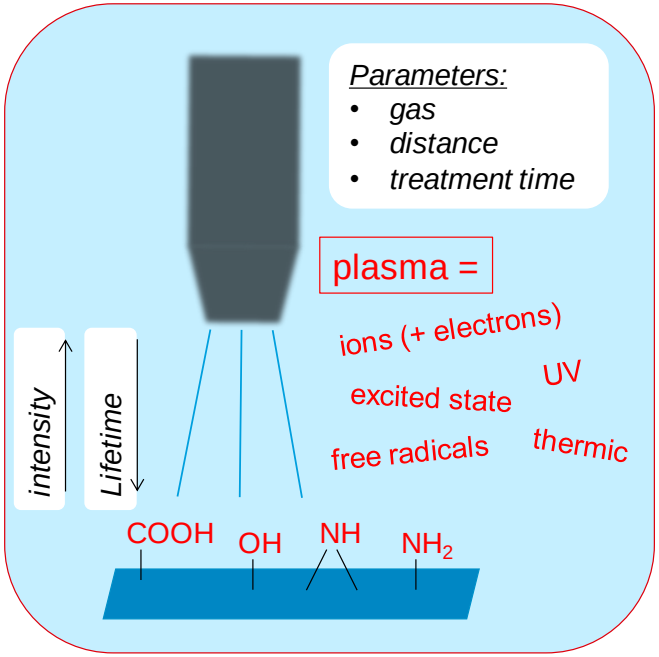
- Plasma as 4th state of aggregation



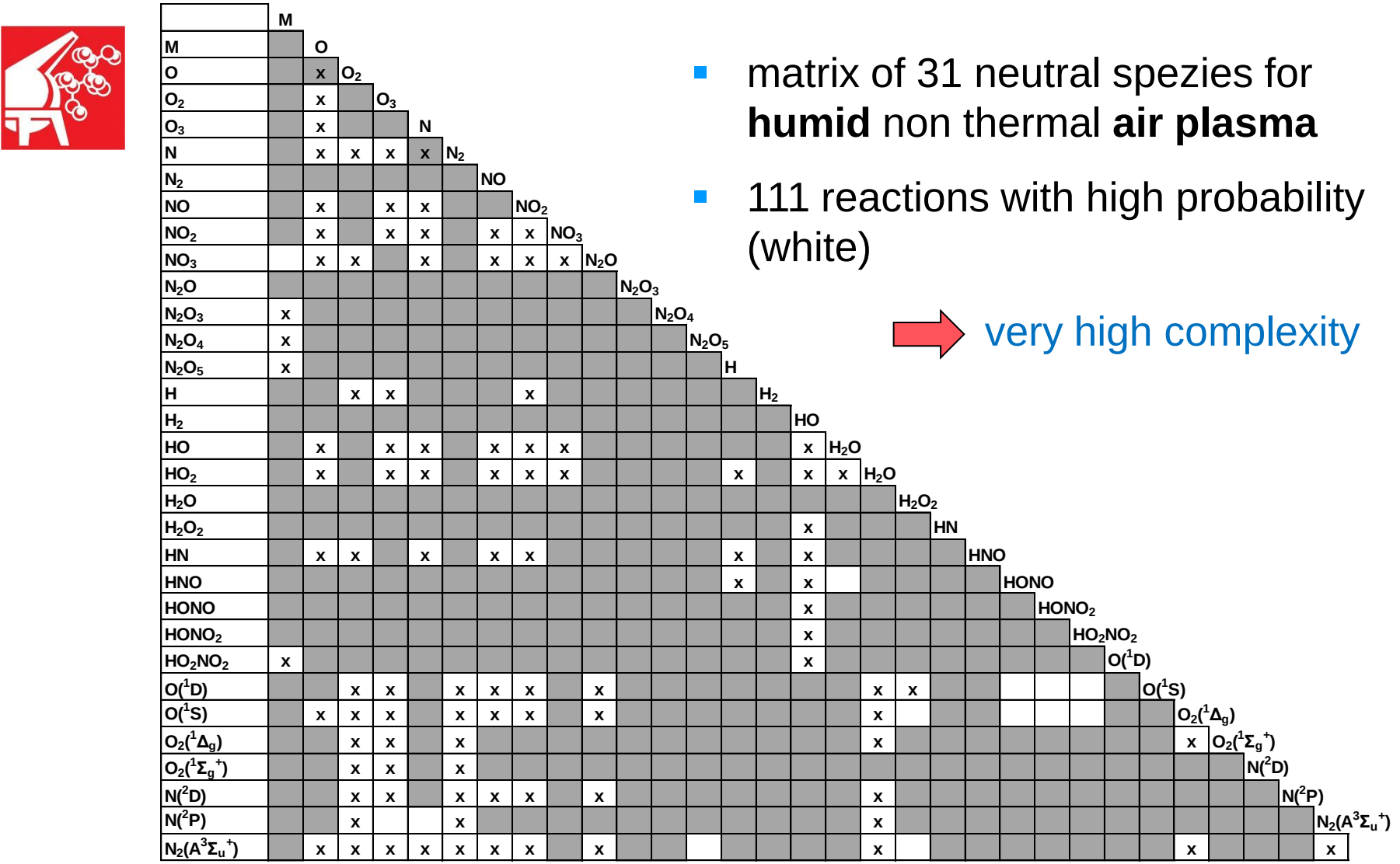
Plasma Effects for Promoting Adhesion

- Two effects dominate:
  - ultra fine surface cleaning
  - chemical surface modification
    - polar chemical groups
    - reactive groups
    - acid-base interactions
    - van der Waals forces





Plasma Chemistry in Gaseous Phase



	M	O	O_2	O_3	N	N_2	NO	NO_2	NO_3	N_2O	N_2O_3	N_2O_4	N_2O_5	H	H_2	HO	H_2O	H_2O_2	HN	HNO	HONO	$HONO_2$	HO_2NO_2	$O(^1D)$	$O(^1S)$	$O_2(^1\Delta_g)$	$O_2(^1\Sigma_g^+)$	$N(^2D)$	$N(^2P)$	$N_2(A^3\Sigma_u^+)$
M																													
O		x																											
O_2		x																											
O_3		x																											
N		x	x	x	x																								
N_2																													
NO		x		x	x																								
NO_2		x		x	x		x	x																					
NO_3		x	x		x		x	x	x																				
N_2O																													
N_2O_3	x																												
N_2O_4	x																												
N_2O_5	x																												
H			x	x				x																					
H_2																													
HO		x		x	x		x	x	x							x	H_2O											
HO_2		x		x	x		x	x	x					x		x	x	H_2O											
H_2O																			H_2O_2										
H_2O_2																x				HN									
HN		x	x		x		x	x						x		x					HNO								
HNO														x		x						HONO							
HONO																x							$HONO_2$						
$HONO_2$																x								HO_2NO_2					
HO_2NO_2	x															x									$O(^1D)$				
$O(^1D)$			x	x		x	x	x		x								x	x							$O(^1S)$			
$O(^1S)$		x	x	x		x	x	x		x								x									$O_2(^1\Delta_g)$		
$O_2(^1\Delta_g)$			x	x		x												x								x	$O_2(^1\Sigma_g^+)$		
$O_2(^1\Sigma_g^+)$			x	x		x																						$N(^2D)$	
$N(^2D)$			x	x		x	x	x		x								x											$N(^2P)$	
$N(^2P)$			x			x												x												$N_2(A^3\Sigma_u^+)$
$N_2(A^3\Sigma_u^+)$		x	x	x	x	x	x	x		x								x								x				x

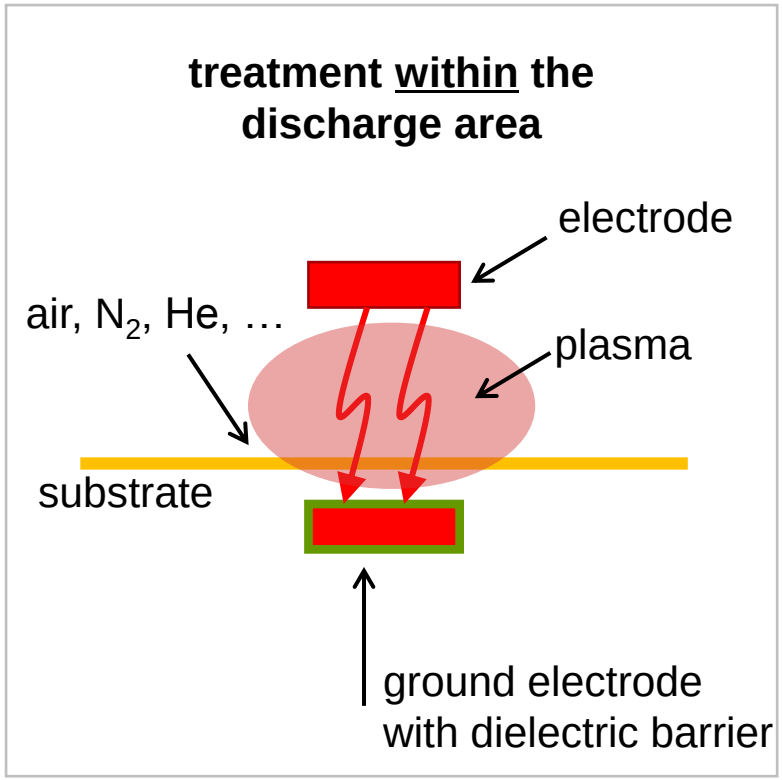
- matrix of 31 neutral spezies for **humid** non thermal **air plasma**
- 111 reactions with high probability (white)

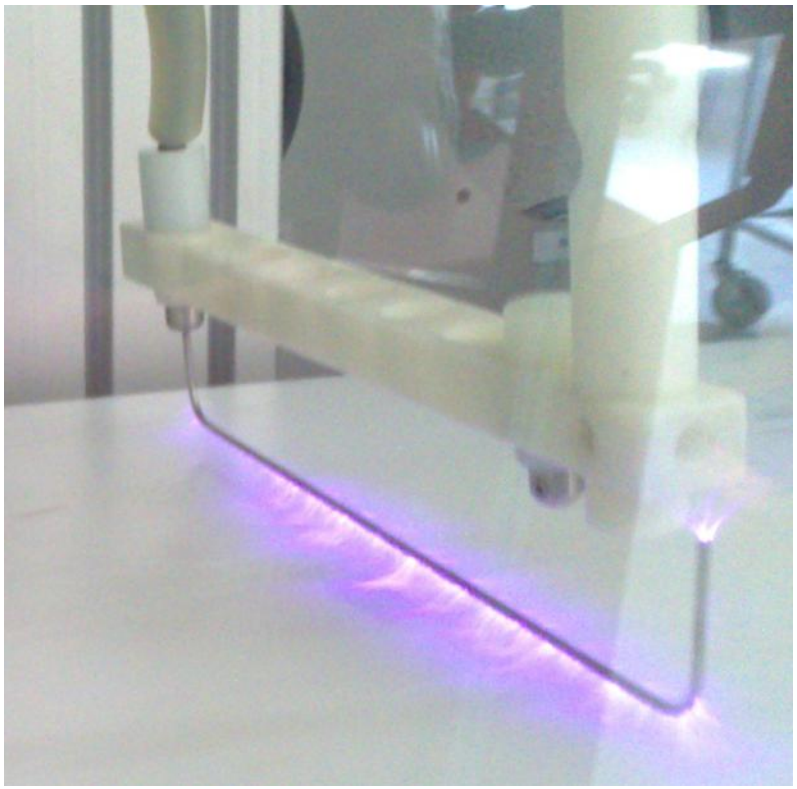
→ very high complexity

Herron et al., *Plasma Chemistry and Plasma Processing* **2001,** 21, 3

Technology Overview (1)

- „**Direct**“ corona treatment (DBD = dielectric barrier discharge)
  - filamentary discharge (e.g. air corona)
  - homogeneous discharge (noble gas corona)

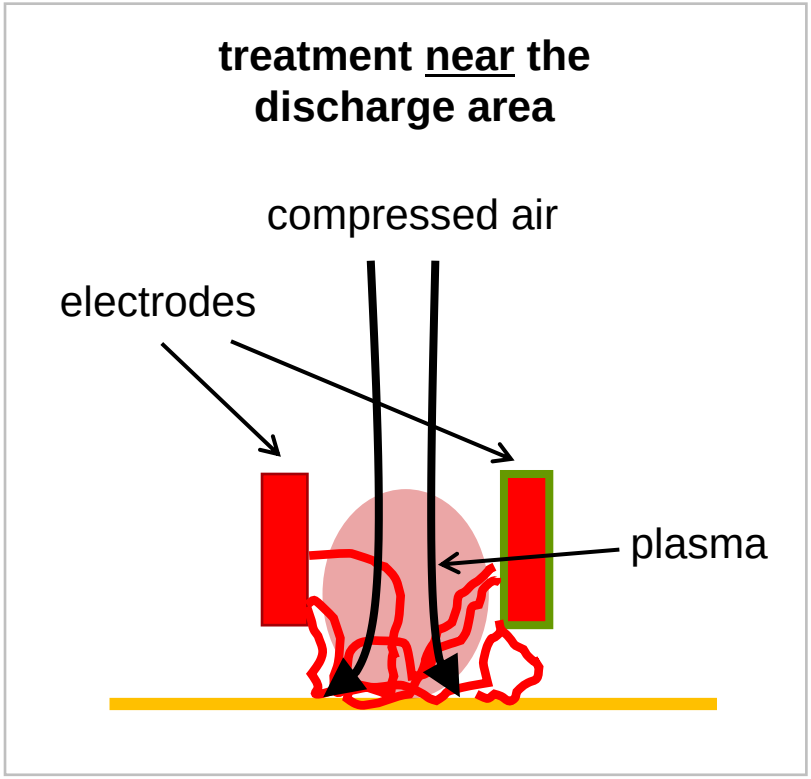


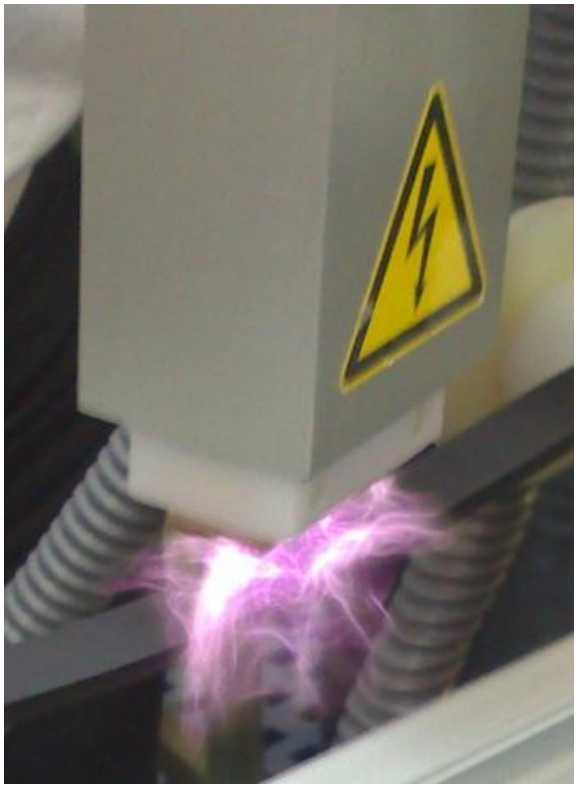


example: wire electrode (Kalwar/Tantec)

Technology Overview (2)

- „**Semi-direct**“ corona treatment (DBD = dielectric barrier discharge)
  - filamentary discharge (air corona)
  - homogeneous discharge (noble gas corona)

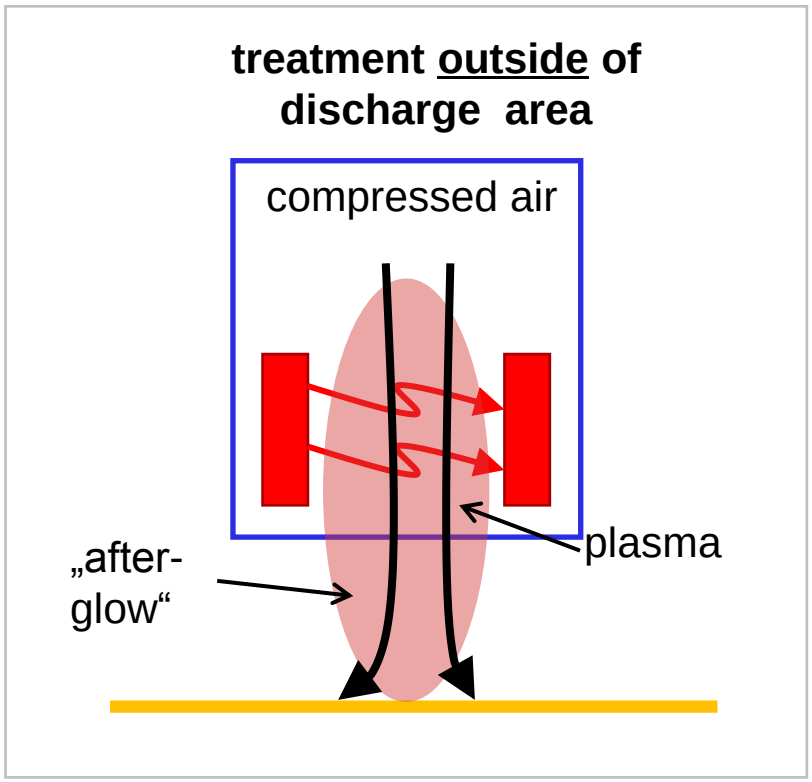




example: SpotTec handheld corona (Tantec)

Technology Overview (3)

- „**Indirect**“ plasma treatment
  - electric arc discharge



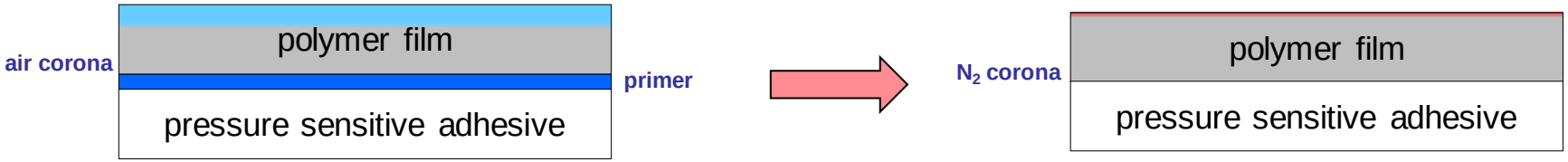
example Plasmajet (Plasmatreat): single nozzle and rotating nozzle

Example: Direct corona within nitrogen atmosphere

- First installed system: Aldyne Plasma System (Softal / Air Liquide)
  - pure N_2-atmosphere (< 20 ppm O_2 necessary)

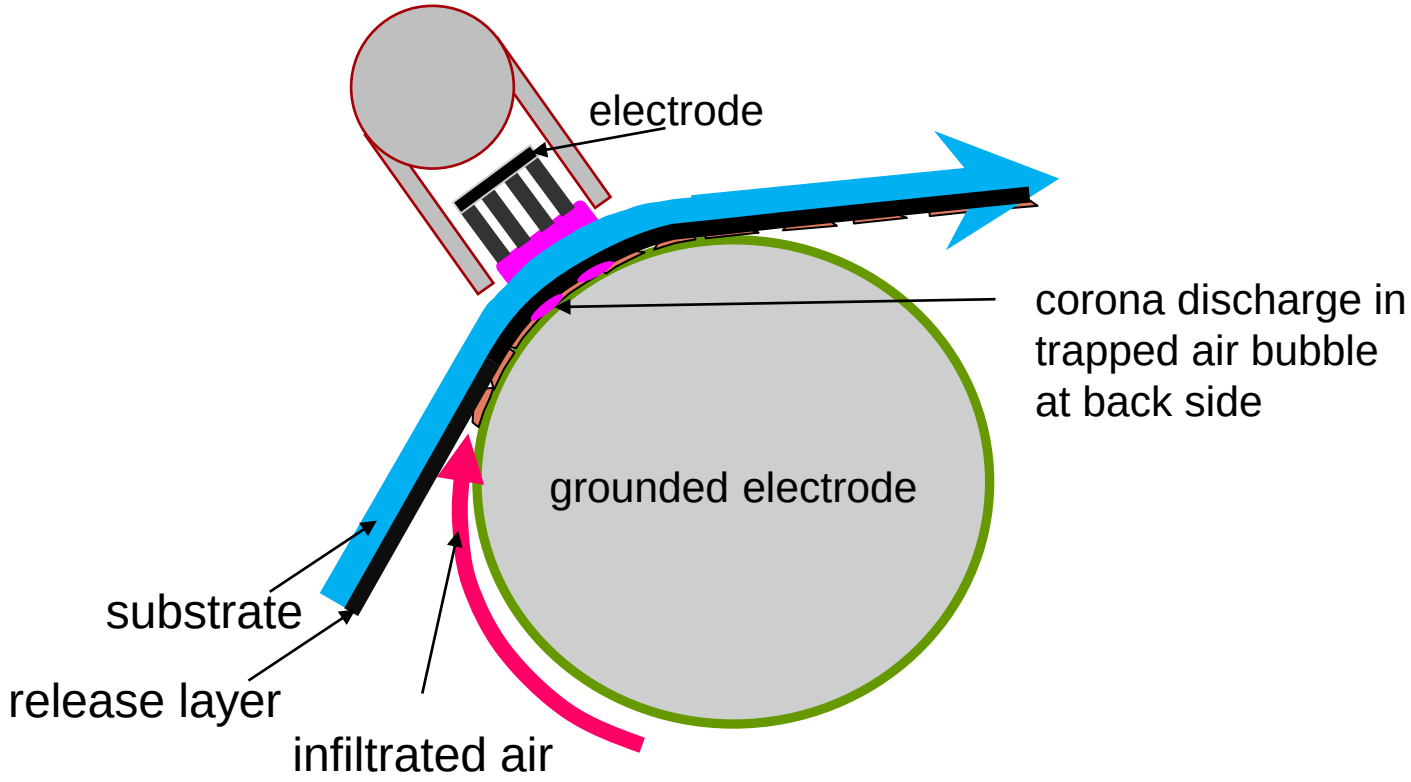
Example: Nitrogen Corona

- tesafilm®:
  - Replacement of primer layer by N_2-Corona



General issue: Back side treatment at Corona

- Unwanted treatment of back side of tape
  - causes problems in unwinding a tape roll due to release layer damage



=> currently not solved properly

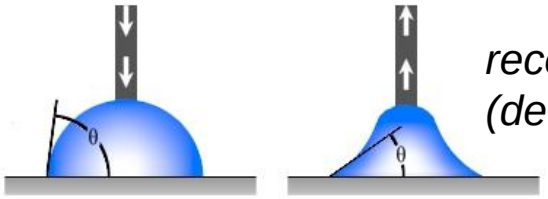
Surface Analysis: Contact Angle Measurements

- Established method to indicate increase of surface energy with plasma treatment

- Observed phenomenon at **nitrogen-corona** treatment of BOPP:
  - measurement by test inks: ➔ 40-60 mN/m
  - static contact angle measurement: ➔ 30-40 mN/m

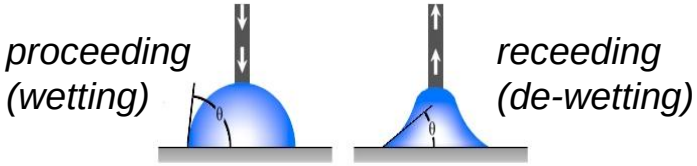
- Clarification by dynamic contact angle measurement

proceeding (wetting)

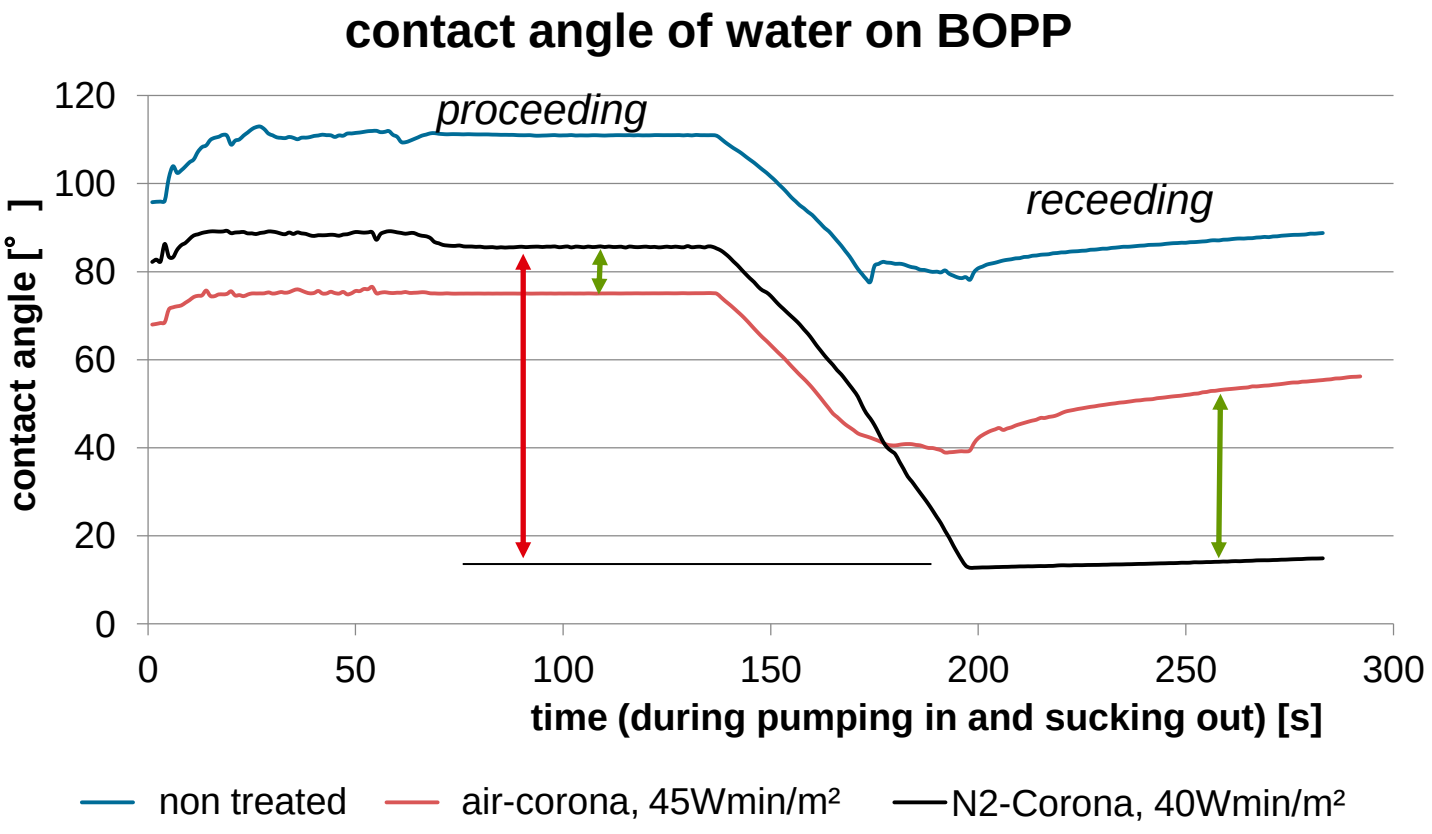


receeding (de-wetting)

Surface Analysis: Contact Angle Measurements



- Dynamic measurements



Surface Analysis: Contact Angle Measurements

- Conclusion:
  - measurements with test inks reflect the receeding dynamic contact angle
  - static measurements are more near to the proceeding contact angle

  - There is a hysteresis on all technical surfaces!
    The „equilibrium angel“ is a fairy tale, there are lots of stable states

- But:
  In current trials for N_2-corona whether the **static contact angle**, nor the **test ink**, nor the OWKR **surface tension**, nor **disperse or polar contribu**tion to the surface energy show a **correlation to peel adhesion**.

Strobel M.: An Essay on Contact Angle Measurements; Plasma Process. Polym. 2010, 7, pp. 8-13
Müller M.: Comments on ‘‘An Essay on Contact Angle Measurements’’; Plasma Process. Polym. 2011, 8, pp.19-24
Di Mundo, R.: Comments Regarding ‘An Essay on Contact Angle Measurements’; Plasma Process. Polym. 2011, 8, pp.14–18
Eral H.: Contact Angel Hysteresis; Colloid and Polymer Science 2013, 291, Issue 2 , pp 247-260

Surface Analysis: ESCA (XPS) investigations

- Chemical analysis of the treated surface necessary
- Comparison between air and nitrogen corona (treated BOPP):

Sample	C [at%]	N [at%]	O [at%]	
without corona	100	-	-	
33 Wmin/m²	99,3	-	0,7	**air**
33 Wmin/m²	95,6	1,9	2,5	**nitrogen**

- more oxygen content in nitrogen treatment than at air treatment
- at air treatment, no nitrogen found on surface

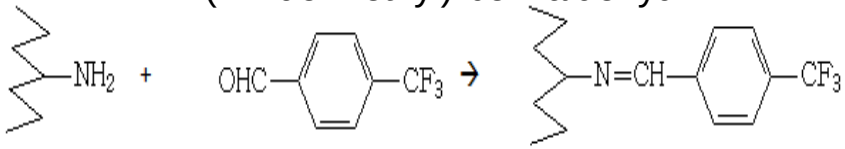
⇒ **Very relevant post plasma processes** !

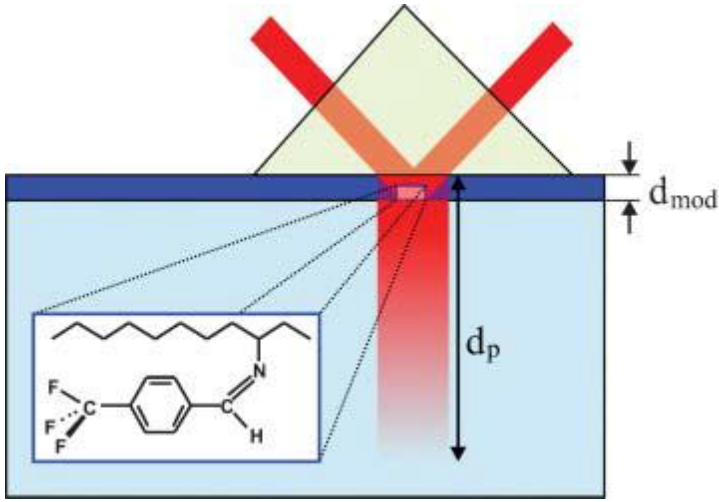
⇒ Remaining question:
What does control adhesion: Nitrogen or oxygen containing groups?

Surface Analysis: Chemical Derivatization

- Derivatization of Amino-groups according to Klages (FhG-IST, Braunschweig)
  - 3 fluorine atoms mark 1 primary amino group

4-(Trifluormethyl)-benzaldehyd



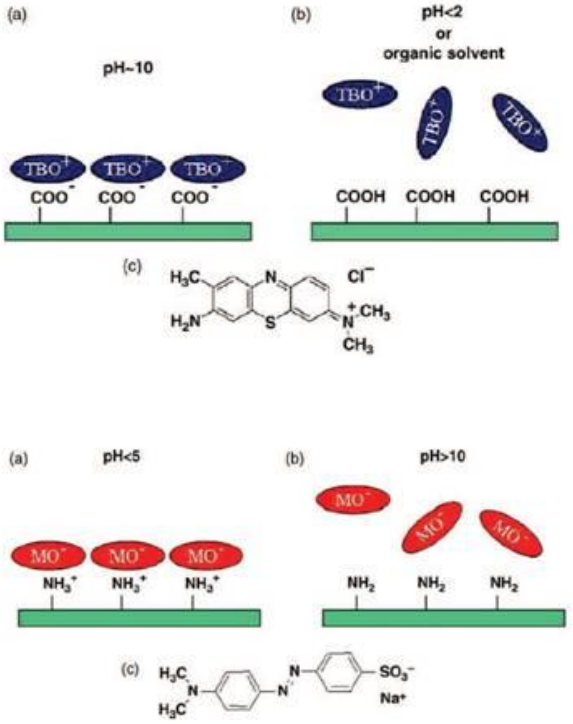


- Verification of successful derivatization with:
  - ATR FT-IR: no valuable results found
  - ESCA: verification successful -> but derivatization not needed

C.-P. Klages, A. Grishin, Plasma Process. Polym. 2008, 5, 359–367
C.-P. Klages, A. Hinze, and Z. Khosravi, Plasma Process. Polym. 10: 948–958, 2013
C.-P. Klages, Z. Khosravi, and A. Hinze, Plasma Process. Polym. 10: 307–312, 2013
IN-SITU FTIR SPECTROSCOPIC STUDIES OF DBD-BASED POLYMER SURFACE NITROGENATION
Claus-Peter Klages, Zohreh Khosravi; HAKONE XIV, Zinnowitz, September 21-26, 2014

Surface analysis: Colorimetric investigations

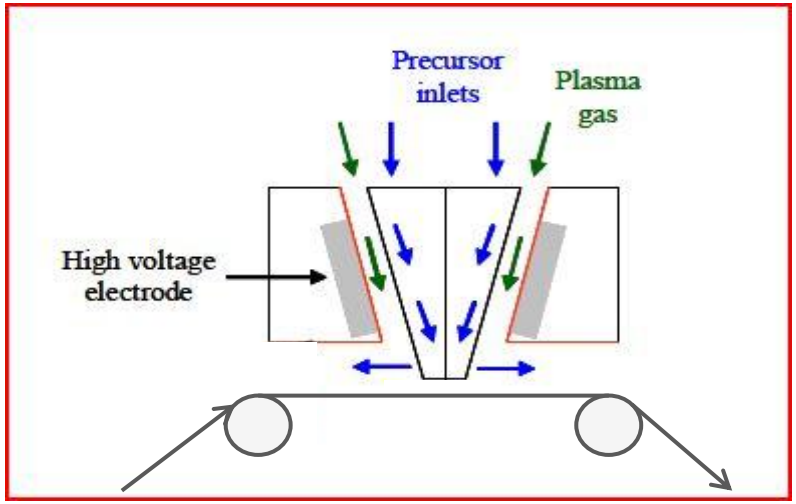
- Established for carboxyl- and amino groups
  - Works by coupling of selective dyes
    - step 1: colouring of defined area
    - step 2: ph-shift releases dye
    - step 3: quantitative determination of amount of dye by spectroscopy
  - Conclusion of first trials:
    - works in general,
      handling of method to be optimized



Habeeb A.: ANALYTICAL BIOCHEMISTRY 14, 328-336 (1966)
Hartwig A.: Adhäsion 1994-38-7/8-p.94
Hartwig A. et. al.: Adhäsion 2000-44-1/2-p.38
Ma Z.: Colloids and Surfaces B: Biointerfaces 60 (2007) 137–157

Technology extension:
Deposition of thin layers by atmospheric plasma

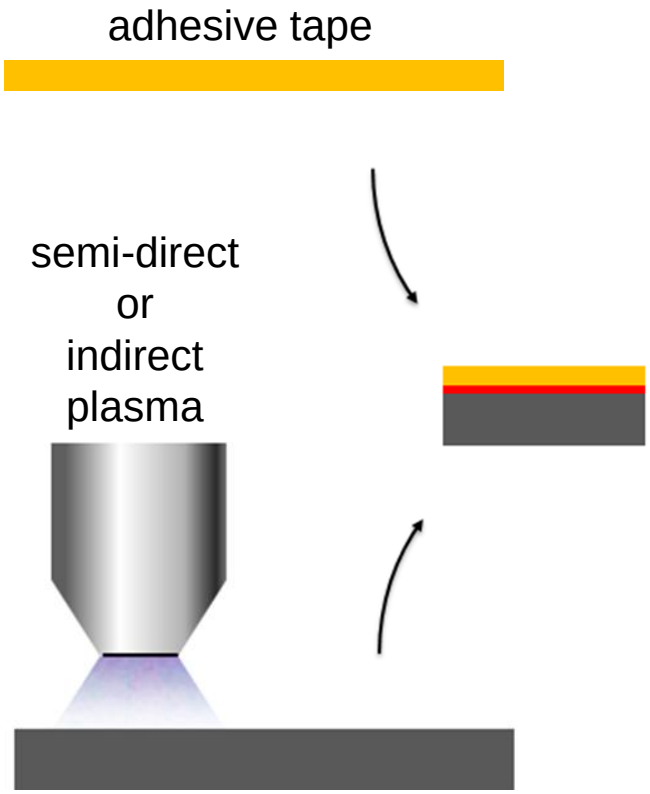
- Vito PlasmaLine:
  Semi-direct DBD in nitrogen atmosphere with additional precursor inlet
  - smooth activation of precursor in after glow
  - relative defined use of chemistry possible in comparison to direct corona technologies

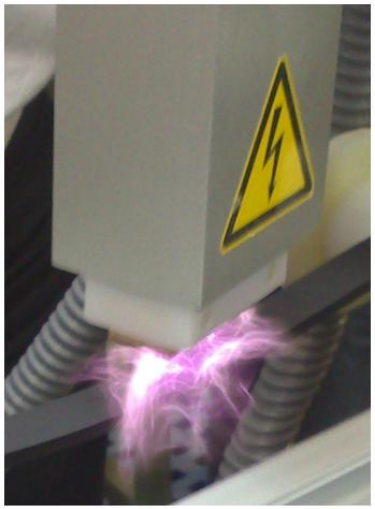


  - Conclusion: Suitable precursors for adhesion promotion available, but very low web speed (< 20 m/min)

Plasma Activation in Customer Tape Applications

- Plasma surface treatment of customer substrates is well established





Comparison Plasma vs. Chemical Primer

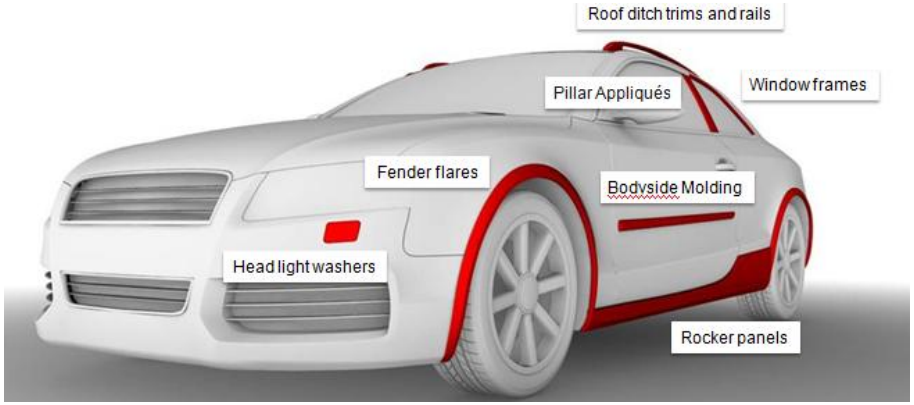
- In high performance tape applications use of chemical primers is common.
- Advantages and restrictions of plasma treatment in general are known:

	Plasma-Primer (OpenAirPlasma Plasmatreat)	**Chemical Primer (tesa-Primer 60150, 60151, 60152)**
Substrates	wide range of materials	wide range of materials, selection of primer needed
Application	automated or semi-automatic treatment easy to implement	manual coating by worker: apply thinly, often wipe of with clean cloth
Tools	plasma equipment, optional positioning table	chemical primer, lint free cloth or brush
Time to bonding	immediate bond handling possible	30 sec to 5 min evaporation time
Open time for bonding	min / several hours	several hours/days
Safety	exhaust of ozone and nitrogene oxides	exhaust of solvent emission, often hazardeous chemical composition

Example: Fixation of Attachment Parts on Painted Body

- tesa ACXplus tape range especially suited for such purposes

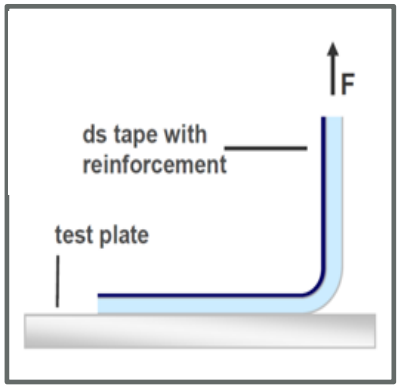
- Challenges:
  - **bonding on polypropylene substrates**
  - low surface energy (LSE) lacquers



Example: Fixation of Attachment Parts on Painted Body

- Materials:
  - substrate: PP GF 30
  - adhesive tape: tesa ACXplus 7076
- Description of problem:
  - batch fluctuations of adhesive strength,
    in the worst case peel adhesion < 10 N/cm
  - required level: significant increase, best: cohesive failure of tape
- Analysis:
  - non-polar impurities on PP GF30
  - analyzed substances:
    - Erucamide (slip agent – carboxylic acid amide)
    - Irgafos 168, Irganox PS802 (processing stabilizer – hydrolytically stable phosphite, heat stabilizer - dialkyl ester of thiodipropionic acid)
    - fatty acids (finger print contamination?)

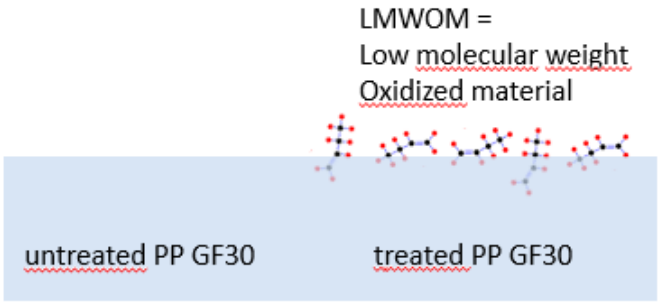
⇒These substances can cause substantial reduction of adhesion



Example: Fixation of Attachment Parts on Painted Body

- Measure: multiple treatments ?

Treatment times	Peel performance [N/cm]
clean (isoprop:H_2O) part treated	
1x	12,3
2x	14,6
3x	16,6



- Corona generates surface damage on PP: LMWOMs
  - LMWOM is non-covalently bond to plastic and water soluble
  - LMWOMs affect the warm-humidity durability

Example: Fixation of Attachment Parts on Painted Body

- Surface treatment: Semi-direct corona
- Corona Parameter
  - actual distance 20 – 25 mm
  - recommended treatment distance (typical): 10 – 15 mm
    - trials:
      - 12 mm, variable speed
      - 5 m/min, variable distance

speed [m/min]	Peel performance [N/cm]
only clean part treated	
2	26,0
5	24,2
10	20,9

distance [mm]	Peel performance [N/cm]
only clean part treated	
6	25,5
12	23,5
20	20,5
24	15,1

Example: Fixation of Attachment Parts on Painted Body

- Breakthrough: Optimization cleaning process
  - w/o cleaning agent: 9,6 N/cm (#04/14)

Cleaning Agent	Peel performance [N/cm]
4 x wiping, > 1 hours waiting	
	cleaned part treated
isopropanol : H_2O (current agent)	10,8 (#04/14)
isopropanol	31,5 (#04/14) 36,4 (#06/14)
petroleum ether	39,6 (#04/14) 51,7 (#06/14) (M)

C = cohesion failure
M= mixture failure

- substantial cleaning necessary
  - improvements with isopropanol and petroleum ether
  - plasma is not able to **clean** surface

Dietrich Ch.: Adhäsion 10/2011, p. 14
Minin E.: Adhäsion 06/2011, p. 38

Wrap-up

- Atmospheric plasma technologies offer great chances in improvement of adhesion.
- It needs much efforts to understand plasma induced effects:
  - effects often depend on the given scenario and could not be generalized
  - analytical tools need to be used and interpretated very careful
- Implementation of plasma technologies in high performance industrial applications need investigations on real substrates
  - effects are very sensitive to substrate qualitiy and depend on the used plasma technology
- Regarding tape applications:
  - first choose the right adhesive tape (without pretreatment)
  - don´t forget cleaning
  - then think about pretreatment

  => support by your tesa representative

Thank you!

tesa SE

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