ActInPak

COST EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

COST is supported by The EU Framework Programe Horizon 2020

COST ACTION FP1405

ACTIVE AND INTELLIGENT FIBRE-BASED PACKAGING – INNOVATION AND MARKET INTRODUCTION (ACTINPAK)

# PROCEEDINGS
# SUMMER SCHOOL
# PRINTING OF FUNCTIONAL APPLICATIONS

Monday 11th - Friday 15th July 2016

Swansea University Bay Campus, UK

## General Information

This Summer School brought together leading speakers from academia across Europe and Industry to deliver an introduction to printable electronics and took place from 11 to 15 July 2016. Location was the magnificent new 65 acre Bay Campus and is located right on the beach on the eastern approach to Swansea City which is the home to the Welsh Centre for Printing and Coating based within the College of Engineering.

This Training School was beneficial for all those who wished to increase their printing knowledge for all processes with an emphasis on printing functional materials such as used in smart packaging, printable electronics and sensors. Presentations and practical sessions were suitable for both industry professionals and academic researchers, and are delivered by selected speakers from industry and leading European academics on the following topics:

- Design and applications
- All major printing processes (flexo, screen, gravure, pad, offset and inkjet)
- Inks
- Substrates
- Curing technology
- Characterisation technologies
- Practical sessions:
    - Screen Printing
    - Flexography
    - Rheology
    - Metrology
    - Ink Making Demo
    - Novacentrix Pulseforge

The Summer School is the first Training School organised by COST Fp1405 ActinPak, and the third time WCPC organised a Summer School in this field.

## INDEX

# 1. Agenda

## Monday 11th July

| | |
|---|---|
| 09:00 | Registration |
| 09:30 - 09:45 | Welcome and Introduction, David Gethin, Welsh Centre for Printing and Coating |
| 09:45 - 10:45 | Lab Tours and Demonstrations |
| 10:45 - 11:15 | Comfort Break |
| 11:15 - 12:00 | Overview of Printed and Coated Functionalities, Tomos Syrový, University of Pardubice |
| 12:00 - 12:45 | Sensor Integration on Flexible Substrates, Grigoris Kaltsas, T.E.I. of Athens |
| 12:45 - 13:45 | Lunch |
| 13:45 - 14:45 | 3D Printing, Tim Mortensen, Welsh Centre for Printing and Coating |
| 14:45 - 15:00 | Inkjet printing, Dave Shaw, Welsh Centre for Printing and Coating |
| 15:00 - 15:15 | Pad printing, James Claypole, Welsh Centre for Printing and Coating |
| 15:15 - 15:45 | Drying and sintering, Davide Deganello, Welsh Centre for Printing and Coating |
| 15:45 - 16:00 | Comfort Break |
| 16:00 - 16:30 | Aerosol Jet printing, Chris Phillips, Welsh Centre for Printing and Coating |
| 16:30 - 17:00 | Photonic Fabrication with PulseForge, Rob Hendriks, Novacentrix |
| 17:00 | Day Close |

## Tuesday 12th July

| | |
|---|---|
| 09:00 - 09:50 | Gravure printing, Gunter Hubner, HdM |
| 09:50 - 10:40 | Flexographic printing, Davide Deganello, Welsh Centre for Printing and Coating |
| 10:40 - 11:10 | Comfort Break |
| 11:10 - 12:00 | Screen printing, Gunter Hubner, HdM |
| 12:00 - 12:30 | Extrusion coated materials, surface treatment techniques, films and foils, Johanna Lahti, Tampere University of Technology |
| 12:30 - 13:00 | Barrier properties, Johanna Lahti, Tampere University of Technology |
| 13:00 - 14:00 | Lunch |
| 14:00 - 15:00 | Advanced Screen Printing, Fernando Zicarelli Fernández, Asada Mesh |
| 15:00 - 15:30 | Comfort Break |
| 15:30 - 16:30 | Colour Measurement, Tim Claypole, Welsh Centre for Printing and Coating |
| 16:30 | Day Close |

## Wednesday 13th July

| | |
|---|---|
| 09:00 - 09:50 | Paper as substrate for printed electronics, Martti Toivakka, Abo Akademi University |
| 09:50 - 10:40 | Inks & formulation, Chris Phillips, Welsh Centre for Printing and Coating |
| 10:40 - 11:00 | Comfort Break |
| 11:00 - 11:30 | Rheology, James Claypole, Welsh Centre for Printing and Coating |
| 11:30 - 12:00 | Electrical Characterisation, Tatyana Korochkina, Welsh Centre for Printing and Coating |
| 12:00 - 12:30 | Surface Characterisation (WLI, AFM & SEM), Chris Phillips, Welsh Centre for Printing and Coating |
| 12:30 - 13:00 | Drying Characterisation and Measurement, David Beynon, Welsh Centre for Printing and Coating |
| 13:00 - 14:00 | Lunch |
| 14:00 - 15:00 | Chemical Measurements, Marta Klanjšek Gunde, National Institute of Chemistry, |

| | |
|---|---|
| | Ljubljana |
| 15:00 - 15:30 | Comfort Break |
| 15:30 - 16:30 | An overview about (nano) cellulose based active paqckaging materials., Carmen Freire, University of Aveiro |
| 16:30 | Day Close |
| 17:30 | BBQ/Buffet at Core, Swansea University Bay Campus |

## THURSDAY 14TH JULY

| | |
|---|---|
| 09:00 - 10:00 | Practical Session 1 |
| 10:00 - 10:30 | Comfort Break |
| 10:30 - 11:30 | Practical Session 2 |
| 11:30 - 12:00 | Comfort Break |
| 12:00 - 13:00 | Practical Session 3 |
| 13:00 - 14:00 | Lunch |
| 14:00 | Day Close |

## FRIDAY 15TH JULY

| | |
|---|---|
| 09:00 - 10:00 | Practical Session 4 |
| 10:00 - 10:30 | Comfort Break |
| 10:30 - 11:30 | Practical Session 5 |
| 11:30 - 12:00 | Comfort Break |
| 12:00 - 13:00 | Practical Session 6 |
| 13:00 | Course End |

## 2. Overview of Printed and Coated Functionalities

Tomas Syrový, University of Pardubice

### Biography

Dr. Syrový is author or co-author of more than 25 IF publications (h-index 7) in peer-reviewed journals and he is also the author or co-author of more than 30 contributions at national and international conferences. There are more than 160 citations of his works. He is the author or co-author of functional samples and utility models for production of sensory element, respectively functional layers and structures (antistatic, antimicrobial, security, health care, etc.). He is experienced in R&D in area of functional printing and coating and he also skilled in transfer of printed/coated functionalities to industrial level, including wideweb. Various functional systems such as printed transistors, electrochromic displays, electroluminescent display panels, sensor elements for measuring relative humidity and various gas detection, photovoltaic cells, printed memory elements, different types of conducting, semiconducting and dielectric layers based conductive/semiconductive, dielectric and nanocomposite materials were prepared as part of his research activities. The various types of functionalities were prepared in many cases by own developed printing/coating formulations and technology condition setup. This is also one of the key roles of his participation in the projects and collaboration, i.e. development of printing/coating ink formulations for functional layers given characteristics made by proper printing/coating techniques (screen printing, gravure printing, flexographic printing, pad printing, ink-jet, aerosol jet printing, spray-coating, spin-coating, spiral bar coating, etc.).

He is a member of the OE-A that associates worldwide scientific and industrial organizations in the field of printed electronics. In 2013 got the award of Rector of UPCE for young scientists under 35 years for beneficial cooperation with the printing industry.

### Abstract

The lecture will be focused for an overview on topic of functional structures fabricated by using printing/coating techniques. It will be highlighted differences in comparison to conventional graphic printing as well as FAQ, requirements, pitfalls accompanying functional printing/coating. The next part of presentation will deal about printing substrates, conductive, semiconductive, dielectric and the others materials, including their ink formulation forms. Likewise will be described typical applications from simple functional layers to more sophisticated multilayer devices. In last part of lecture will be presented an overview of printing and coating techniques, their basic parameters and examples of their usage for various applications. At the end of presentation will briefly mentioned selected approaches of drying/sintering/annealing for functional layers.

flexprint

SuBaTex
Energy Harvesting for Smart Textile

# Overview – printed/coated functionalities

ActInPak

cost

Tomáš Syrový
Department of Graphic Arts and Photophysics
tomas.syrovy@upce.cz, +420 604 615 734

**Swansea Early Researcher Summer School 2016**

T A Č R
Technology Agency of the Czech Republic

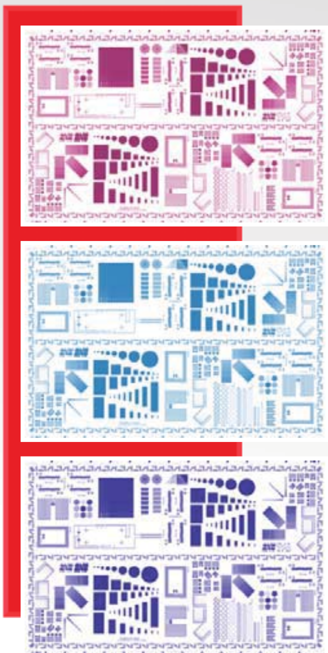
Program **Centra kompetence**

Program **Alfa**

Department of Graphic Arts and Photophysics

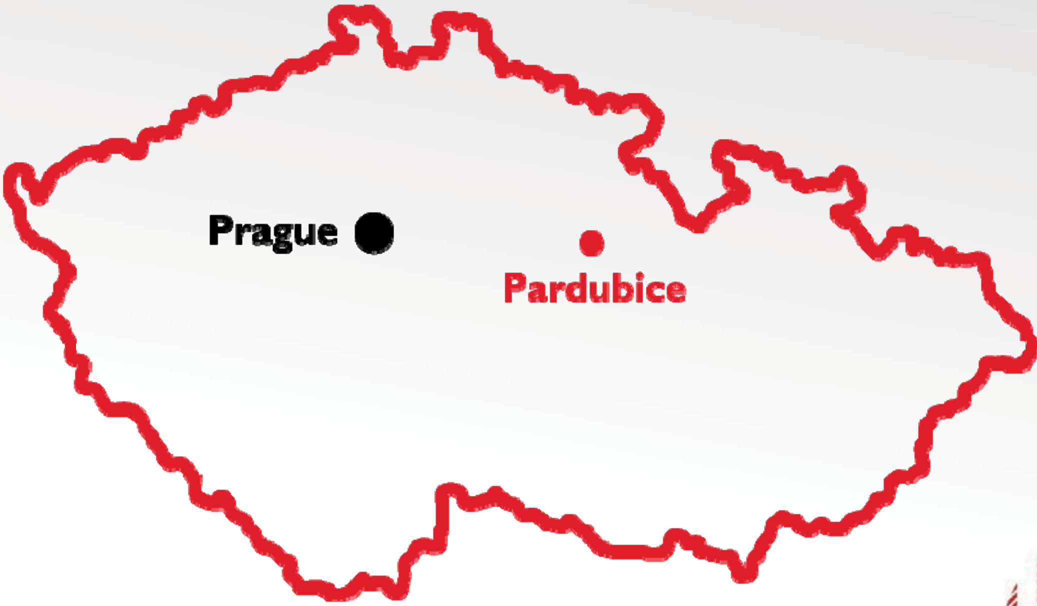
## Agenda

- Interduction of R&D activities
- Challenges and aspects of printed/coated functionalities
- Materials
- Selected devices/functionalities
- Coating techniques
- Printing techniques
- Drying/Sintering techniques
- Conclusion



Syrovy

## Pardubice






## University of Pardubice

- 1950 – Institute of Chemistry
- 1994 – University of Pardubice
- 2014 – 7 Faculties
  - Jan Perner Transport Faculty
  - Faculty of Economics and Administration
  - Faculty of Electrical Engineering and Informatics
  - Faculty of Arts and Philosophy
  - Faculty of Chemical Technology
  - Faculty of Restoration
  - Faculty of Health Studies
- www.upce.cz

# Department of graphic arts and photophysics

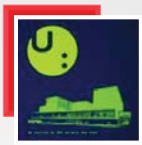
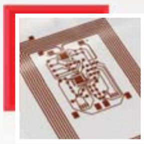
- 1984 – Founded
- 2013 – 170 students
- 10 academicals, 2 researchers, 6 lab. and admin. stuff
- The only department in the Czech Republic providing university studies, research, and testing in the whole field of printing
- Close cooperation with the industry
- Member of IARIGAI, IC (of Educational Institutes for Graphic Arts Technology and Management), OE-A





Department of Graphic Arts and Photophysics

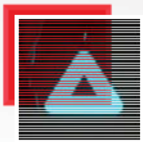
# R&D activities


- Simple functional layers
  - Antistatic, Antimicrobial, Security Luminescent, Photochromic
- Passive components
  - Resistors
  - Capacitors, Coils
  - Etc.
- OECT, OFET
- Printed batteries
  - Alkaline, Li-on

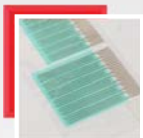






- Sensors
  - Temperature s.
  - Rel. humidity s.
  - Gas s.
  - Air/Gas flow s.
  - Acceleration s.
  - Tactile s.
  - Light s.
- Display elements
  - LEC, OLED
  - Electrochromic
- Smart Labels

With NFC communication over Android devices

- Experiences
  - R&D of Inks & printing/coating technology process
  - Upscaling, Lab2Fab experineces incl. Wide Web
- Core Projects - TE01020022 www.flexprint.cz

TA04010085 - Flexible autonomous energy harvesting systems for smart textiles

Contact: tomas.syrovy@upce.cz, +420 604 615 734

## R&D activities, printing/coating techniques competency

- R&D of technology of preparation of functional structures
- R&D of ink formulation and benchmarking of comercial ink formulation
- Personally 400-800 mixed/tested ink formulations per year for several type of printing/coating techniques and applications

- Screen printing (Sheet fed, R2R)
- Flexo
- Gravure
- Pad printing
- Offset
- IJ
- Spin coating
- Dip coating
- Spiral bar coating
- Spray coating
- Zone casting
- AJP
- Negative patterning – lasers – UV/VIS, NIR, IR

- Lab2Fab experiences
- Narrow web (410 mm), Wideweb production trials, pilot plant trials incl. high speed materiál printing (1.3 m, 320 m/min)



## Why coating and printing technologies?

- The printing and coating techniques should provide cheap and fast production of low cost and low-end functionalities
- Printed/coated functionalities are sometimes tens years behind to products made by traditional technologies in terms of their characteristics

SOMA

## Differences to conventional coating/printing process?

- Safety - printing materials, fabrication process
- Printing/coating materials, printing substrates
- Printing forms
- Interaction of materials
- Strict observance of technology
- Printing/coating process quality/stability
- Post treatment condition
- Storing of the products
- Long term stability
- Never-ending and limitless opportunities to use or characterize anything

Syrovy

(NASA)

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## Printed/coated functionalities

### Active components/structures

- Battery (primary, secondary)
- Battery Charger
- Photovoltaic – PV – (OPV, DSSC)
- Display, Light source – OLED, EL, electrochromic, thermochromic, electroforetic
- Sensor – chemical, bio, climatic, pressure, etc.
- Memory
- RFID
- diodes
- Transistors – OFET, OECT
- ISS – Smart Objects, Smart Sensor, Smart Textiles

### Passive components

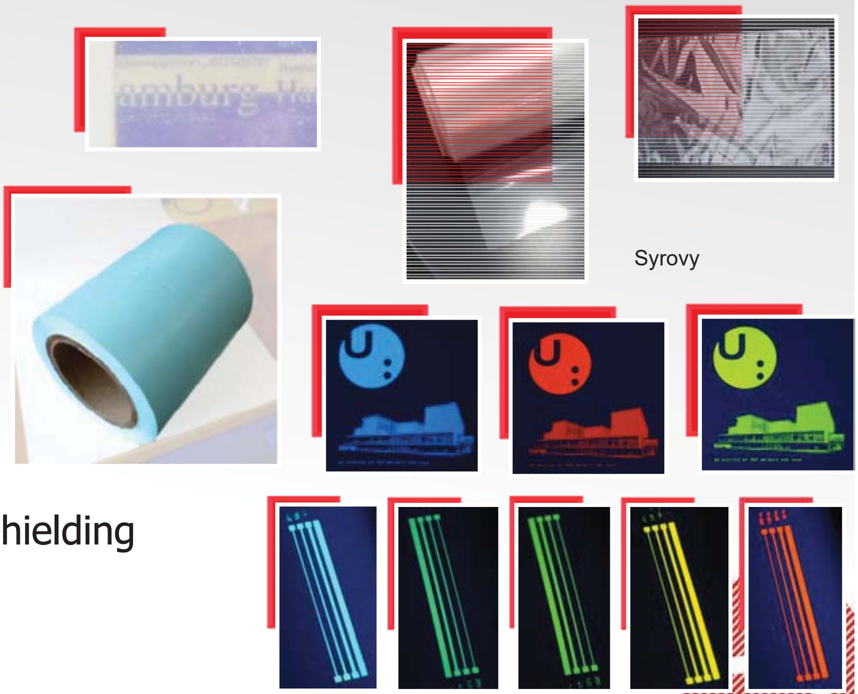
- Electronic circuits
- Antennas – RFID
- Capacitors, resistors, induction coil, transformers

### Functional layers

- Healtcare aplication
- Drugs
- Termochromic, photochromic
- Catalytic layer
- Textile finishing layers
- Explosives

## Simple functional layers

- Antistatic
- Antimicrobial
- Barrier
- UV protective
- Luminescent
- Thermochromic
- Photochromic
- Electromagnetic shielding

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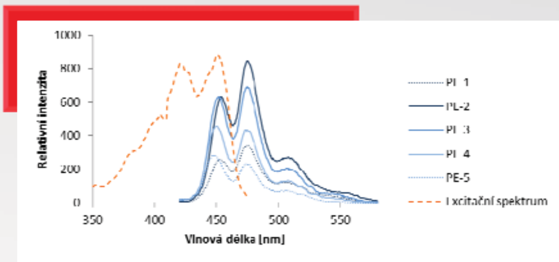
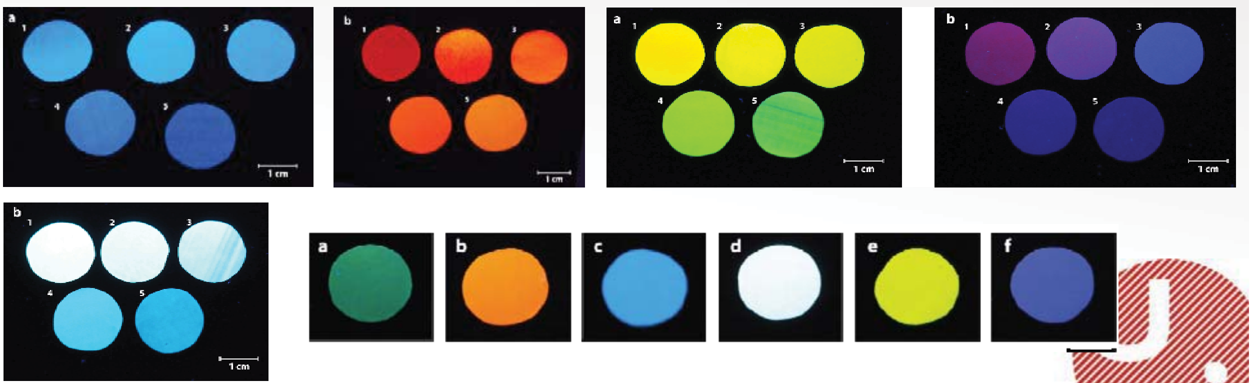
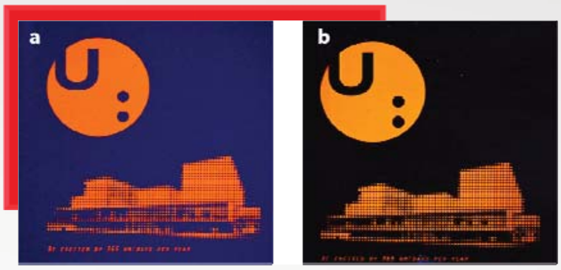
## Luminiscent materials

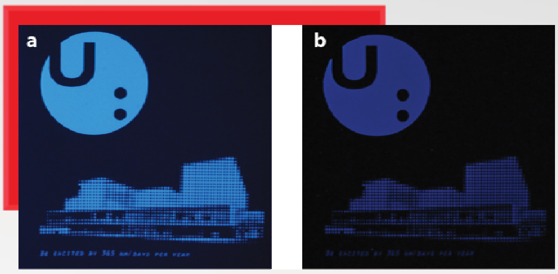
- R&D of specific effect layers
  - Fluorescencent

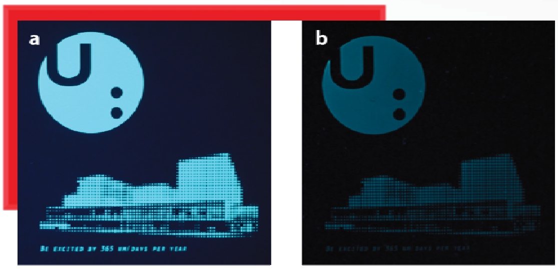


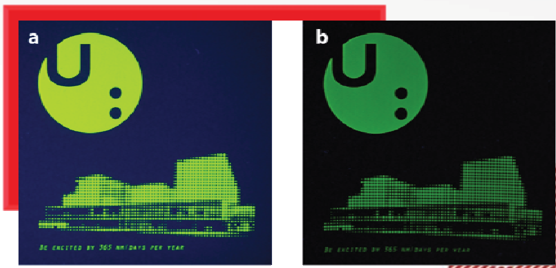



# Luminiscent materials - Fluorescence

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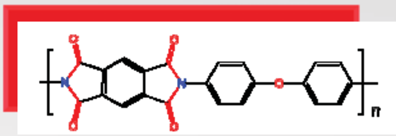
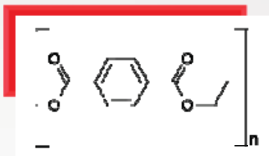
# Substrates for printed functionalities/electronics

- Flexible
  - PET, PEN, PI (Kapton, Neopulim), PC, PVC
  - Polyolefins - PE, PP
  - Synthetic papers – Pretex (PES/PA), Synaps (PES), Tyvek (HDPE), Teslin (polyolefin)
  - Paper – un/coated paper, primer
  - Nanocellulose
  - Glass – 25 to 100 µm
  - Metals
- Rigid
  - Paper - heavy ream weight
  - Cardboard
  - Thick polymeric susbtrate (PET, PEN, PI, PC, PE, PP, etc.)
  - Glass – float, quartz, etc.
  - Ceramic – $Al_2O_3$ (Rubalit, Alunit), AlN, etc.
  - Metals



Polyimide

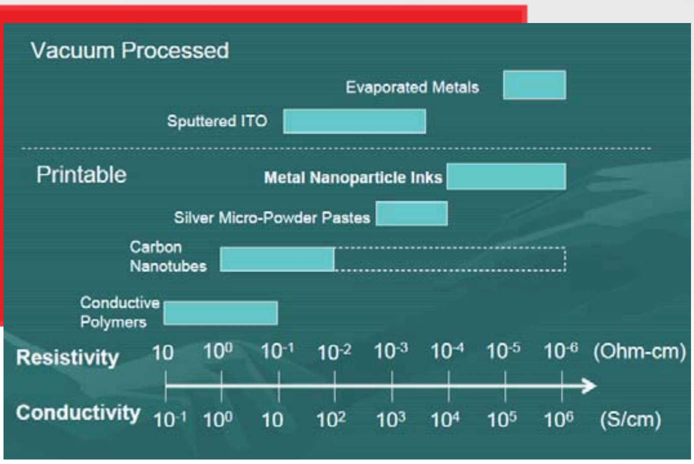


PET

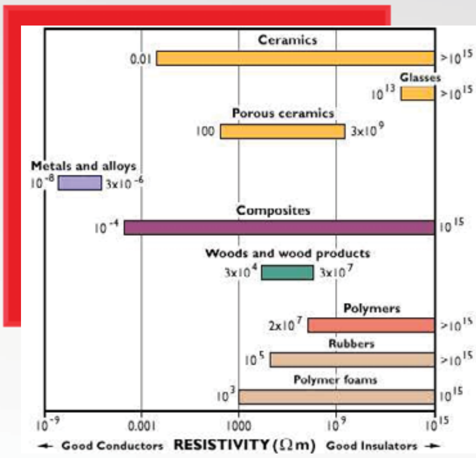
Ultra-Thin Glass - SCHOTT

CeramTec

# Materials for printed/coated structures




Yang

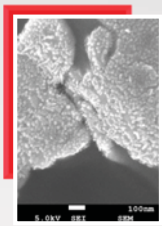


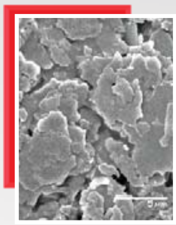

www.lehigh.edu

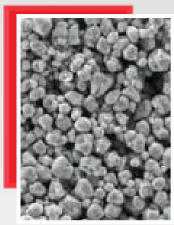


# Materials for printed/coated structures

- Conductive
  - Metal composite – based on (Ag, Cu, Au, Ni, Pt, etc.)
    - Different shape and sizes of particles (globular, flakes, rods, wires)
    - Ag based most used
      - Up to 30 % of conductivity of bulk Ag
    - Cu – usually based on precursors CuO
      - Photonic sintering, reduction agents
    - Other metal for specific purposes
  - High temperature firing – Ag, Au, Pt, etc.
  - Precursors of metals
  - Carbon composite (graphite, carbon black, etc.)
  - Carbon based (graphene, GNP CNT (SWCNT, MWCNT))







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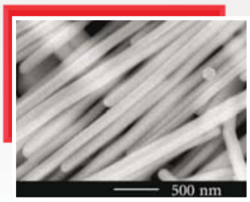


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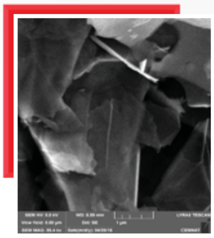

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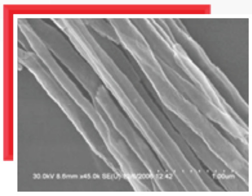
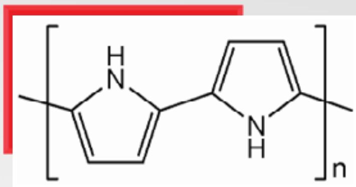


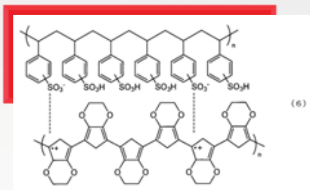
mntl.illinois.edu

## Materials for printed/coated structures - (Semi)conductive

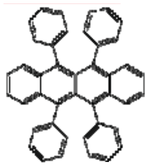
- Polymers
  - PEDOT:PSS – (in-situ 3000 S/cm, disp. 1000 S/cm)
  - Polyaniline
  - Polyacetylene
  - Polypyrrole
  - Polythiofene
  - MEH-PPV
  - PVK, etc.
- Small molecules
  - TIPS - Pentacene
  - Rubrene
  - Phtalocyanines
  - Diketopyrrolopyrrole
  - Perylenes
  - Alq3, NPD, TPD, Ru cpx
  - Some others
  - Fullerenes

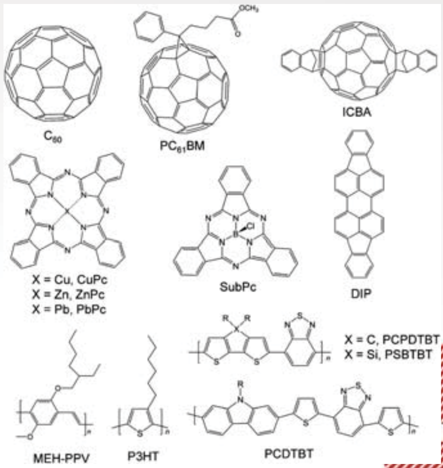


polypyrrole



PEDOT:PSS






2014, Xue et Al.

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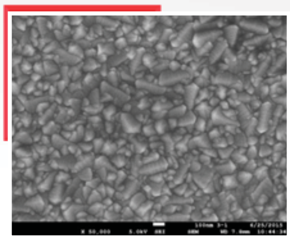
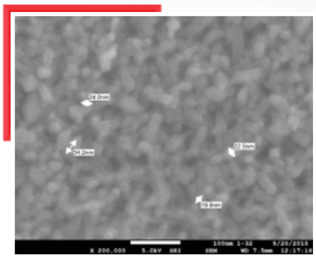
## Materials for printed/coated structures - semiconductive

- Inorganic semiconductors
  - ZnO, ZnS, $As_2S_3$, $TiO_2$, $WO_3$, $MoO_3$, etc.
  - Si dispersions
  - **TCO**
    - Sn doped oxide s ITO, FTO, ATO
    - Zinc doped oxide AZO, GZO
    - Mainly as a transparent conductors
    - Prepared by sol-gel, nanoparticles ink, CVD

ITO/PET
www.opticalfiltersusa.com/



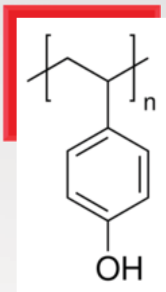
ITO



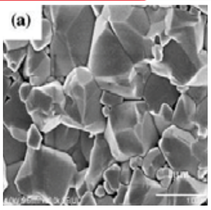
$TiO_2$

# Materials for printed/coated structures - dielectrics

- Polymer based
  - From solution/dispersion of various polymers
    - PVC (ε′ ~ 3)
    - PC (ε′ ~ 2.8 – 3.4)
    - PVDF (ε′ ~ 6)
    - PMMA (ε′ ~ 3)
  - Radiation induced polymerization (UV, EB) (Acrylate based (ε′ ~ 3))
  - Thermally induced polymerization (PVP, acrylates with proper iniciators)
- Composites
  - Based on particles of inorganic materials with high dielectric constant
    - $BaTiO_3$ (ε′ ~ 1000)
    - $SrTiO_3$ (ε′ ~ 300)
    - $TiO_2$ (ε′ ~ 100)
    - $Al_2O_3$, MgO (ε′ ~ 9)
    - $HfO_2$ (ε′ ~ 20)




Poly(4-vinylphenol)




Kharisov et Al.

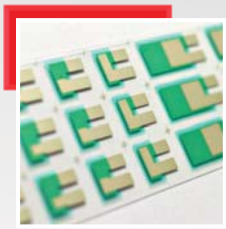


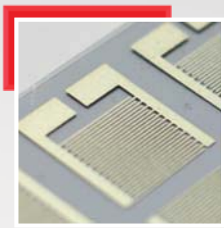
# Passive electronic components

Resistors

Capacitors

Circuits and conductive structures





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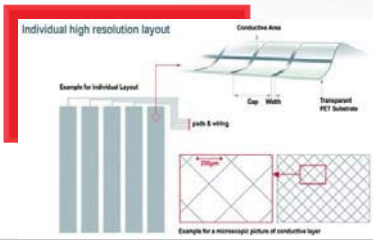
Transparent conductive electrode

- (Semi)conductive polymers
- CNT, graphene based layers
- Metals nanowires layers
- high-resolution conductive metal (metal mesh)

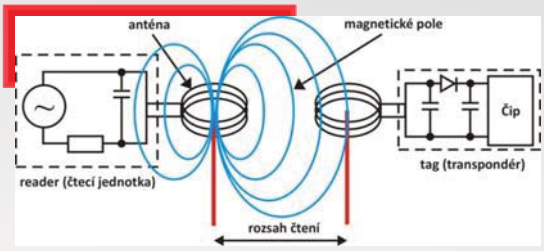
Syrovy



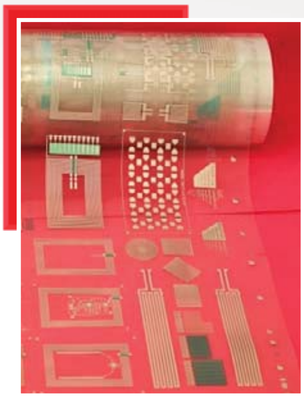

PolyIC

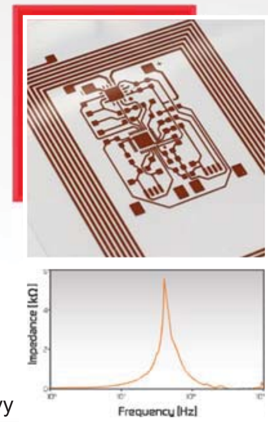
# RFID

- RFID (Radio Frequency Identification) – system which through the radio-frequency electromagnetic fields transfer data, usually for the automatic identification and tracking tags attached to objects.
- The datas are stored inside tag. These datas is possible to read or rewrite in dependance to type od tag.
- Every TAG has an unique EPC.
- Implementation of RFID requires except tag, readers and „middleware" (Central systém for data exchange, storing, it is gate to MIS)




(Hrachovcová)






Syrovy



# RFID – type of TAGs

## Active TAG

- Battery is a main source of the energy, which limit lifecycle.
- This type of TAG is usually equiped by MCU, sensors, I/O ports.
- It is used for more advance type of aplication – ISS. Usually has a higher price due to more complicated production than for passive tags.
- Tag start the communication as a first, followed by response of reader, peridodically transmits its ID signal.
- The active tags are used for identification, localization of fast moving object too.
- The read distance is in range of hundreds meters.

## Semi-active TAG

- For transfer of datas use energy emmited by readers. Communication is activated by reades, the battery source is used for data transfer to higher distances.
- The read distance is in range of tens of meters (UHF, MW).
- Identification, localization of fast moving object.
- Longer lifecycle than for active tag.

# RFID – type of TAGs

## Passive TAG

- The communication starts reader.
- Energy for communication is obtained from electromagnetic filed generated by reader.
- Low cost, more simple structure, durability and resistance to extreme condition (temperature to 200 °C, acids, bases)
- The passive tag consist from antenna and chip. At higher frequencies there are difficulties with interferences and identification close to metals and liquids.
- The passive tags are cheaper and smaller in comparison to active tags.
- Usability –logistics (material flow), personal ID cards, passports, credit cards, identification of vehicles, animals, books in libbraries

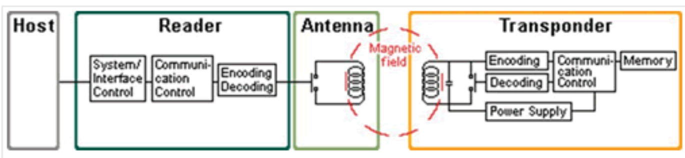



Figure 1. RFID System--Reader/Writer, Antenna, Tag

2012, Schmoldt

Department of Graphic Arts and Photophysics

# RFID – Frequencies

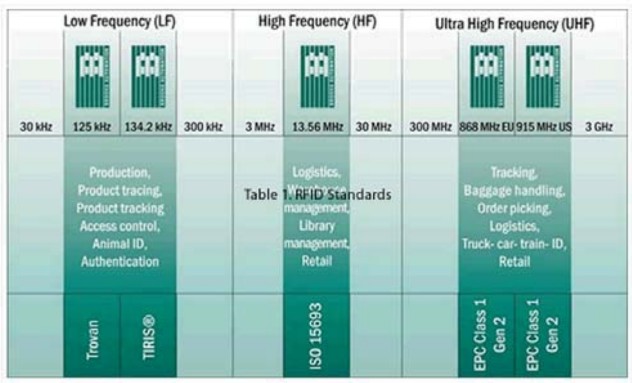



Table 1. RFID Standards

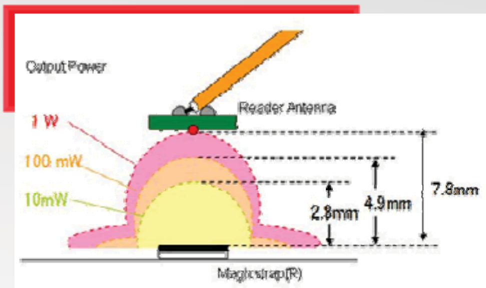



Figure 3. Output Power versus Read Range

2012, Schmoldt

- Read distance – Induction (Near Field Comunication), reflection (Far Field)
- Memory - Tag RO (Read-Only), Tag WORM (Write Once Read Many), Tag RW (Read-Write)
- Class – according abilities, Class 0 - 5

## RFID - Frequencies

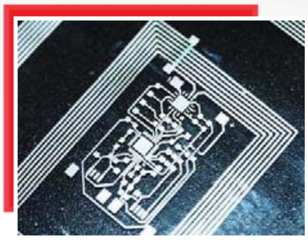
| | |
|---|---|
| **Low Frequency**<br>125 a 135 KHz<br>LF Tag | - Read distance up to 0,5 m, low communication speed<br>- High cost of production<br>- no difficult to read when placed within a few millimetres of a metal or liquid surface<br>- ID card, animals identification |
| **High Frequency**<br>13,56 MHz<br>HF Tag | - Read distance up to 1 m, moderate communication speed<br>- High cost of production<br>- Difficulties with reading through the liquid<br>- logistics, identification of goods |
| **Ultra High Frequency**<br>868 MHz<br>UHF Tag | - Read distance up to 3 m, high communication speed<br>- Low cost production<br>- Difficulties with reading through the liquid and metals |
| **Microwave**<br>2,45 a 5,8 GHz<br>MW Tag | - Read distance up to 10 m<br>- identification of fast moving objects<br>- High cost of tag |

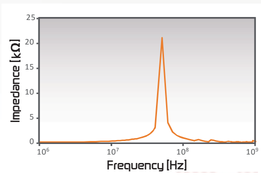


## RFID – Production

- Etching Cu, Al (18 – 35 µm)
- Galvanic metallization of vacum evaporated/sputtered structures
- Laser ablation – negative patterning
- Printing technique
  - Silver, copper (precursor) based inks
  - Screen printing – the most used
  - Gravure
  - Flexography

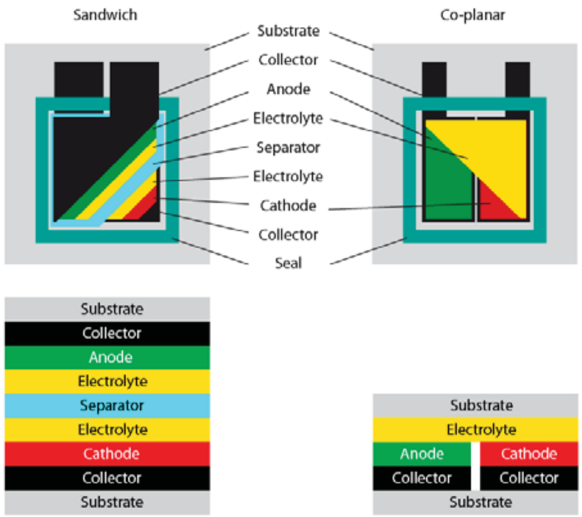
OTK Group





# Printed batteries

- Based on typical materials and chemistry as for conventional batteries
- Flexible, Thin - usually below 1 mm
- R2R compatible production process
- Capacity in range of tens of mAh
- Voltage in dependence to electrode materials and electrolytes
- Basic patrameters – Nominal Voltage, Capacity, short-circuit current, UI characteristics
- For device with low consumption of electrical energy < 1 mW
- Usage – ISS, RFID, sensors, chip cards, etc.




Syrovy



# Printed baterries, accumulators - materials

## Primary

- $Zn/MnO_2$ Zn + 2MnO + $H_2O$ ZnO+ 2MnO(OH)
- Electrolyte $ZnCl_2$, $NH_4Cl$, KOH, NaOH, thickener (PEO, CMC, HEC)
- 3V battery

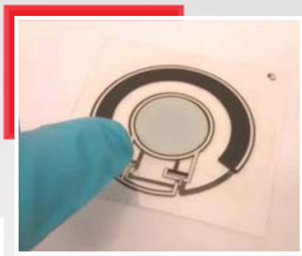
| | |
|---|---|
| Enfucell | 10 mAh@4 mAh/cm$^2$ |
| Fraunhofer ENAS | 8 mAh@1 mAh/cm$^2$ |
| Blue Spark | 5 mAh @ -- mAh/cm$^2$ |
| Flexprint | 11 mAh@1.7 mAh/cm$^2$ |

- $Zn/Ag_2O$ Zn + $Ag_2O \rightarrow$ 2 Ag + ZnO

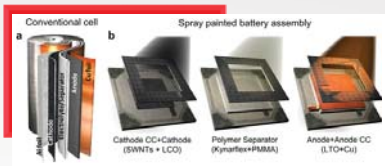
## Rechargeable

- Lipol battery
  Anode $LiCoO_2$, $LiMn_2O_4$, cathode Li, electrolyte Li salt + polyethylene oxide
  $Li_{1-x}CoO_2 + x\,Li^+ + x\,e^- \rightarrow LiCoO_2$
- All-solid polymer lithium (ITSUBO/Hatanaka), 45 mAh, operation voltage 1.8 V
- Nickel metal hydride
  Alloy(H)+ 2 NiOOH $\rightarrow$ Alloy + 2 $Ni(OH)_2$
- Varta 32 mAh


Blue Spark



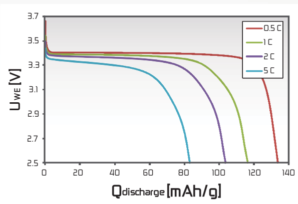
Syrovy. Fraunhofer ENAS




(Singh at Al.)

ITSUBO

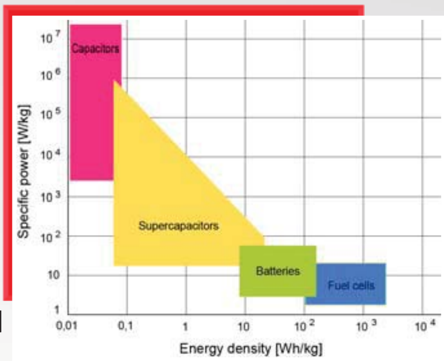
Varta




Syrovy

# Supercapacitors, Hybrid capacitors

- Charge/discharge current is in range 1-100 A.
- Very low value of internal resistance
- 10 times higher energy density in comparison to clasic capacitors.
- Charging time is in orders shorter to batteries.
- Capacity is directly proportional to the area and inversely proportional to the distance between the electrodes
- Capacity is given by electrodes materials too.
- Usability – ISS, RFID, sensors, chipcards, etc.
- Basic patrameters – Nominal Voltage, Capacity, short-circuit current, UI characteristics



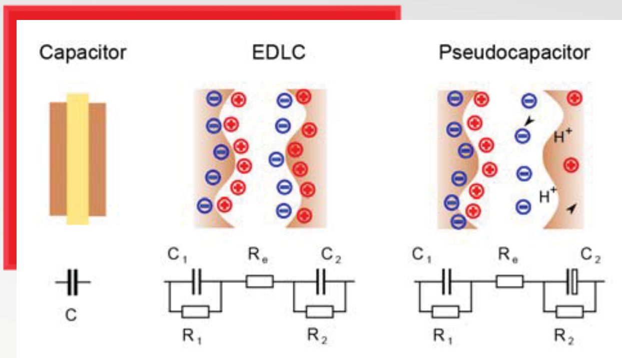

Dvorak

| Parameter | Batteries | Capacitors | Supercapacitors |
|---|---|---|---|
| Energy density [Wh/kg] | 100 | 0,2 | 10 |
| Specific power [kW/kg] | 1-3 | 500 | 10 |
| Charging time | 5 h | 0,001 s | 10 s |
| Life cycle | 100 | 1 000 000 | 1 000 000 |

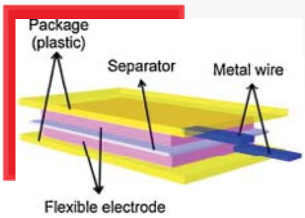


# Storage principles

- Pseudocapacitance storage of the electrical energy based on reversible redox reactions with charge-transfer.
- EDLC (Electric Double Layer Capacitor) Based on separation of charge in a Helmholtz double layer.




Dvořák



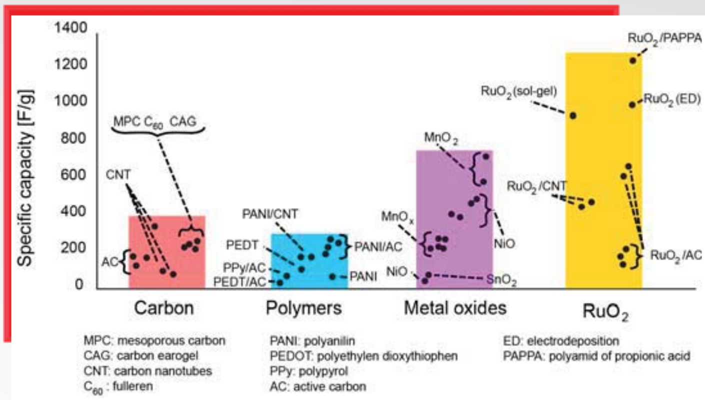

ScienceDirect

Syrovy

# Electrode materials, electrolytes

## Electrode materials

- Carbon based materials with large specific surface (> 1000 $m^2/g$)
- (Semi)conductive polymers
- Metal oxides




Dvořák

## Electrolytes

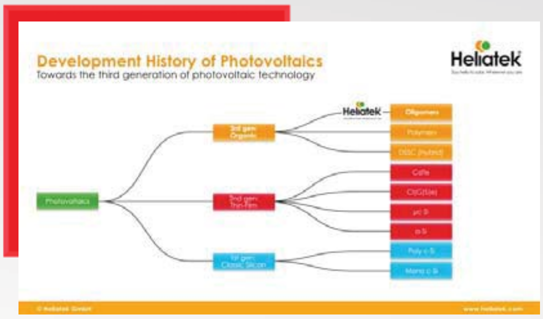
- Water based solution of acids ($H_2SO_4$. $H_3PO_4$), bases (KOH) and salts ($NaClO_4$, $LiClO_4$, $LiAsF_6$)
- High specific conductivity (100-1000 mS/cm), Low operation window ~ 1 V per electrode, low operation temperature.
- Organic solvents – the most often solvents are propylene carbonate, ethylene carbonate, tetrahydrofuran, diethyl carbonate, γ-butyrolactone. Salts - $LiClO_4$, $Et_4NPF_6$, $Bu_4NPF_6$.
- An advantage of organic solvents is higher operation voltage (up to 4 V). The electrical conductivity of electrolytes based on organic solvents is lower (10 to 60 mS/cm). Energy density increases with the square of the voltage.



# Photovoltaic cells

## DSSC

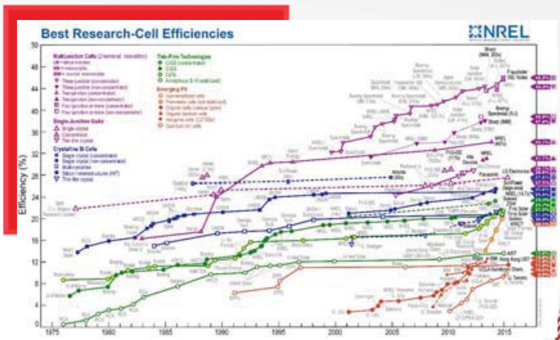
- „Grätzel cell" – 1991
- High efficiency up to 12 %
- 2014 DSSC with perovskite up to 20.5 %




Heliatek

## OPV

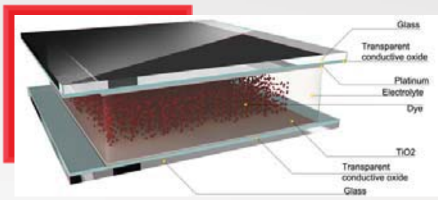
- Commercial avaiable from 2009 with Wp 1 – 28 W
- Efficiency at 12 % is comparable with 15 % for conventional Si panels
- Integration of OPV from 2010

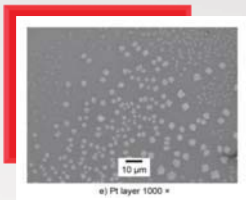


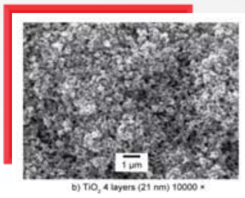

NREL

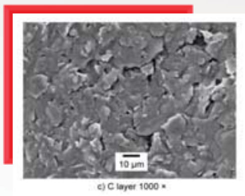
# DSSC - materials

- Photoelectrode $TiO_2$, $ZnO$, $Fe_2O_3$, $ZrO_2$, $Nb_2O_5$, $Al_2O_3$, $CeO_2$, $SrTiO_3$, $Zn_2SnO_4$
  - Shapes of particles - globular, microsheets, nanorods, nanotubes, nanorods
- Sensibilizing dyes
  - Bipyridyl ruthenium complex
- Counter electrode
  - Platinum ($H_2PtCl_6$)
  - Carbon based (graphite, CNT)
  - (Semi)conductive polymers
- Electrolytes
  - Liquid, gel, solid state
  - redox systems $I/I_3^-$, $Br^-/Br_3^-$, $SCN^-/SCN_2^-$, $SeCN^-/SeCN_2^-$, 1-hexyl-3-methylimidazolium iodide
  - Acetonitrile, propionitrile, methoxyacetonitrile, NMP, EG, etc.
  - polyethylene glycol (PEG), 1,3:2,4-di-O-dimethylbenzylidene-D-sorbitol (DBS), poly(acrylic acid)-poly(ethylene glycol) (PEG-PAA), polyvinylpyridine (PVP), polyacrylonitrile (PAN)



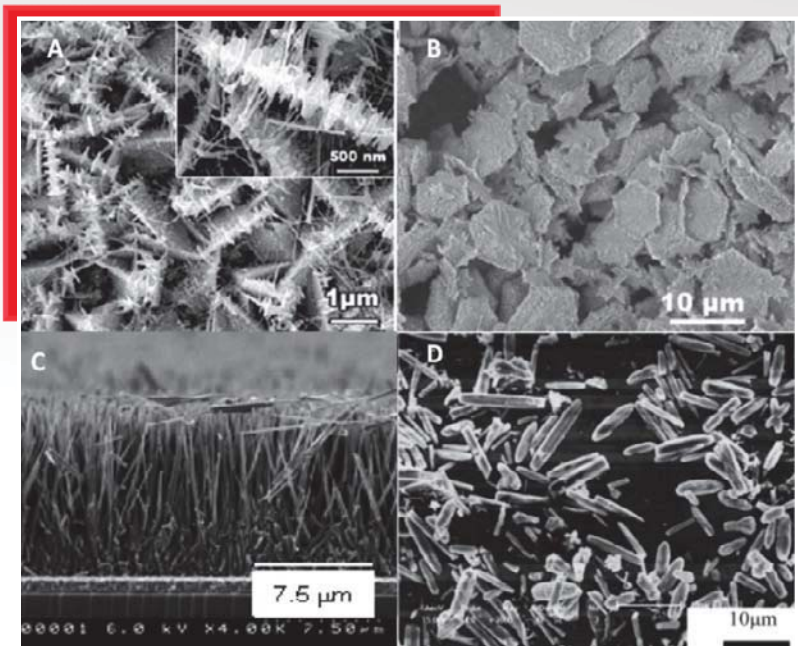




Syrový et Al.

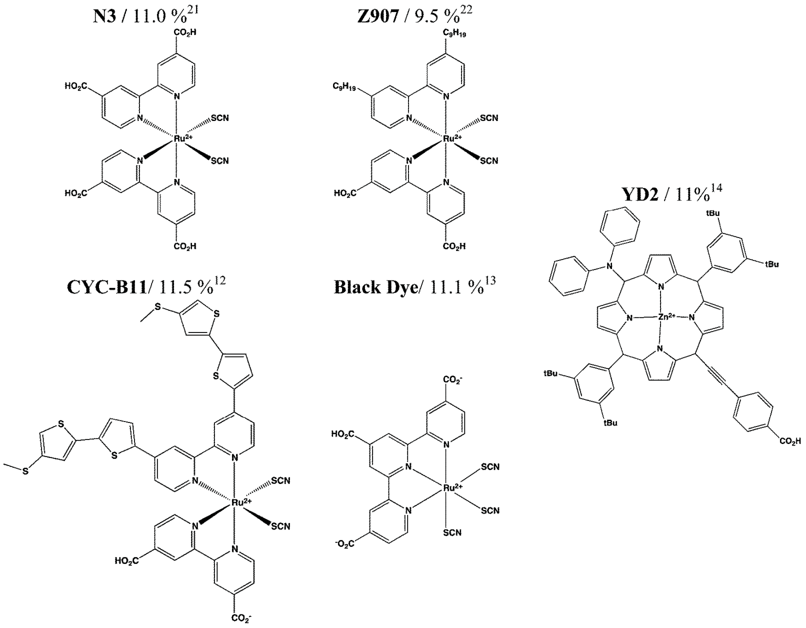


# Photoelectrode

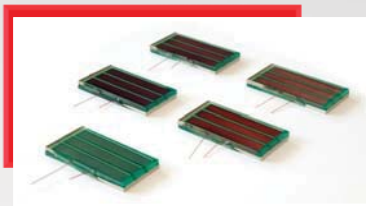



Xu et al., 2010;
Wang et al., 2010;
Gao et al., 2007;
Pang et al., 2007

# Sensibilizing dyes




Le Bahers et Al.

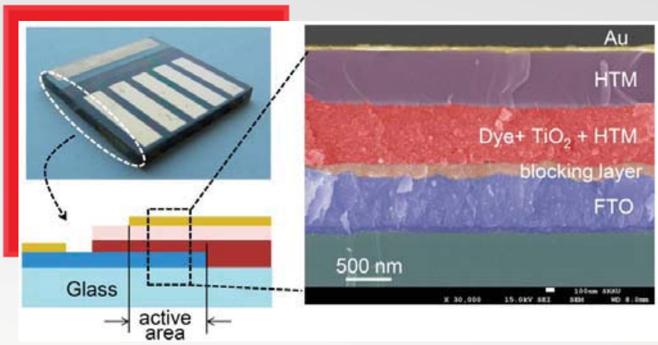


Hatala, Syrovy

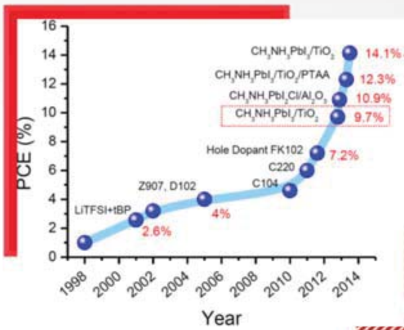
Department of Graphic Arts and Photophysics

# DSSC with perovskite

- In 2009 3.8% efficiency
- Based on $TiO_2$, $Al_2O_3$ photoelectrode
- Perovskite acting not only as a light absorber, but as a charge-carrying semiconductor
- Organometal halides $CH_3NH_3PbI_3$ with perovskite structure
- efficiency approaching 20% is realistically possible from a solid-state mesoscopic solar cell based on CH3NH3PbX3
- In tandem cells with silicon based panel efficiencies should be expected 30% or more
- Extremely sensitive to oxygen, water vapor dissolves the salt like perovskites

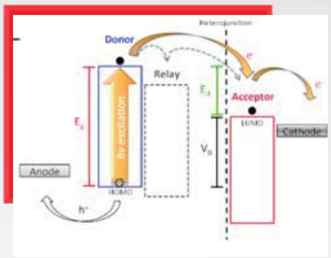



Park

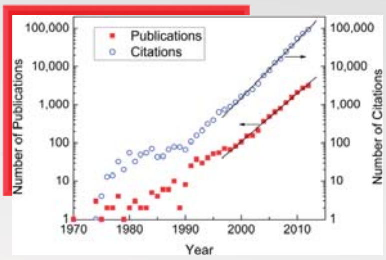


# OPV

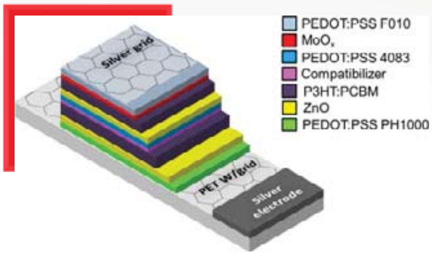
- Based on p-conjugated small molecules or polymers
- Typical energy gaps of 1 to 3 eV between LUMO and HOMO
- Power conversion efficiency (PCE, ηP) has steadily increased over the years from about 6% to 14%



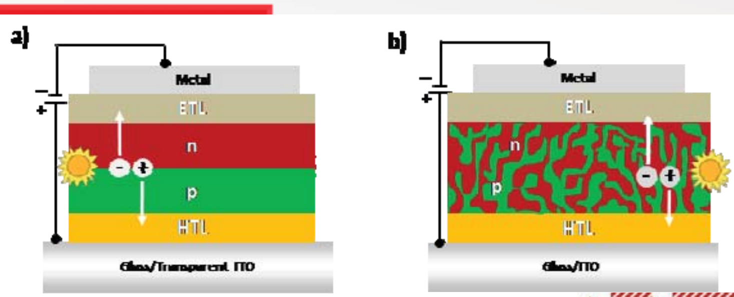

2014, Bessette




2014, Xue et Al

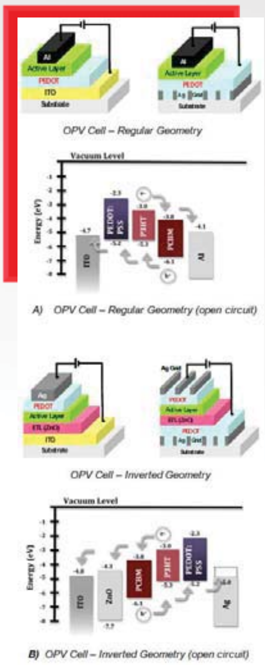



2014, Andersen

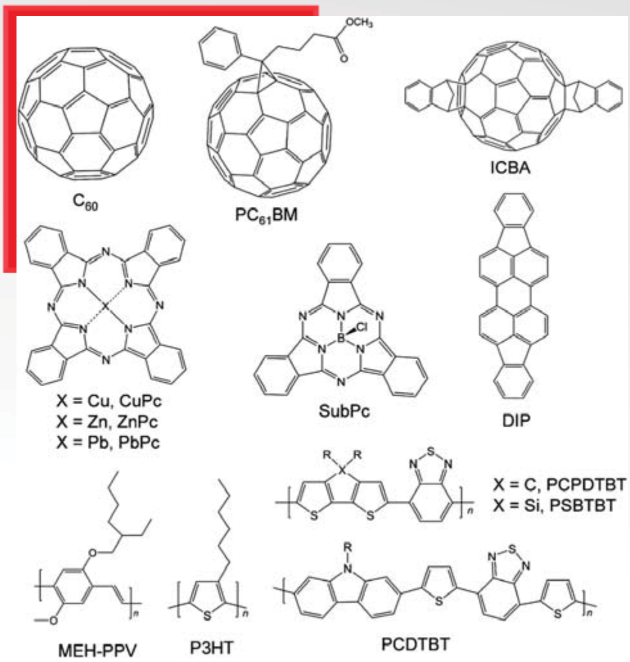





# OPV - materials



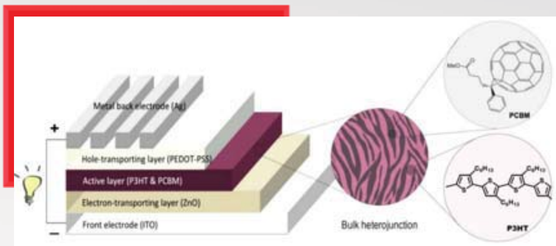

Vanmaele



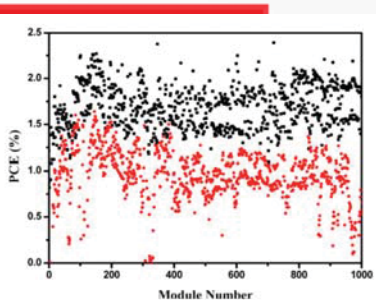

2014, Xue et Al.

## OPV R2R fabrication

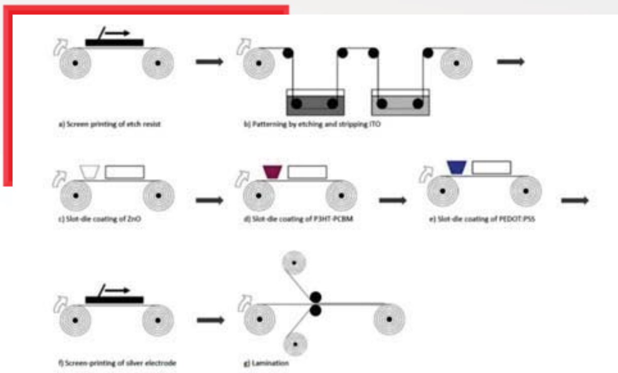
- Typical eficiency ~ 2 %
- Project in progress to achieve 4-5 % efficiency in R2R process.
- Lifecycle 1-2 years




2014, Xue et Al.




2011, Krebs

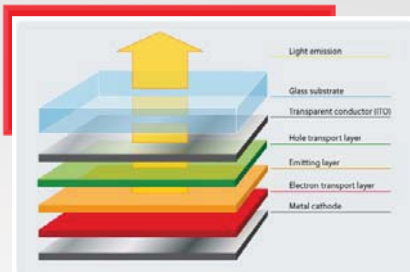


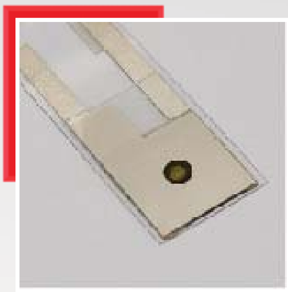
2012, Lauritzen



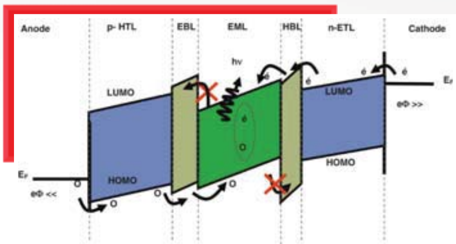
## OLED

- Several types called PMOLED, AMOLED, PHOLED, WOLED, FOLED, TOLED, SOLED
- High efficiency 50.7 lm/W at 1000 cd/m$^2$, 140 lm/W for SOLED
- Up to 200 000 cd/m$^2$

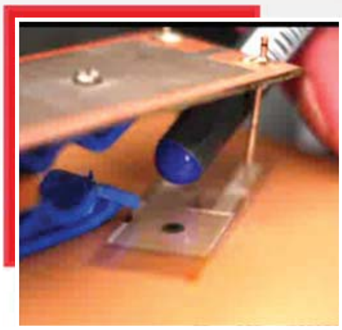


Novaled



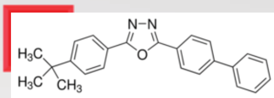

Guaino



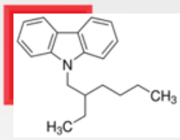
Syrovy

# OLED – materials

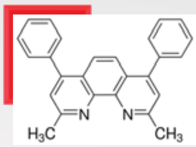
- Cathode – Al/Li, Ag/Mg, LiF/Al/Ag, LiF/Al, Ca/Al
- ETL – Bphen, Alq3, BCP, PBD, PVK, EHCz, TAZ
- EML – $Alq_3$, Alq3/TPP, Rubrene, PtOEP, MEH-PPV, $F_2Irpic$, QD
- HTL – HMTPD, TPD, NPD, PVK, CBP, TAPC



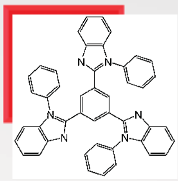
Butyl-PBD



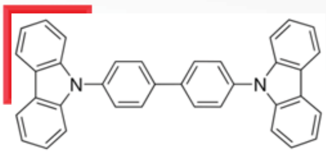
EHCz



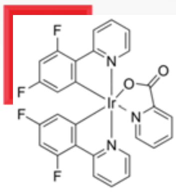
BCP – Bathocuproine



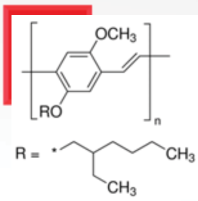
TPBI



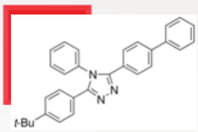
CBP



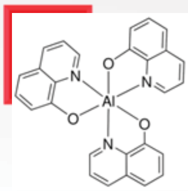
$F_2Irpic$



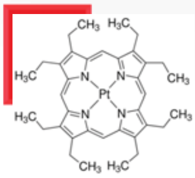
MEH-PPV



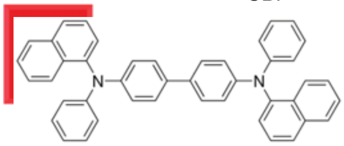
TAZ



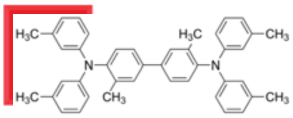
Alq3



PtOEP



NPD



HMTPD

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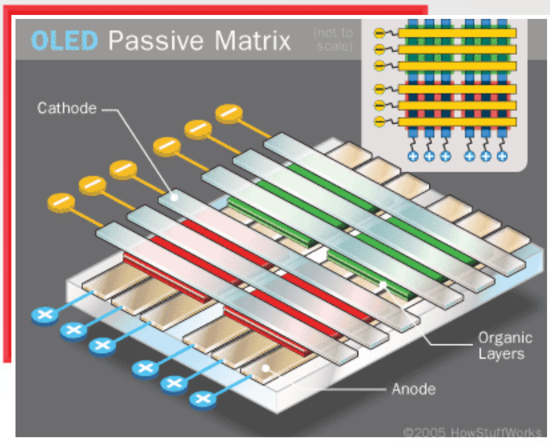
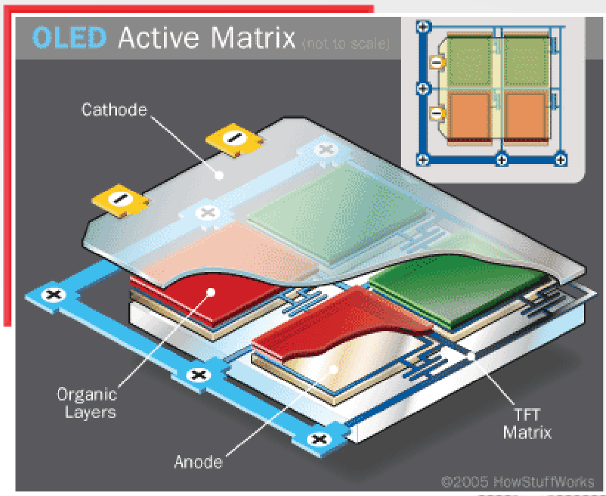
# OLED

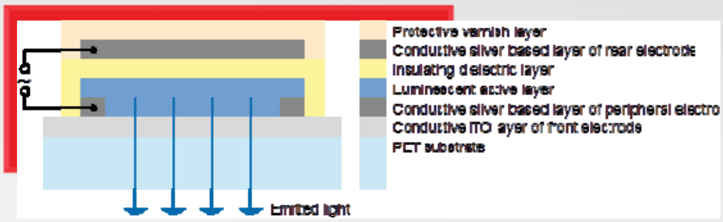



HowStufWorks



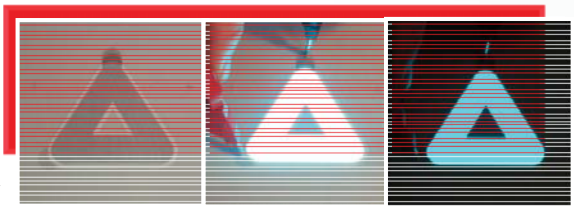
# Light emmiting capacitors - LEC

- Based on doped luminofors of ZnS, SrS, etc.
- High efficiency up to 37 %, rsp. 160 lm/W, low consumption 34 W/m$^2$
- Life cycle > 12 500 hour
- Backlight for advertising displays, decorative lighting, security lighting, backlighting dashboards.




Syrovy

Syrovy



Syrovy

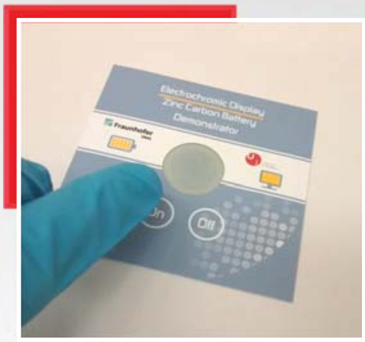


# Electrochromic, electroforetic displays

## Electrochromic displays

- Switching of redox states generates new or different visible region bands.
- Metal oxide films – $WO_3$, $MoO_3$, $V_2O_5$ $Nb_2O_5$, $Ir(OH)_3$
- Conducting polymers (PEDOT:PSS, PANI, PPY, Polythiophenes)
- Dyes (Ethyl Viologen, heptyl viologen, Prussian blue, Phthalocyanines)

Guaino

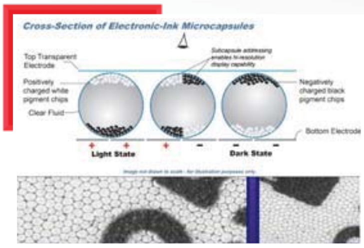




Syrovy, ENAS

## Electroforetic displays

- Reflective displays
- Based on bistable states
- Low consumption
- Encapsulated pigments




AMEPID

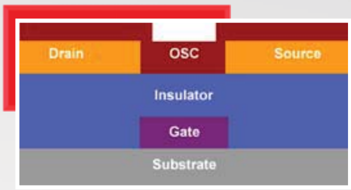
Eink

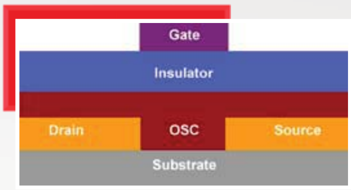
# OFET

- Based on formation of a conduction channel between source and drain at the insulator-semiconductor interface
- Solution processed, low temperature manufacturing
- Two main architecture – Top-Gate and Bottom gate
- The main parameter is mobility (graphene 3900 $cm^2/Vs$, Si 1450 $cm^2/Vs$, organics 1-40 $cm^2/Vs$)

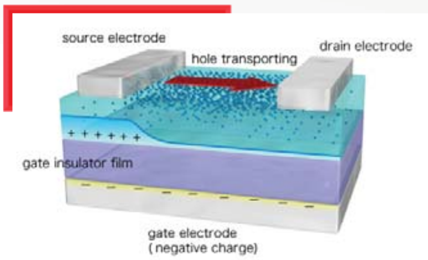
## Challenging factors

- Mobility Performance
- Switching characteristics
- Process-ability
- Solubility
- Long-Term Stability
- Facilitate Hopping Process
- Impurity charge traps




Silvaco

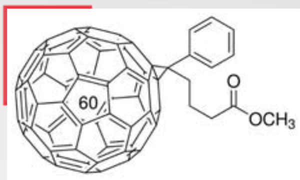



Kyushu University

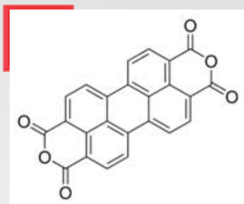


# OFET – materials

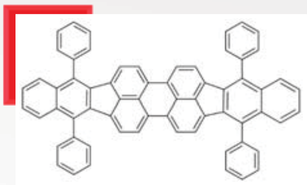
- n type – PTCDA, PCBM, DBP, BBL
- p type – P3HT, PQT, PTAA, TIPS pentacene, CuPc, Caronene, Rubrene
- Dielectric – PMMA, PS, etc.



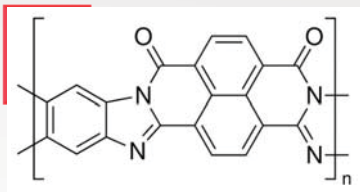
PCBM



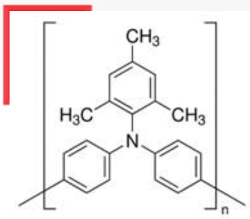
PTCDA



DBP

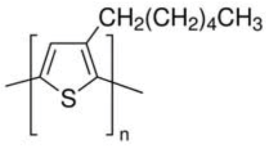


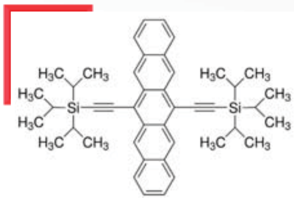
BBL



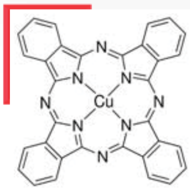
PTAA

P3HT





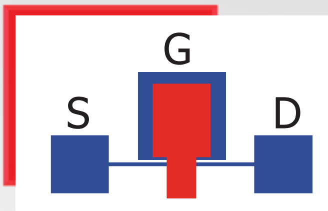
TIPS P.

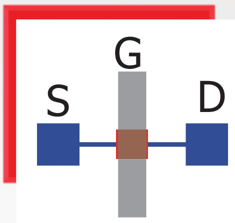


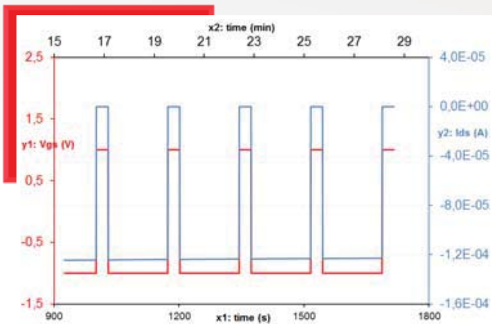
CuPc

# OECT

- Switching of redox states of channel affects Ids, resistivity of channel respectively.
- Two main architecture – Latteral, sandwich
- Low voltage operation, On/OFF up to $10^5$
- Response time in ms




Syrovy



# Sensors

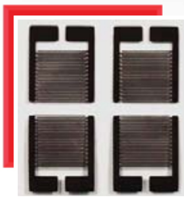
- Temperature
- Relative humidity
- Gas detection – $NO_2$, $SO_2$, $H_2$, $NH_3$, $H_2S$, Ethylene, hydrocarbons
- Movement sensors, acceleration sensors
- Tactile sensors, pressure sensors
- Light sensors
- Biosensors
- Electrochemic
- Microfluidic





Syrovy





# Others printed functionalities

## Printed memory

2013, Jung

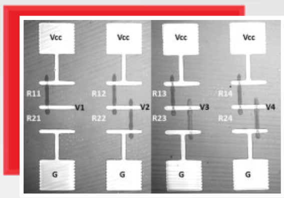
- ROM, WORM, NVRAM

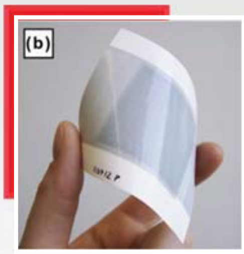
## Printed speakers

- Electromagnetic induction
- Piezoelectric

## Electro active polymers

- Artificial muscles
- Tactile sensors
- Haptic feedback
- Tactile displays „artificial skin"
- Energy generator



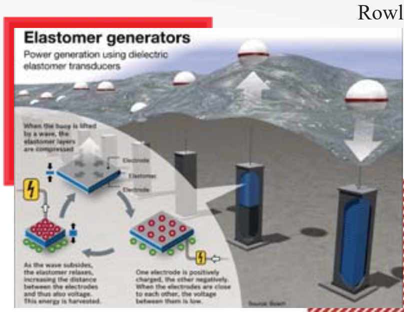



Hübler

Rowland

OE-A

Heydt



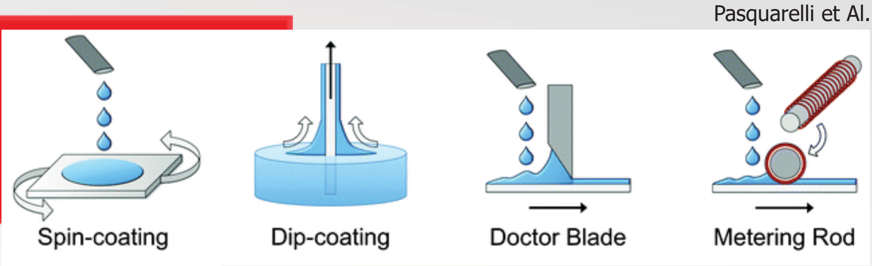

Bosh

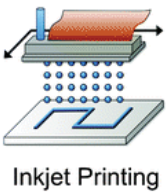


# Coating and printing techniques – laboratory

- Spin coating
- DIP coating
- Doctor blade, Bar Coating
- Spray coating
- Ink-Jet
- Aerosol printing
- Electro-Hydrodynamic and Reciprocating System

Pasquarelli et Al.



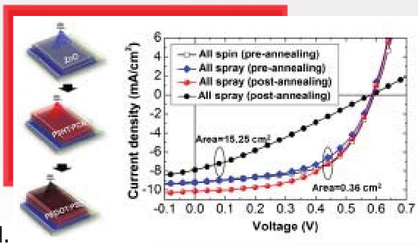


Optomec

## Laboratory scale Printing/Coating techniques in photovoltaics

- Spin Coating. Spray Coating, Blade Coating, Spiral Bar Coating
  - DSSC – $TiO_2$ photoelectrode, counter electrode
  - OPV – HIL layer, ETL, BHJ layer
  - Transparent conductive layers
  - Metal bus bars, wiring


PEMS




Kang et al.

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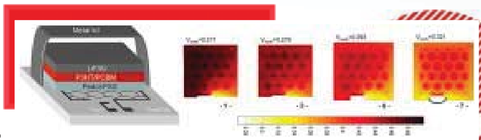

Yulia Galagan et al.

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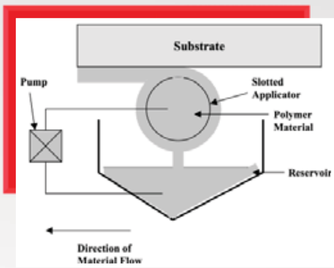
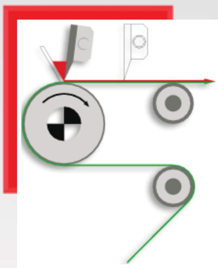
## Coating techniques

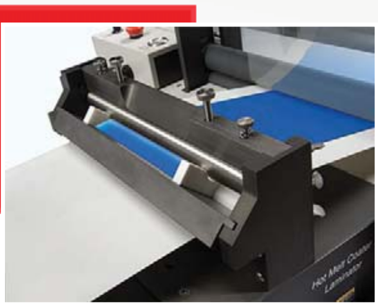
- Knife-over-edge/Blade coating
- Mayer Bar, Spiral Bar Coating, Stripe coating
- Meniscus coating




www.3dit.de



Coatema

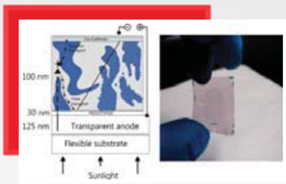


www.chemsultants.com

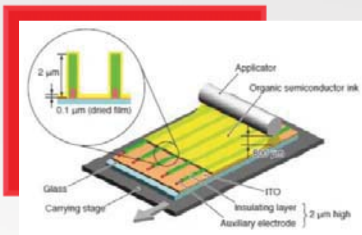

PEMS Co.,Ltd

# Coating techniques

- Knife-over-edge/Blade coating, Mayer Bar, spiral bar coating
  - DSSC – $TiO_2$ photoelectrode, counter electrode, gel electrolyte
  - OPV – HIL layer, BHJ layer
  - OLED – emissive layer, transparent and rear electrode
  - Sensors – gas, bio
  - Batteries – electrode material, electrolyte
- Meniscus coating
  - Photoelectrode - $TiO_2$
  - Transparent conductive layers
  - Sensors




Wengeler et Al.




Toshiba

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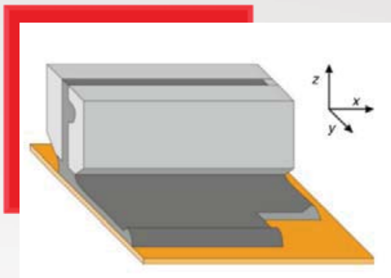
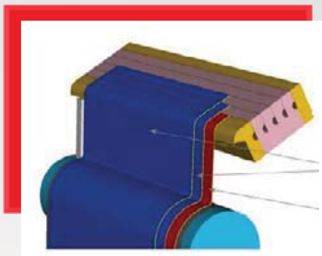
# Coating techniques

- Slot Die
- Curtain coating
- Multiple slot
- Slide coating




Schmitt et Al.



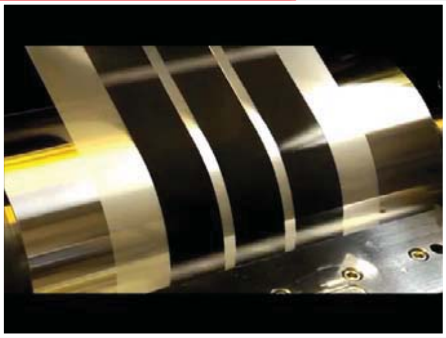
www.packaging-int.com

plasticphotovoltaics.org

| | |
|---|---|
| Media Format | R2R, Sheets |
| Ink Waste | Low |
| Coating Speed | 100- 500 m.min$^{-1}$ |
| Ink Viscosity | 10-25 000 mPa.s |
| Wet Thickness | 5-500 µm |
| Dry Thickness | 0.01-100 µm |
| Resolution | Given by shim |

# Coating techniques applications

- OPV – transparent electrode, BHJ layers (P3HT:PCBM), ETL
- Lamination adhesives – pressure sensitive
- HTL (PEDOT:PSS), ETL layers ($TiO_2$, ZnO)
- Electrochromic display
- OLED – PLED – emissive layers, HIL layers, ETL
- Battery – electrode layers, collectors



Frontier

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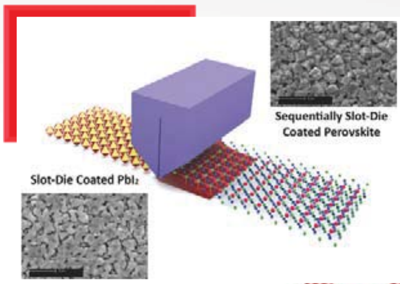
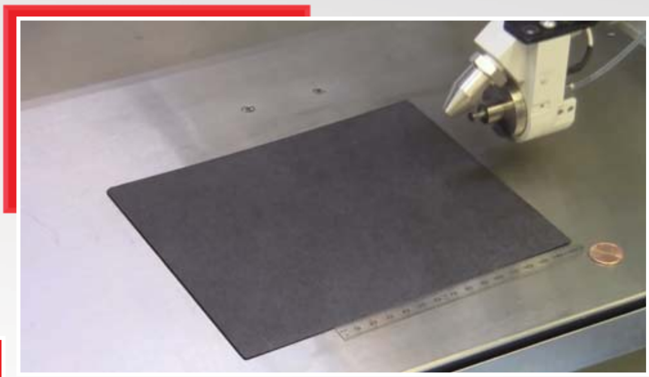



Hwang et Al.



# Coating techniques – Spray Coating

+ High uniformity of layers
+ Deposition to 3D object
+ Relatively high range of thickness of layers



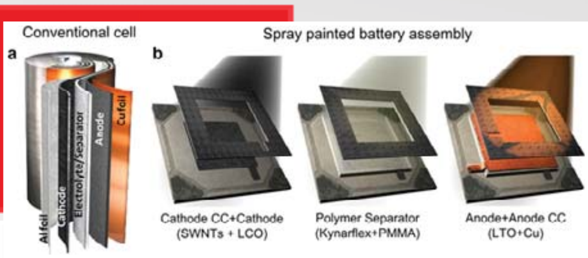
Sono-tek

- Ink Waste
- Complicated patterning
- Low resolution of patterning

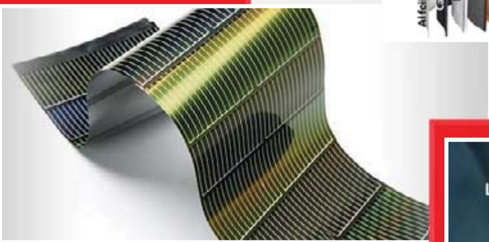
| | |
|---|---|
| Media Format | Sheets, R2R |
| Ink Waste | moderate |
| Coating Speed | Up to 100 m.min$^{-1}$ |
| Ink Viscosity | 10-1000 mPa.s |
| Wet Thickness | 1-500 µm |
| Dry Thickness | 0.01-100 µm |
| Resolution | Tech. Sol. dependent |

# Coating techniques – Spray Coating

- OPV - HIL, BHJ, ETL
- Transparent conductive layers (CNT, PEDOT:PSS, PANI:HCl)
- Memory
- OFET
- Battery
- OLED




Singh at Al.



Sono-tek



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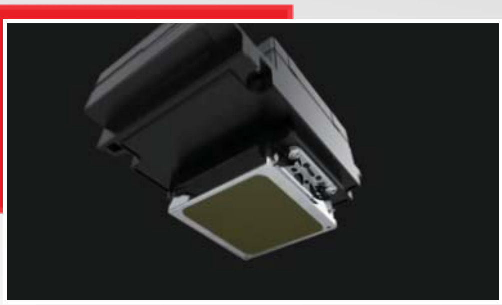
# Printing techniques - InkJet

+ Absence physical printing form
+ Relatively high resolution and high precise registration
+ Relatively high range of thickness of printed layers



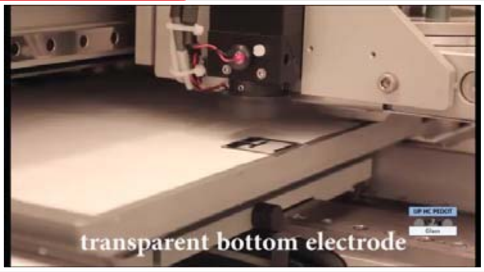
Epson

| | |
|---|---|
| Media Format | Sheets, R2R |
| Ink Waste | Low |
| Printing Speed | Up to 280 $m.min^{-1}$ |
| Ink Viscosity | 1-50 mPa.s |
| Wet Thickness | 1-500 µm |
| Dry Thickness | 0.01-100 µm |
| Resolution | 10 µm |

– Problems with clothing of nozzles
– Quality strongly influenced by printing speed
– long time run stability
– Large amount of interfaces

# Printing techniques - InkJet

- BHJ, ETL (PFN, ZnO, $TiO_2$), HTL (PEDOT:PSS, $MoO_3$)
- Transparent conductor (Ag nanowire, CNT, SWCNT, Graphene, ITO, AZO, ATO)
- Sensors
- Catalytic layers
- Conductive (Ag, Cu), semiconductive, dielectric layers for several type of devices
- Transistors – OFET, OECT
- OPV, DSSC
- OLED – POLED, SMOLED
- Piezoelectric elements – micropumps, tactile
- Baterries, supercapacitors
- Memory
- Reactive colors




Holst Centre

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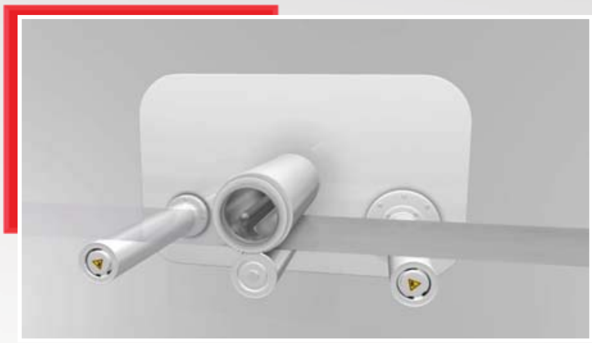
# Printing techniques – Screen printing

+ Most used production technique
+ Variety of thickness of layers
+ Relatively easy preparation of stencil

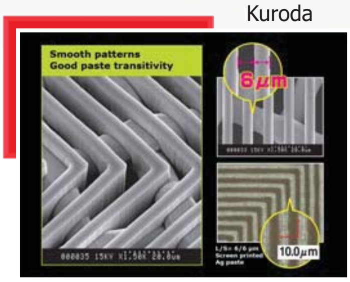


3D-Micromac AG

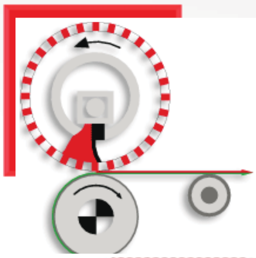
| | |
|---|---|
| Media Format | Sheets, R2R |
| Ink Waste | Low |
| Printing Speed | Up to 50 $m.min^{-1}$ |
| Ink Viscosity | 100-20 000 mPa.s |
| Wet Thickness | 3-1000 µm |
| Dry Thickness | 0.02-1000 µm |
| Resolution | 6 µm |

– Printing speed, high viscosity

Kuroda




Coatema



# Printing techniques – Screen Printing

- Photocathode ($TiO_2$, ZnO, etc.)
- Counter electrode (PEDOT:PSS, PANI, PPY, CNT, Graphene, Ag)
- Conductive patterns (Ag, Cu)
- Electrolytes
- BHJ layers, ETL, HTL
- Sealing layers, Barrier layers
- Sensors
- Catalytic layers
- Conductivee, (Semi)conductive, dielectric layers for several type of devices
- Transistors – OFET, OECT
- OPV, DSSC
- OLED – POLED, SMOLED
- Batteries, supercapacitors
- Memory
- Reactive colors
- Piezoelectric elements – micropumps, tactile


Plasticphotovoltaic.org

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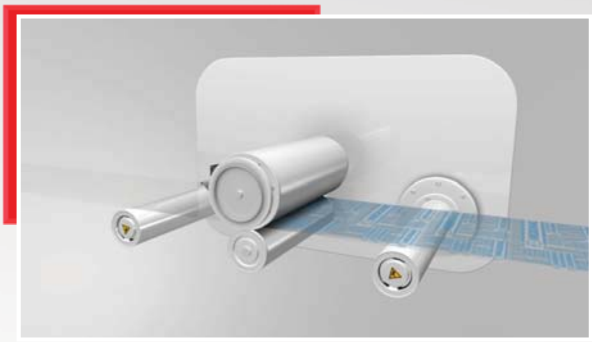
# Printing techniques – Gravure

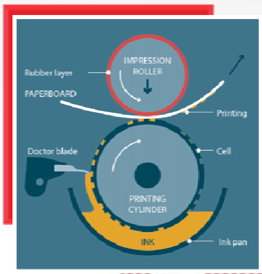
+ Very stable printing process
+ Highest printing quality
+ High printing speed
+ Printing form resistant to solvents
+ Reverse gravure for precise coating

| | |
|---|---|
| Media Format | Sheets, R2R |
| Ink Waste | Low |
| Printing Speed | Up to 500 $m.min^{-1}$ |
| Ink Viscosity | 10-20 000 mPa.s |
| Wet Thickness | 5-80 µm |
| Dry Thickness | 0.02-80 µm |
| Resolution | 3 µm |



3D-Micromac AG

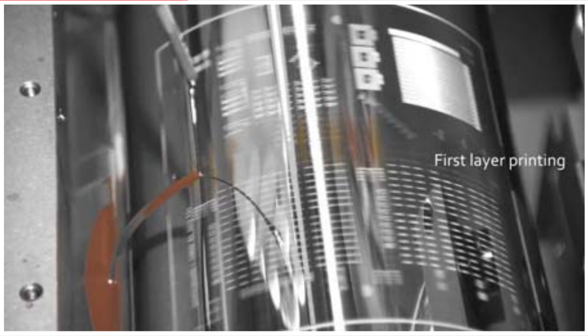
– Expensive printing form/ cyllinder
– Mainly gravure is suited to flexible substrates



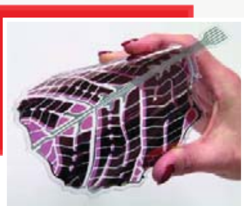

www.iggesund.com

# Printing techniques – Gravure

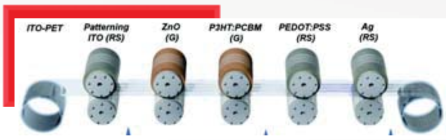
- HIL ($MoO_3$, PEDOT:PSS), BHJ
- ETL ($ZnO_2$, $TiO_2$)
- Conductive tracks (Ag, Cu)
- Dielectrics
- OLED – SMOLED, PLED – emissive layer
- OFET – ID structures, Dielectric layer, Semiconductor layer,
- RFID antenas
- Sensors – RH, Biosensing layer
- Voltage multiplier circuits
- Memory
- Antistatic layers
- Microfluidic chanells




CSEM



VTT

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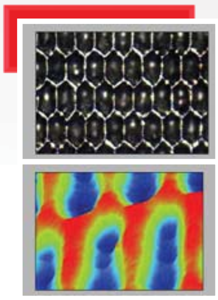
# Printing techniques – Flexography

+ Stable printing process
+ High printing speed
+ Rigid and flexible substrates
+ Relatively inexpensive printing form

Altana


| | |
|---|---|
| Media Format | Sheets, R2R |
| Ink Waste | Low |
| Printing Speed | Up to 1000 $m.min^{-1}$ |
| Ink Viscosity | 10 -1 000 mPa.s |
| Wet Thickness | 5 - 30 µm |
| Dry Thickness | 0.03 - 10 µm |
| Resolution | 30 µm |

Simec Group



– Limited thickness of layers
– Uniformity of topology of fine lines
– NIP pressure is crucial

## Printing techniques – Flexography

- Conductive interconnection,
- Transparent conducive layers (CNT, PEDOT:PSS), conductive grids
- HTL (PEDOT:PSS, $V_2O_5$)
- RFID antennas
- Biostatic layers
- Dielectric layers (OFET, RFID)
- Laudspeakers
- Fuid-guiding channels
- Drug delivery systems


Syrovy


Plasticphotovoltaics.org

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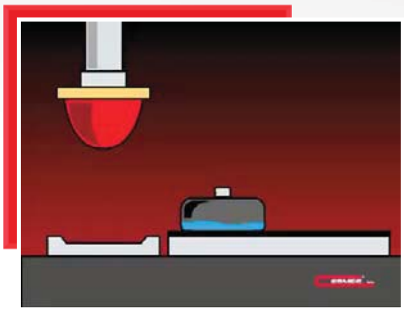
## Printing techniques – Pad printing, offset gravure

+ Rigid and flexible substrates
+ Printability of 3D surface
+ Printing quality
+ Printing speed

| | |
|---|---|
| Media Format | Sheets, R2R |
| Ink Waste | Low |
| Printing Speed | Up to 120000 parts/hr |
| Ink Viscosity | 10 -1000 mPa.s |
| Wet Thickness | 5- 80 μm |
| Dry Thickness | 0.05 - 20 μm |
| Resolution | 25 μm |

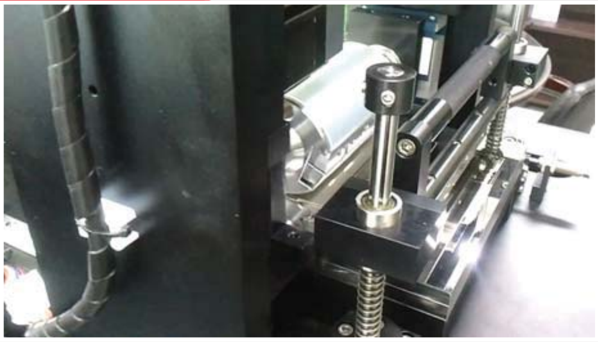

Tampoprint



TRI Elektronik

# Printing techniques – Pad printing, offset gravure

- Conductive interconnection (Ag)
- BHJ layer (P3MHOCT/ZnO)
- transparent conducive layers (CNT, PEDOT:PSS), conductive grids



PEMS

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# Printing techniques – Offset printing

\+ Printing speed

\+ High resolution

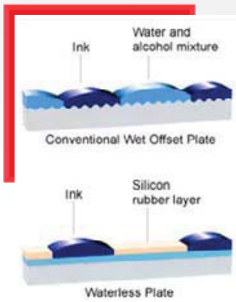
\+ inexpensive printing plates fabrication

\+ Frequently used printing technique

Kim

www.brancher.com

| Media Format | Sheets, R2R |
|---|---|
| Ink Waste | Low |
| Printing Speed | Up to 1000 $m.min^{-1}$ |
| Ink Viscosity | 10 -100 Pa.s |
| Wet Thickness | 10 µm |
| Dry Thickness | 3 µm |
| Resolution | 25 µm |



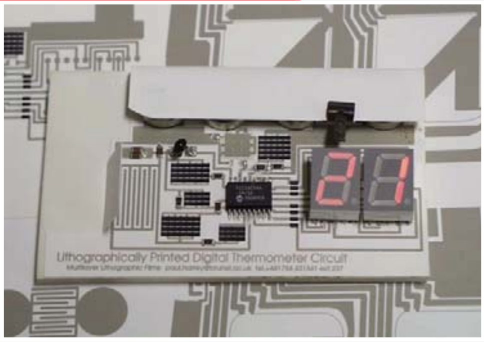

– Limited thickness of layers

– High resistivity of conductive layers

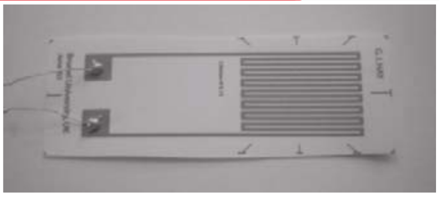
– Lack of commercial functional ink

## Printing techniques – Offset printing

- OFET ID structures
- Conductive circuits
- Passive components
- Sensors
- Thermochromic display
- Battery
- OPV




Brunel University



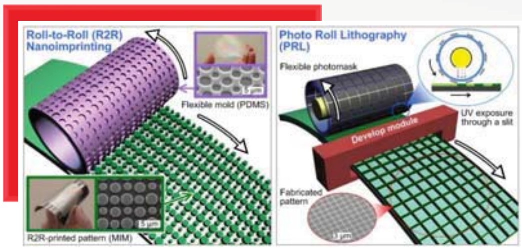
Brunel University



## Others „printing" techniques for μ-Patterning

- Nanoimprinting lithography NIL
- Soft Lithography
  - Microcontact Printig μCP
  - Micromolding in Capillaries MIMIC
  - Nanotransfer printing nTP
  - Replica molding REM
  - Microtransfer molding μTM
  - Solvent-assisted micromolding SAMIM

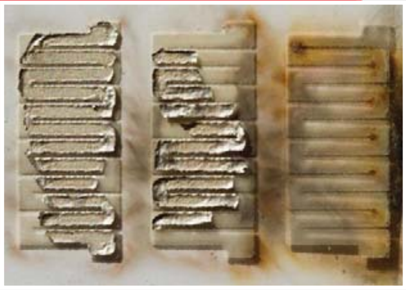
www.miplaza.com

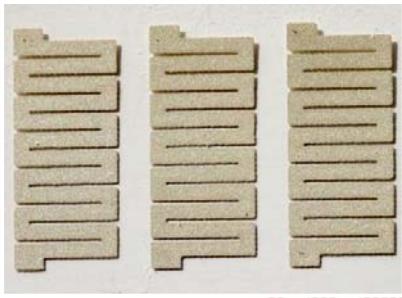



OKNANOLAB

# Possibilities for rapid drying or sintering process

- Hot-air drying/sintering
- IR drying/sintering
- Curing by UV radiation or EB
- Photonic sintering
- Microwave drying/sintering
- Electrical sintering (DC or contactless AC)





Syrovy

Department of Graphic Arts and Photophysics

flexprint

Program Centra kompetence

T A Č R
Technology Agency of the Czech Republic

# Thank you for your attention

cost

ActInPak

## 3. Sensor Integration on Flexible Substrates

Grigoris Kaltsas, T.E.I. of Athens

### Biography

Dr Grigoris KALTSAS received his B.Sc. degree in Physics from National University of Athens in 1993. He joined the Institute of Microelectronics of National Center for Scientific Research (NCSR) "Demokritos" in 1993 as a Ph.D. student, after he has obtained a corresponding scholarship from the Institute. He received his Ph.D. entitled "Integrated gas and gas flow sensors fabricated by using porous silicon technology", from the National Technical University of Athens (School of Applied Mathematical and Physical Sciences) in 1998. He joined the Department of Electronics of the Technological Educational Institute of Athens (TEI-A) in 2003 as Assistant Professor and he is now Professor in the same Department. He is also affiliated (since 2003) with the Institute of Microelectronics of NCSR "Demokritos", as a research associate, having a close collaboration with several members of the Institute staff.

Dr. G. Kaltsas has participated and coordinated several European and National research projects funded by various foundations (EU, GSRT, Ministry of Education, etc) and industries (Unilever UK, i-Tax). He has collaborated with many European research groups from various countries within the frame of several projects. He has also participated in various committees and boards related to electronics – microsystems - sensors research and education.

He has published over 100 papers in refereed journals and major conferences and he is an author of 5 patents, two of them being PCTs. He has given 3 invited talks in major international conferences in the field of microsystems - microfluidic devices and sensor technology. In 2004 he has been awarded from the minister of development by the General Secretariat for Research and Technology for the patent "Flow meter and special designed packaging for use in medical equipment for breath control", for the contribution to the technological progress of the country. He has over 600 citations with an h-index of 13.

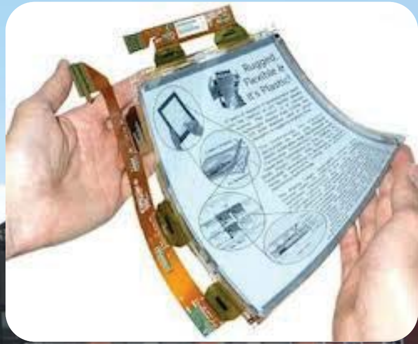
### Abstract

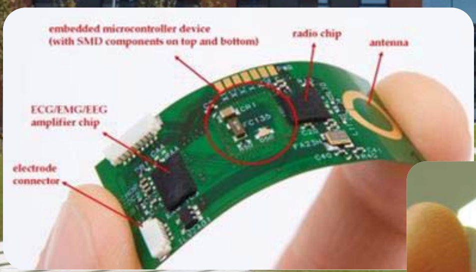
n/a

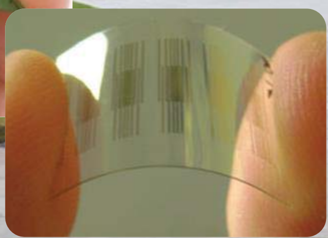
# Sensors integration on Flexible Substrates

Grigoris Kaltsas
G.Kaltsas@ee.teiath.gr

Technological Educational Institution (TEI) of Athens,
Department of Electronic Engineering,
12210 Egaleo, Athens, Greece
*microSENSES Lab* - http://microsenses.stef.teiath.gr/





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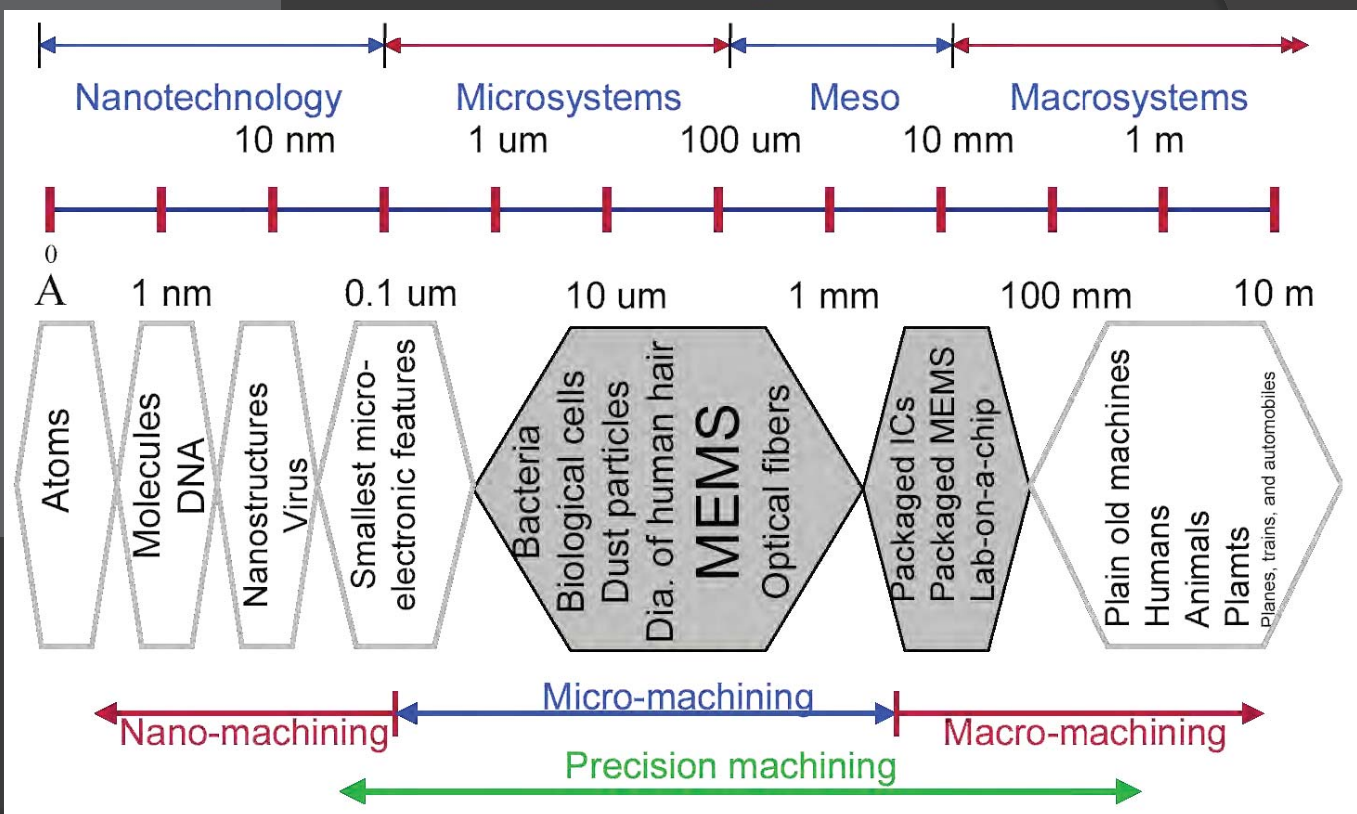
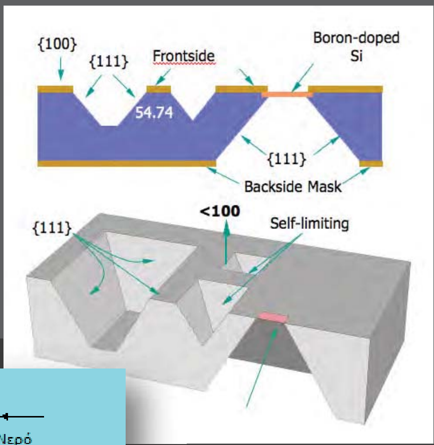
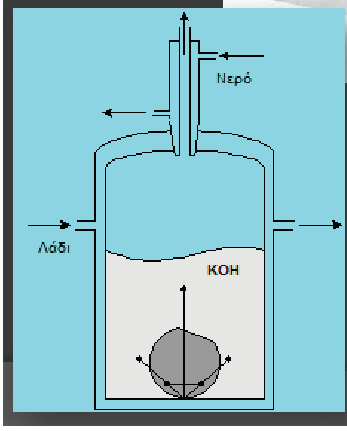
## When SIZE actually matters ...



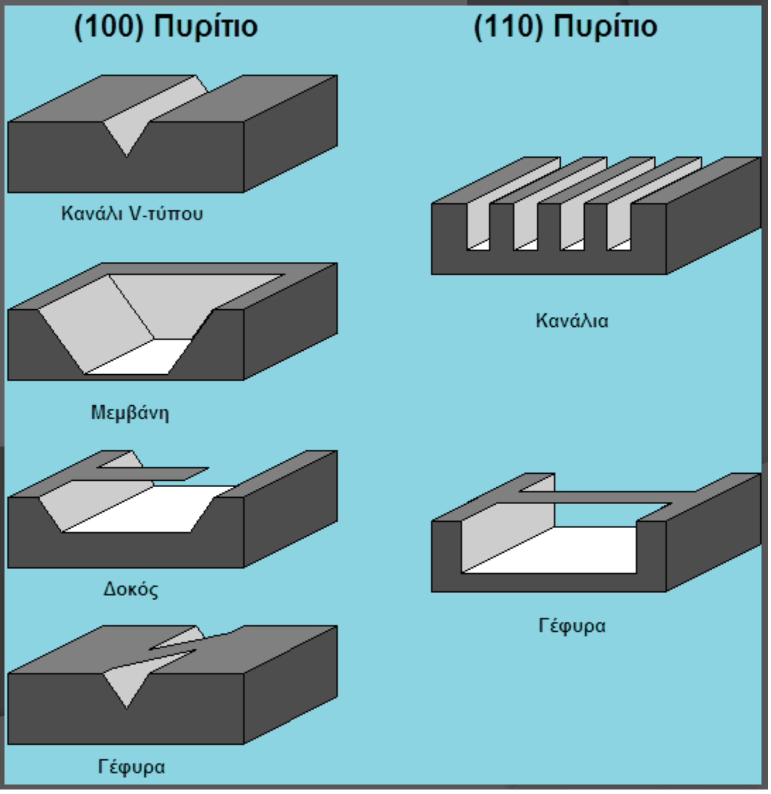
# MEMS Fabrication – Bulk Micromachining

## Fabrication Method




## Basic Structures

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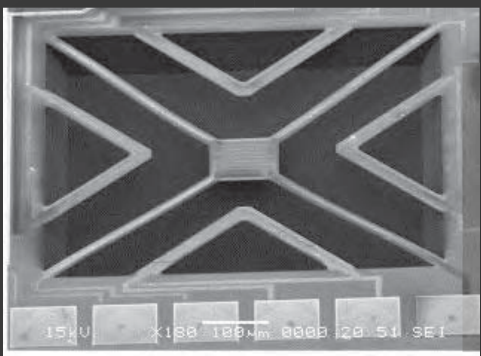
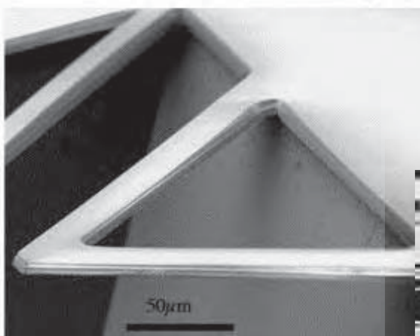
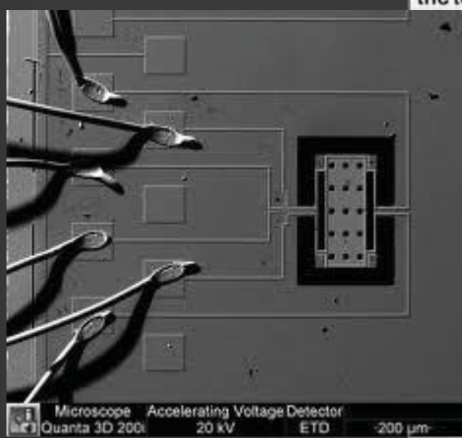
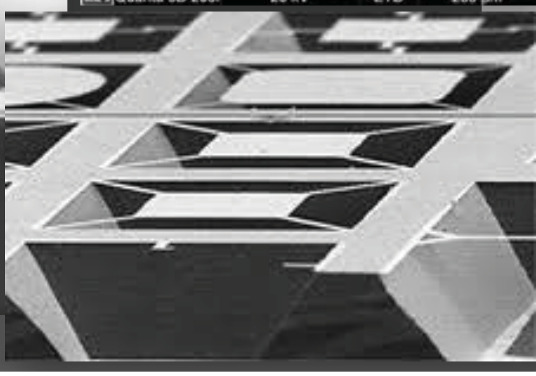
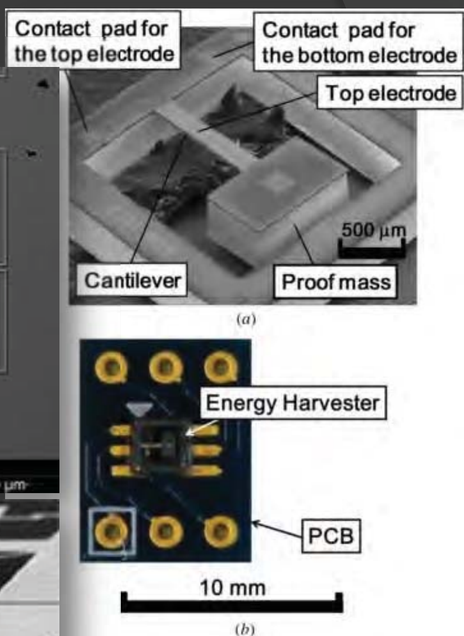
# Bulk Micromachining Structures



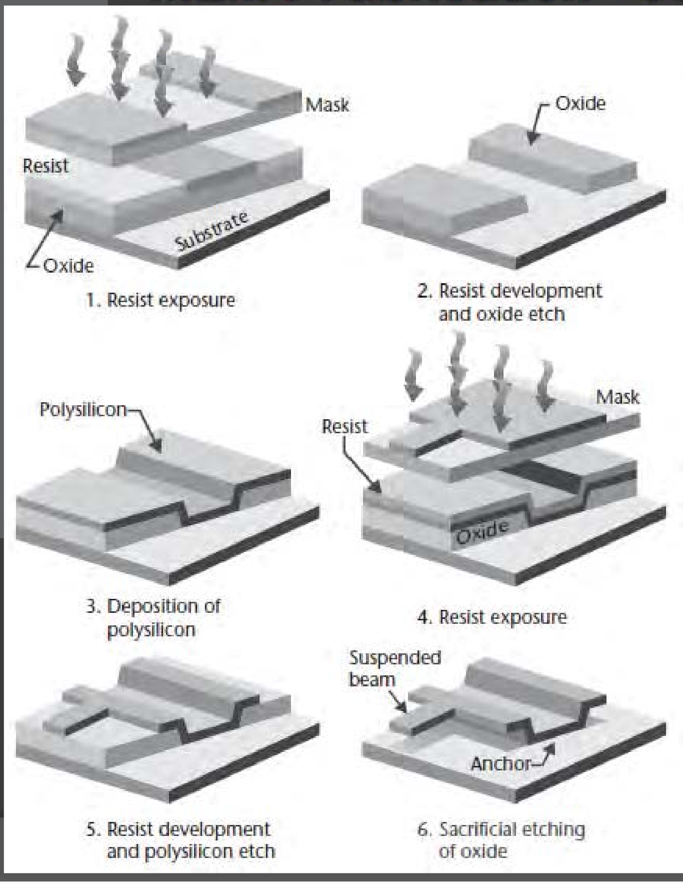





# MEMS Fabrication - Surface Micromachining




- ❑ The Si wafer is not etched, since the structures are formed through sacrificial epi-layers.
- ❑ The basic idea was applied initially to metallic substrates from H. C. Nathanson in the late 60s
- ❑ The full application of the technology in silicon was demonstrated through the integration of an NMOS/polysilicon commercial device in 1984.
- ❑ The term “surface micromachining” was suggested by P. W. Barth in the late 85s

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Department of Electronic Engineering
microSENSES Lab
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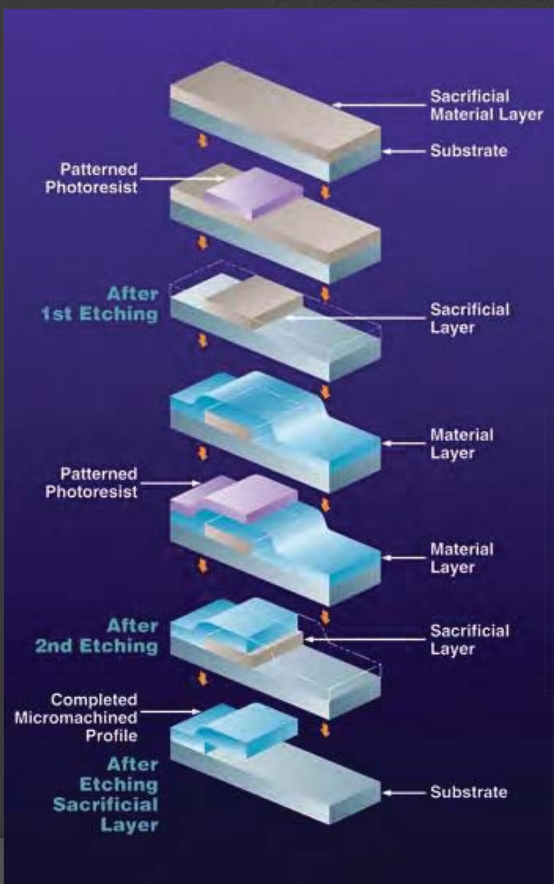
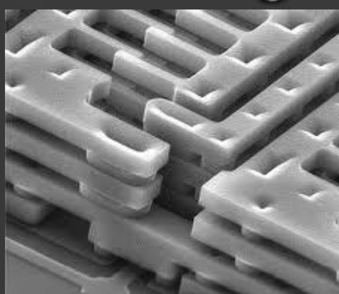
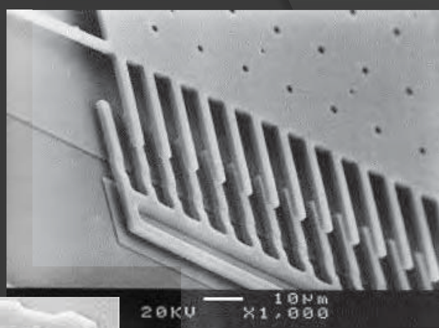
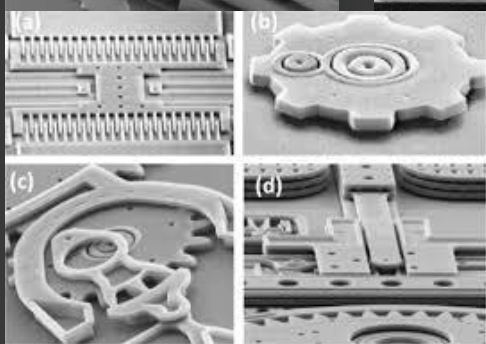
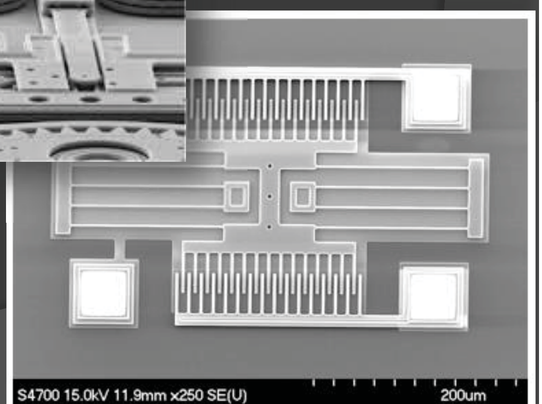
# Surface Micromachining Structures



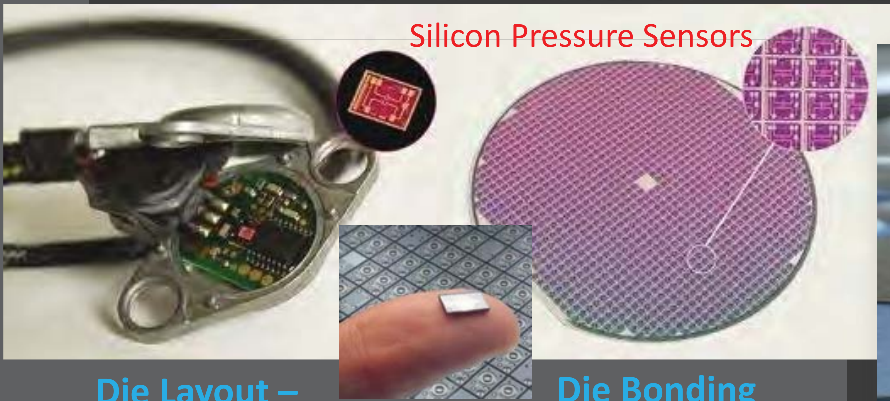


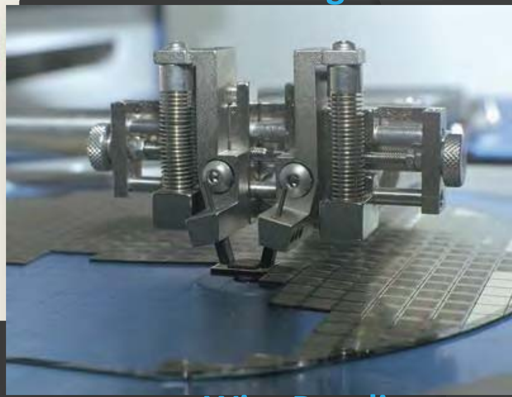



# Silicon MEMs: Fabrication – Wafer – Die - Chip

Silicon Pressure Sensors



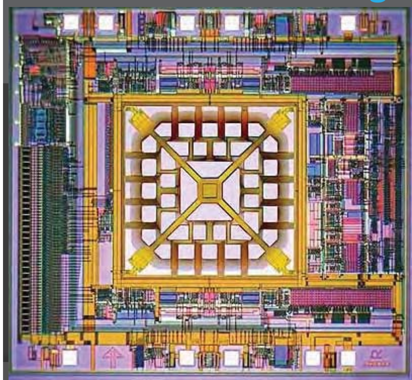
Die Cutting

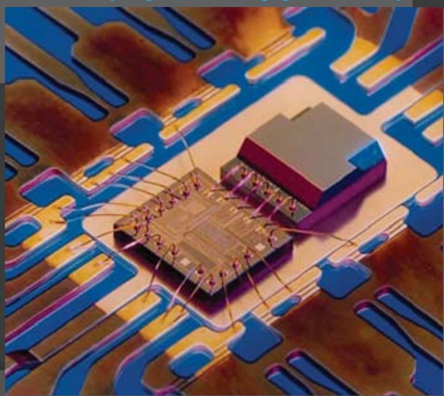


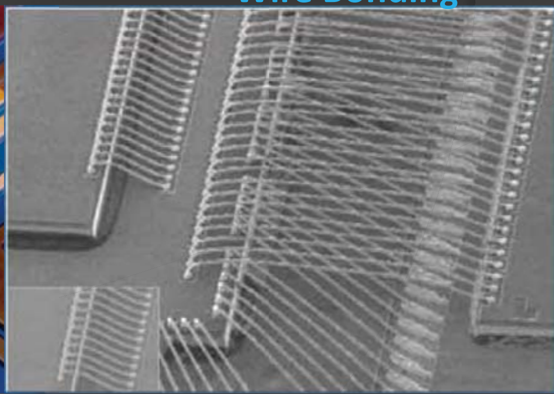
Die Layout – Electronic Interfacing

Die Bonding (Hybrid Approach)

Wire Bonding







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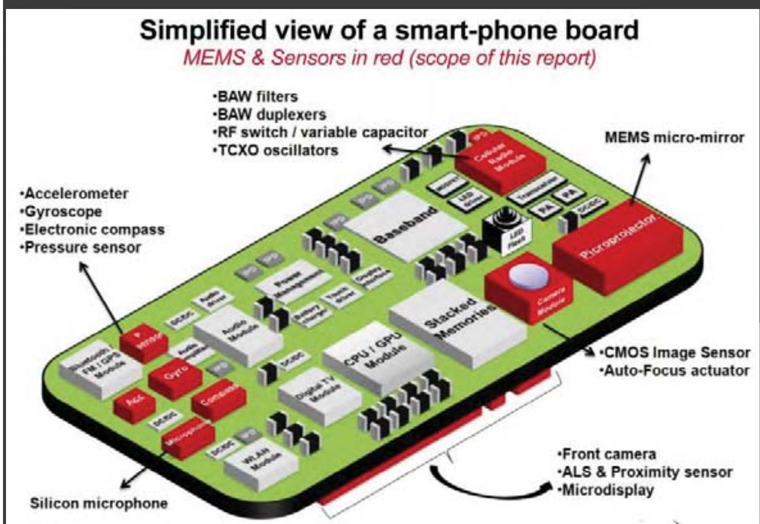
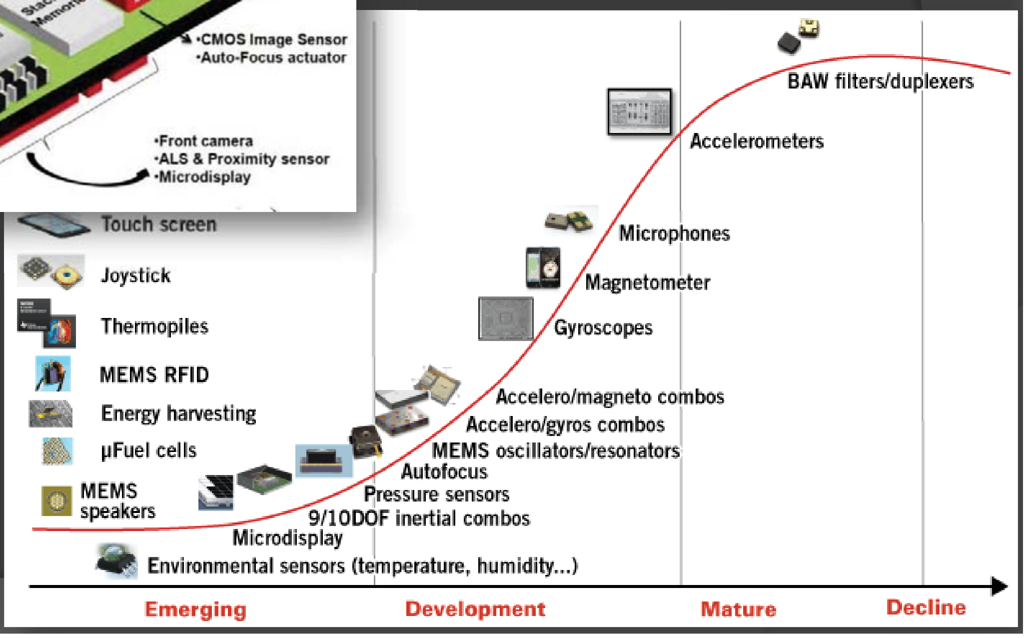
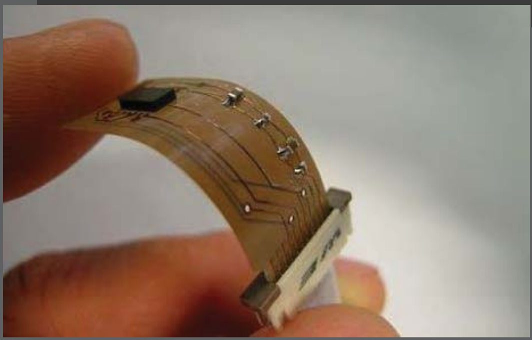
# MEMS Applications

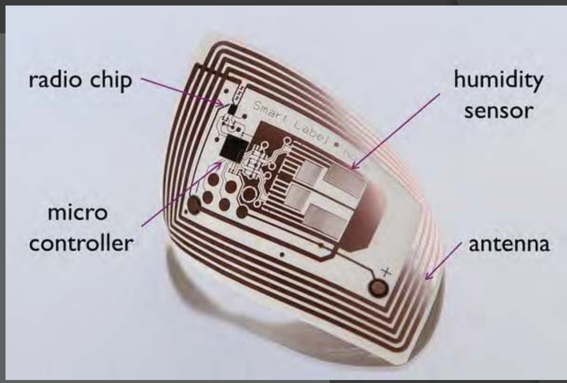


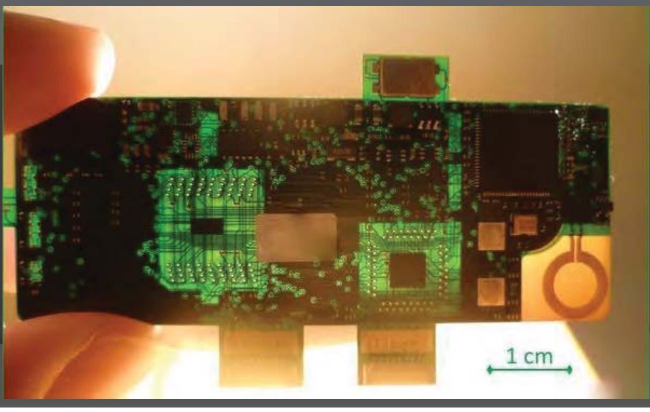
# Hybrid Sensor's Integration on Flexible Substrates



Multi-Parametric and Smart Sensing Platform on Flexible Substrate
*EPFL 2013*




Smart label with two chips and all 10 passive components embedded in a 250µm thick, flexible substrate
*Centre for Microsystems Technology, University of Gent*




A smart sensor node featuring two embedded off-the-shelf ICs, embedded in the flexible circuit board using UTCP Technology
*Centre for Microsystems Technology, University of Gent*

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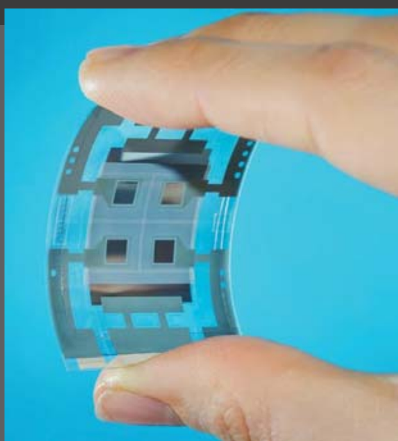
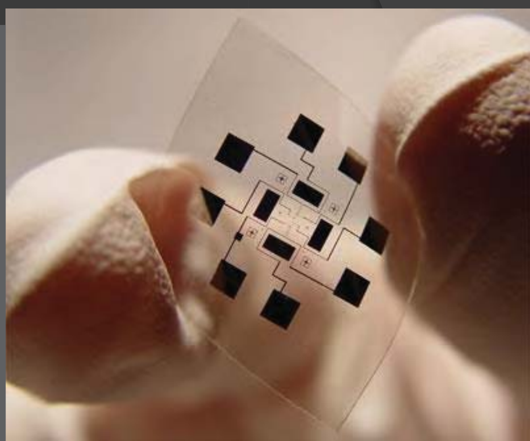
# Direct Sensor's Integration on Flexible Substrates

Electronic fingertips to allow virtual sensations
*John A. Rogers, University of Illinois, 2012*



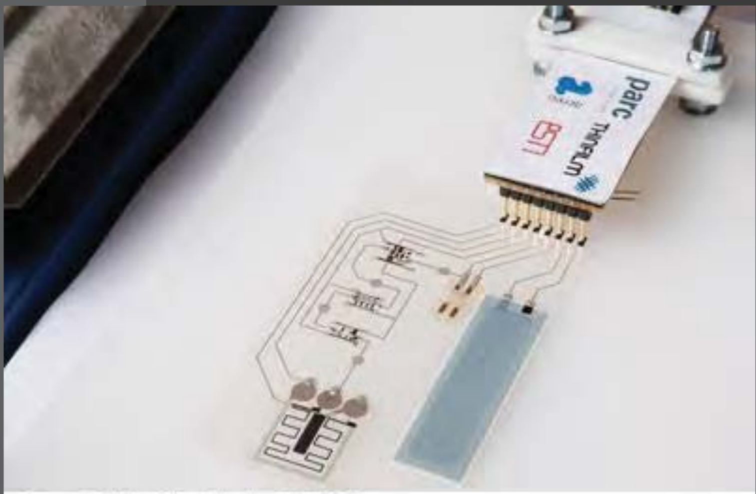
Organic photodiodes on flexible substrate
*© Fraunhofer COMEDD, 2014*



'Electronic nose' composed of nanowire device arrays on flexible plastic
*Photograph of the flexible sensor chip (Image: Heath Group, Caltech), 2007*

A Really Flexible X-ray Sensor
*IMEC and Holst Centre, 2013*

# 1st Integrated Printed Electronic System

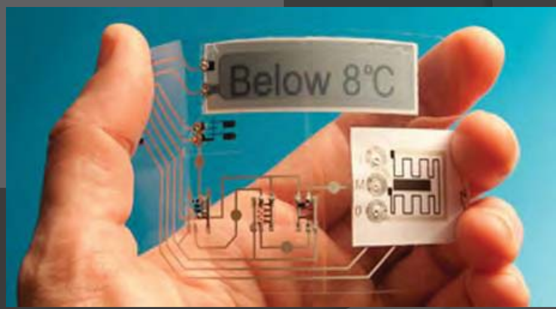


Source: Thin Film Electronics ASA

Source: www.thinfilm.no

Integration of:

- ✓ rewritable memory (Thinfilm)
- ✓ organic logic circuitry (PARC),
- ✓ temperature sensor (PST Sensors)
- ✓ electrochromic display (ACREO)




- Thin Film Electronics ASA, Oslo, Norway
- Leader in the development of printed electronics
- The first to commercialize printed rewritable memory
- December 2012 - the first prototype of an integrated printed electronic tag based on rewritable memory

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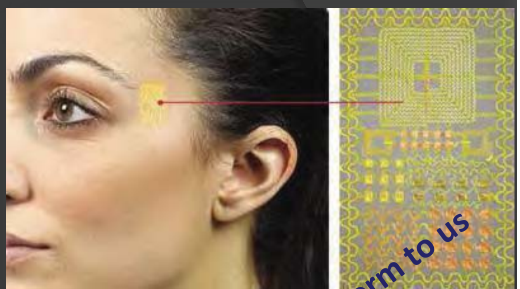
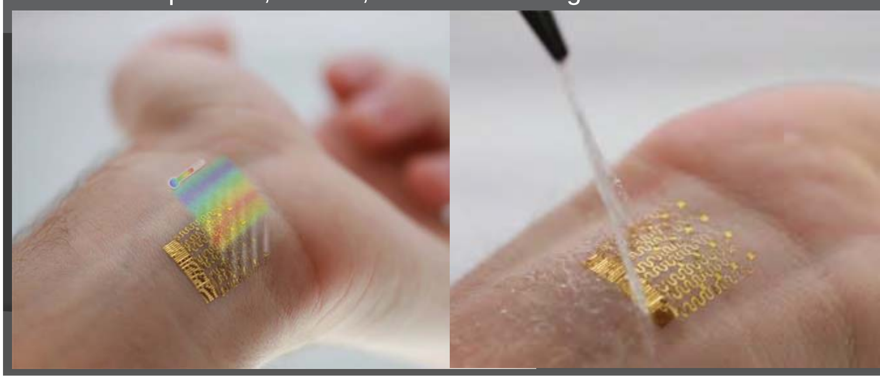
# "Electronic tattoo" by MC10

- "EPIDERMAL ELECTRONICS"
- Devices consisting of ultrathin electronics, sensors, electrodes, wireless power and communication systems
- Before: Devices applied to elastomer backing (easily detached by water)
- NEW SOLUTION: Printing device on the skin
- Technology: Rubber stamp prints the ultrathin mesh electronics directly to skin
- Protection: Commercial „spray-on-bandage" thin protective and bonding layer (durability: 2 weeks)
- Applications – health, sport, welness monitoring: temperature, hydratation, blood pressure, insulin level, sun exposure, strain, wound healing



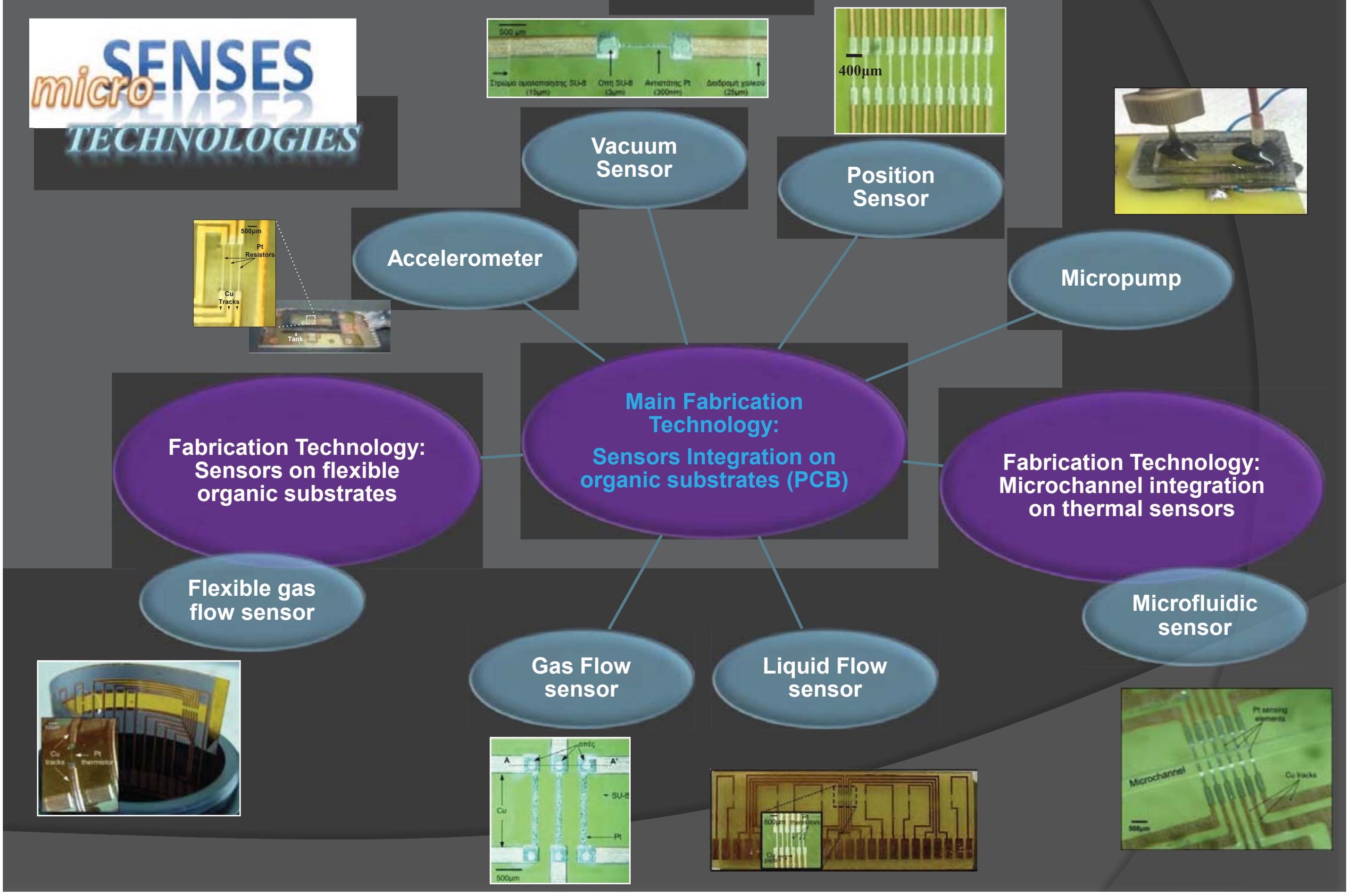
Making electronics to conform to us

*Source: www.technologyreview.com*
*www.mc10inc.com*



Flexible Thermometer Laminated Onto Skin for Continuous, Area-Wide Temperature Monitoring

*John A. Rogers, University of Illinois, 2013*

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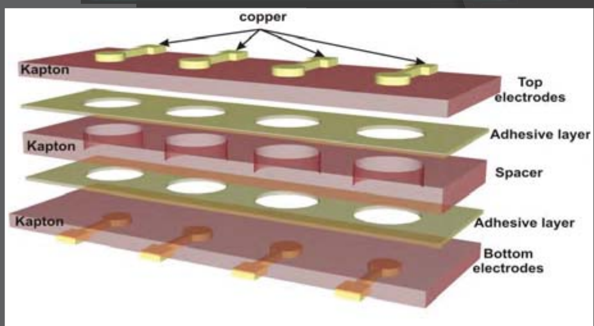
# Capacitive Sensor Fabricated By Flexible Substrates

## Device Structure

- The pressure sensor array consists of a sequence of three flexible layers.
- The capacitor electrodes are defined by the copper patterning on the upper and the lower Kapton layers. Cavities of pre-defined size are formed in the intermediate layer.
- The Kapton layers are bonded together through a standard lamination process.
- A pressure-depended capacitor is formed by the copper electrodes and the sealed cavity in between.

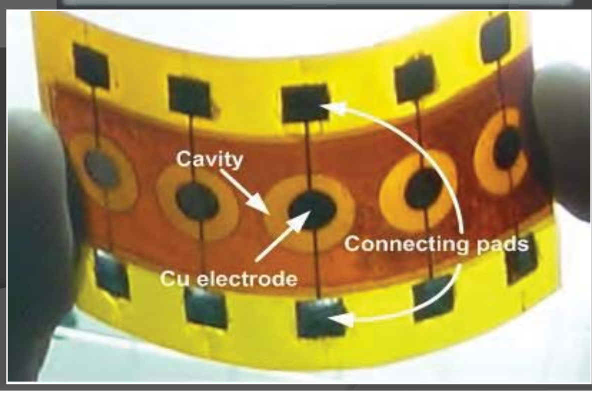
## Structure Schematic




## Technology Benefits

- Direct device integration with the corresponding electronics
- Structure flexibility
- Direct modification of the final geometry
- Process simplicity

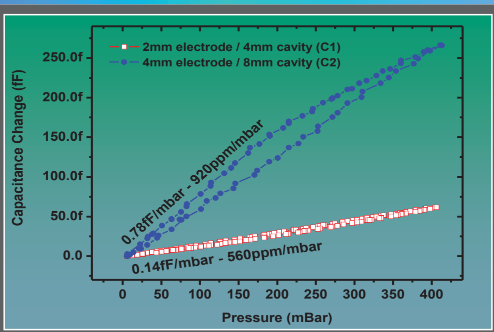
## Photograph of the Sensor Array



# Capacitive - Tactile Flexible Sensor

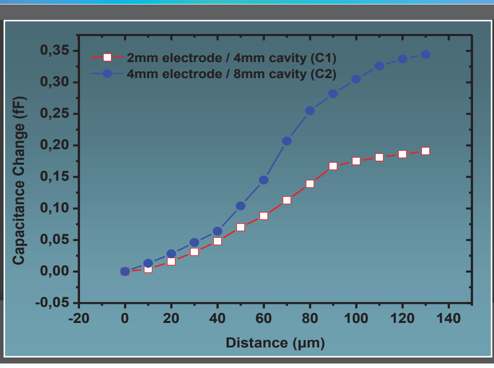
## Results

### A. Pressure Determination

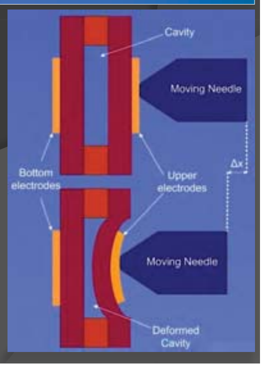



- High sensitivity: 0.14 fF/mbar (C1) and 0.78 fF/mbar (C2)
- Relatively small hysterisis
- Relatively low initial capacitance value ($C_{01}$=248fF, $C_{02}$=848fF)

### B. Displacement Determination




- Needle in contact with the surface electrode moves in steps of defined distance (resolution: 1μm).
- Measurement of the capacitance change caused by the pressure induced by the needle movement
- The measurement range is determined by the thickness of the intermediate layer

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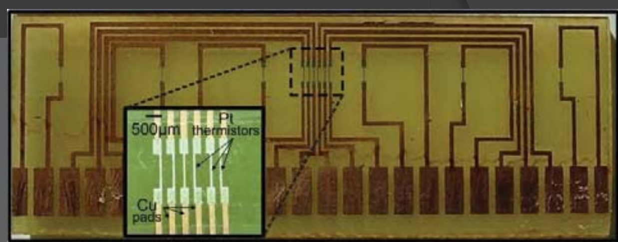
# Thermal Sensors Fabrication Process

Patterned PCB

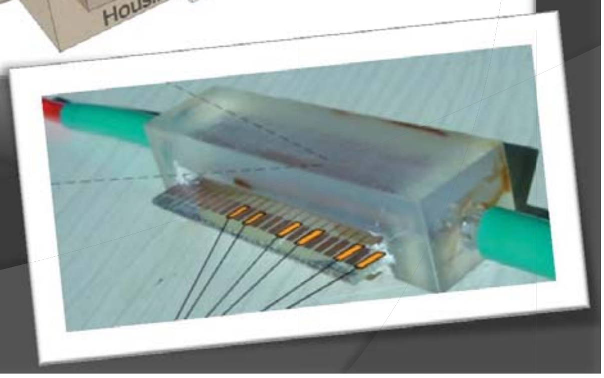
SU-8 Planarization layer

ma-N lithography.
Sensing element definition.

Pt sputtering and lift-off.
Formation of the Pt sensing elements.

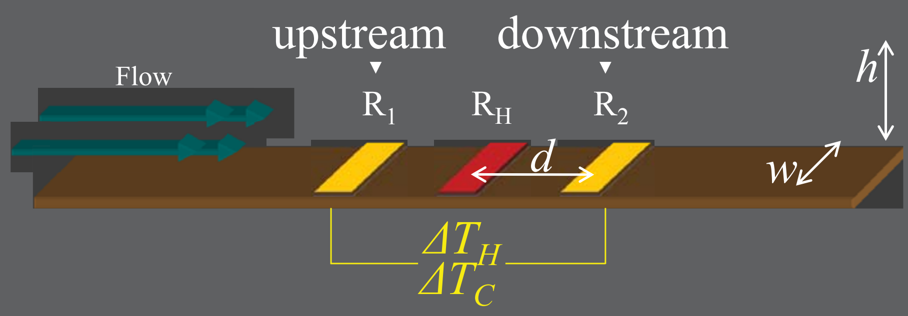






## Flow Sensors Operating Principles

**Hot Wire Principle** | **Calorimetric Principle**




$$Sensor\_Signal = \frac{R - R_o}{R_o} \propto \Delta T_H$$

$$Sensor\_Signal = \frac{R_1 - R_{1,o}}{R_{1,o}} - \frac{R_2 - R_{2,o}}{R_{2,o}} \propto \Delta T_C$$

## Parameters of interest

- Heater Power/Current, $P_h / I_h$
- Sensing element distance, ***d***
- Tube height and width, ***h*** and ***w***
- Fabrication Materials

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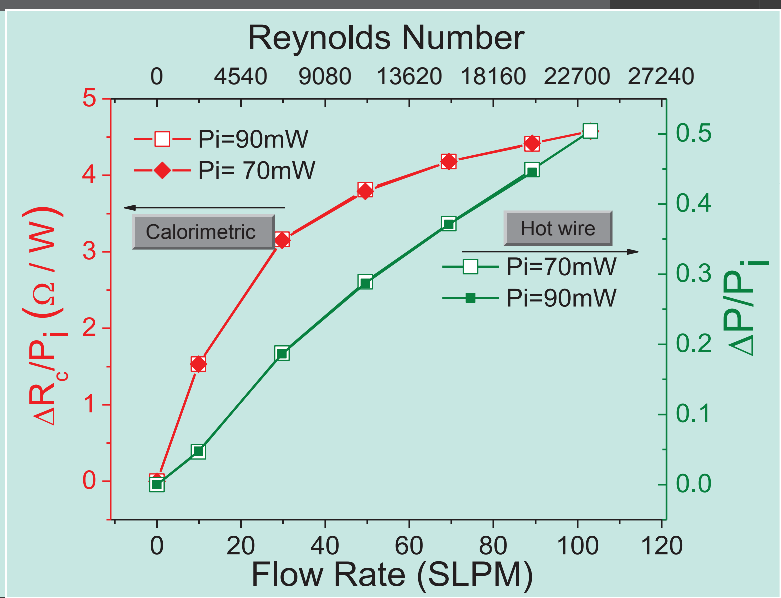
## Overall Characterization (0-100 SLPM)



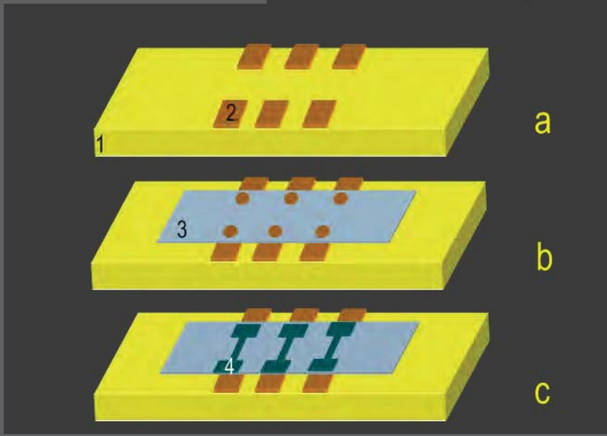

- Calorimetric: *High sensitivity in the low flow rate region*

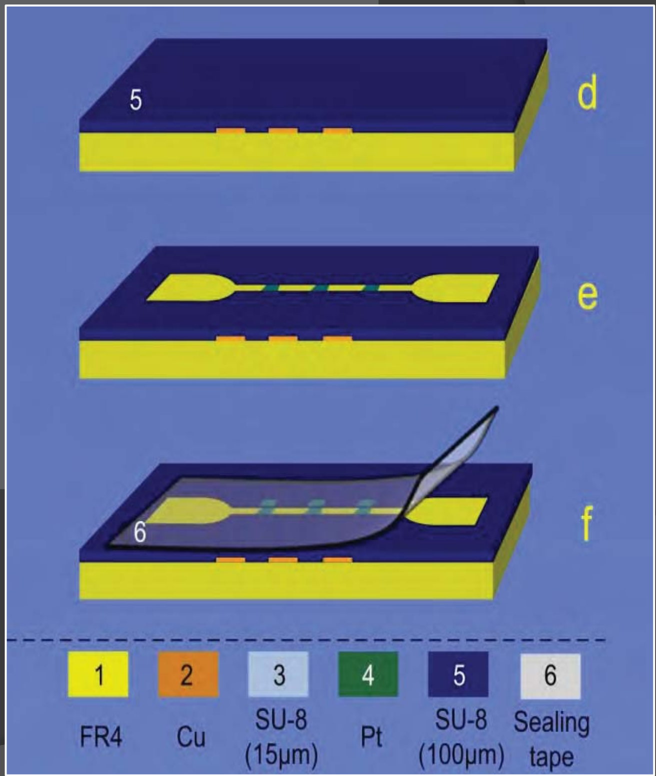
  Maximum Resolution: < 0.05 SLPM (*1.2 cm/s*)

- Hot Wire: *Expanded measurement range*

  Maximum Range: > 100SLPM (*24 m/s*)

# Microchannel Direct Integration




d. Thick SU-8 layer spin coating

e. Lithography definition of the microchannel

f. PMMA spin coating. Sealing of the microchannel's upper surface

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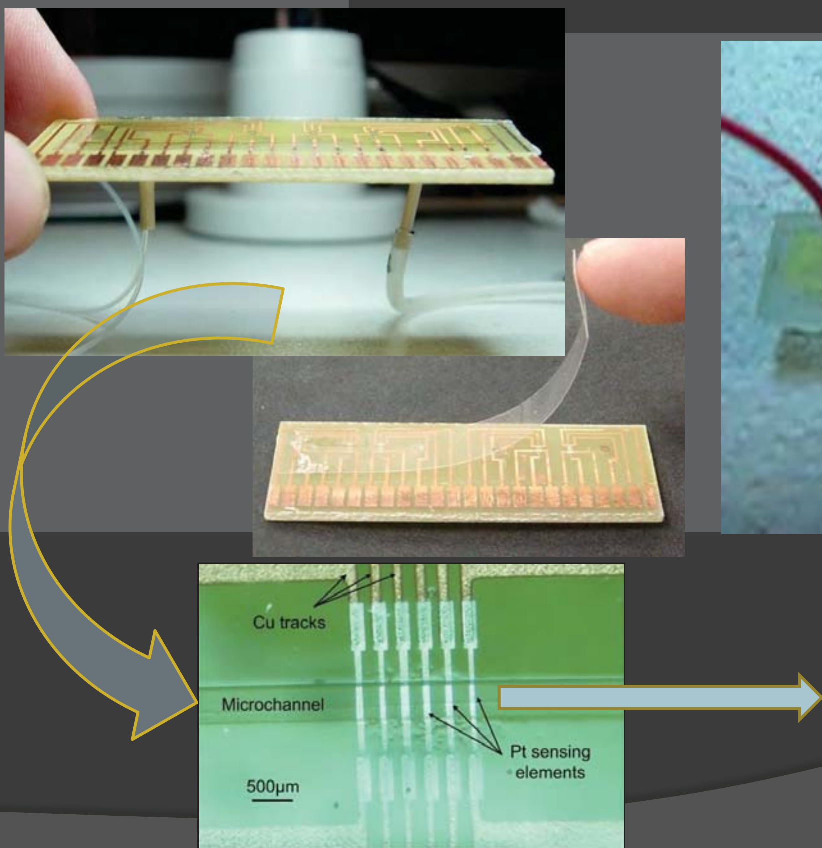
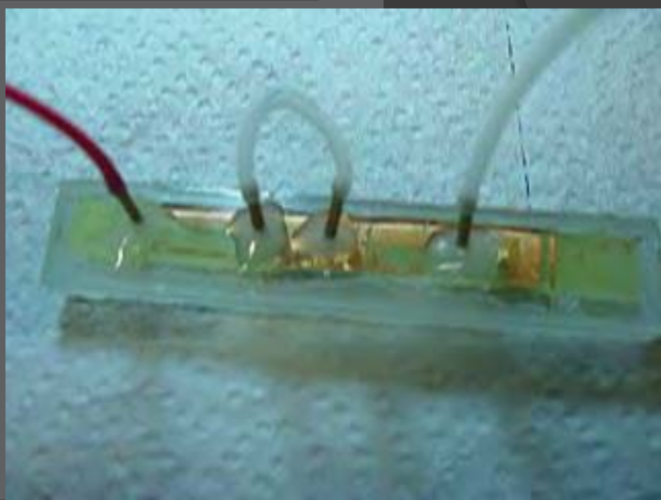
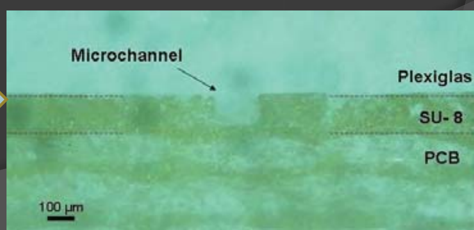
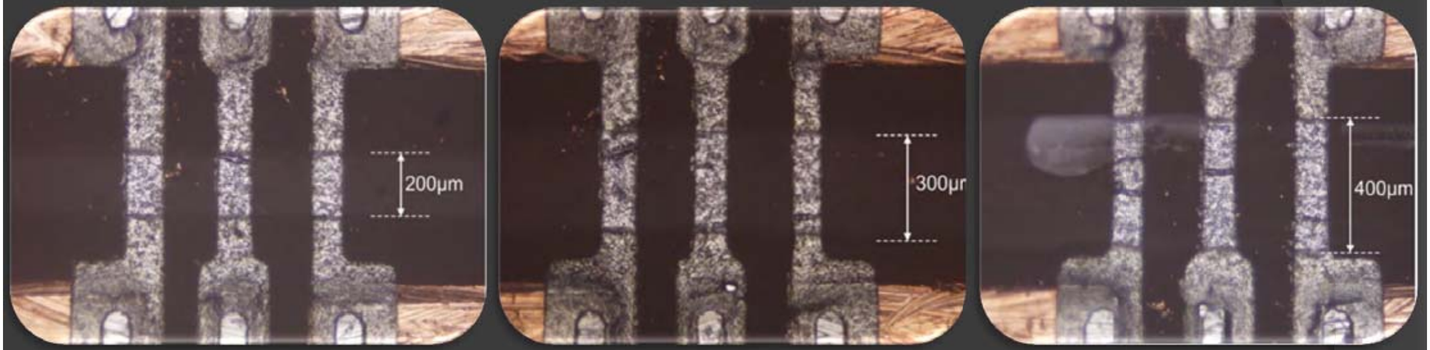
# Microfluidic Flow Sensor

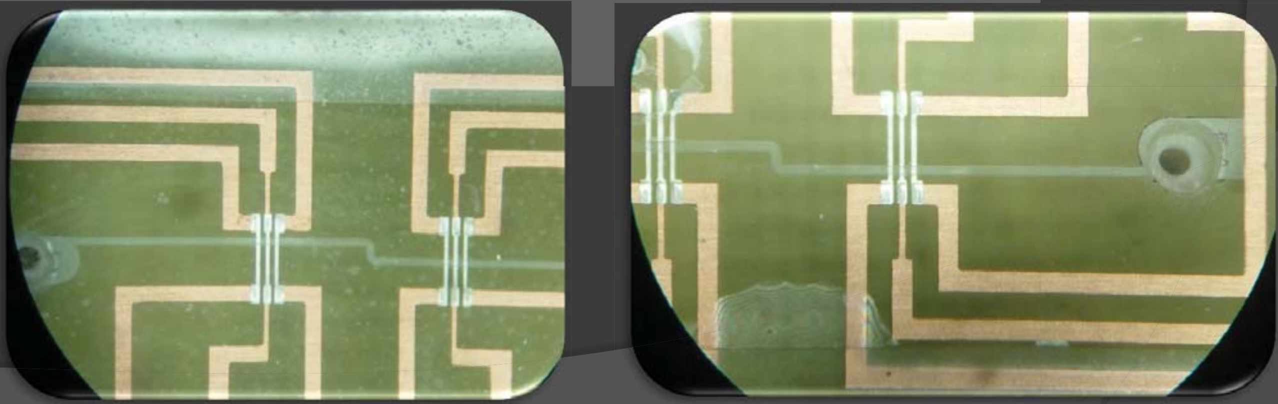




# Microchannel Engineering



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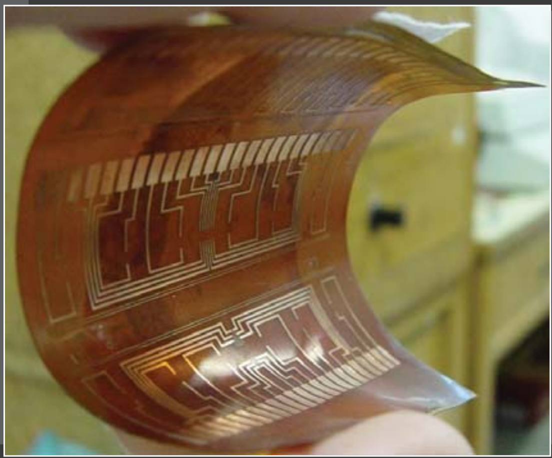
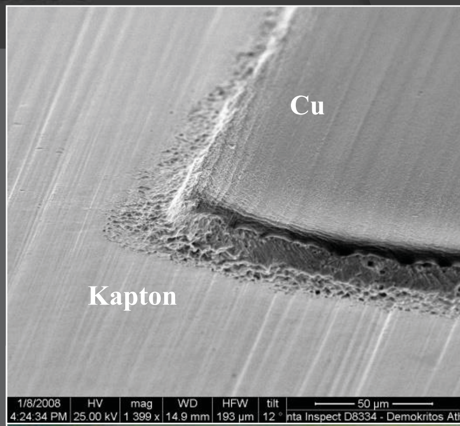
# Remarks - Discussion

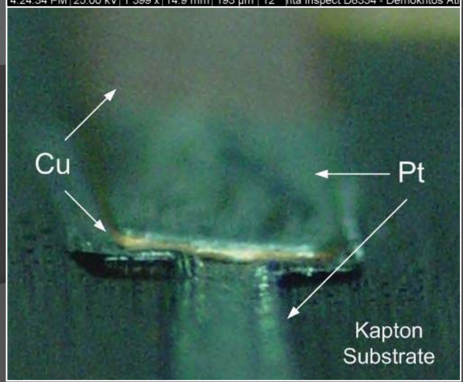
| Flow Rate | 150nl/min | 1µl/min | 5µl/min | 20µl/min | 40µl/min | 140µl/min |
|---|---|---|---|---|---|---|
| Input Current | | 30mA | 40mA | | 60mA | |
| Operation Mode | | Calorimetric | Composite | | | Hot wire |
| Microchannel Height | | 25µm | 60µm | 115µm | | |
| $D^{down}$ | 300µm | | | | 5000µm | |

- ✓ For low flow measurements → Calorimetric mode (sensitive in the region of ~1µl/min)
- ✓ For flows up to 20µl/min → Composite mode (more sensitive)
- ✓ For flows higher than 20µl/min → Hot wire (more extensive measurable range)

# Transfer of the Developed Fabrication Technology Into Flexible Substrates





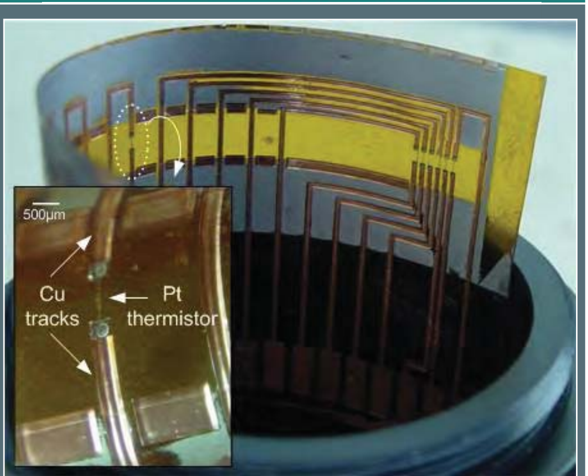




- ✓ Formatted flexible Kapton substrate (*100μm*) with a Cu layer on top (*25μm*)
- ✓ Planarization layer needed prior to Pt deposition



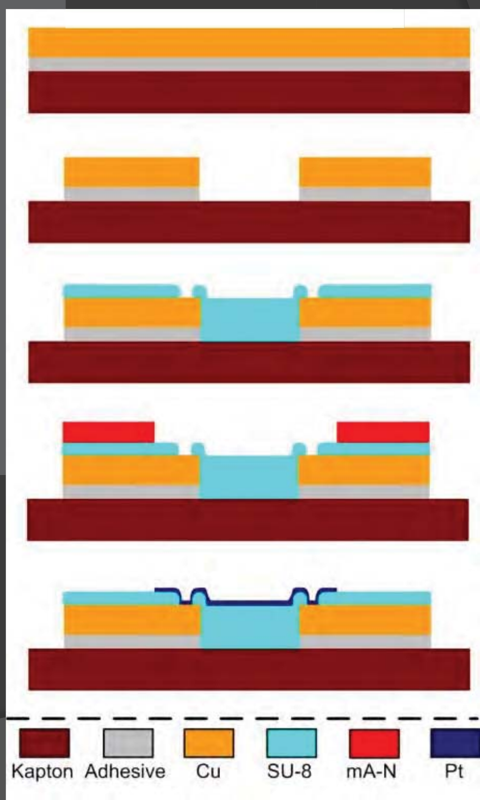
# Flexible Flow Sensor

## Device Characteristics




Cu thickness: 15 μm
SU-8 thickness: 15 μm
Vias depth: 3 μm
Ti thickness: 30 nm
Pt thickness: 300 nm
Thermistors' width: 100 μm
Thermistors' length : 1.5 mm

## Process Flow



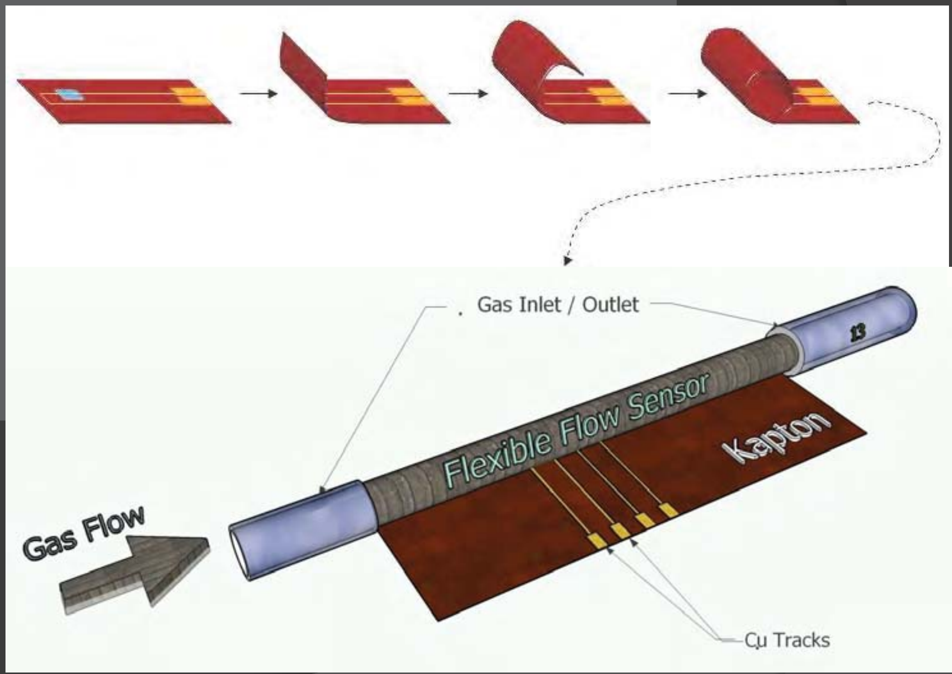
# Measurement Set-up

**$N_2$ Flow measurements within the range 0 - 10 SLPM**

The sensor adjusts to the tube curvature

Minimal invasion to the flow field

Direct communication to the macroworld

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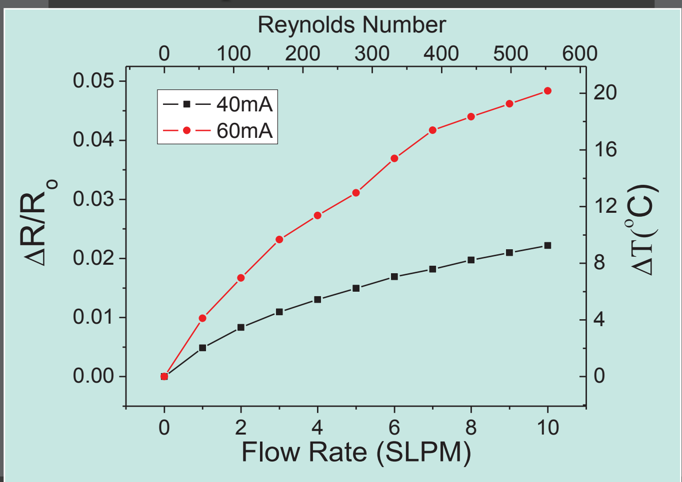
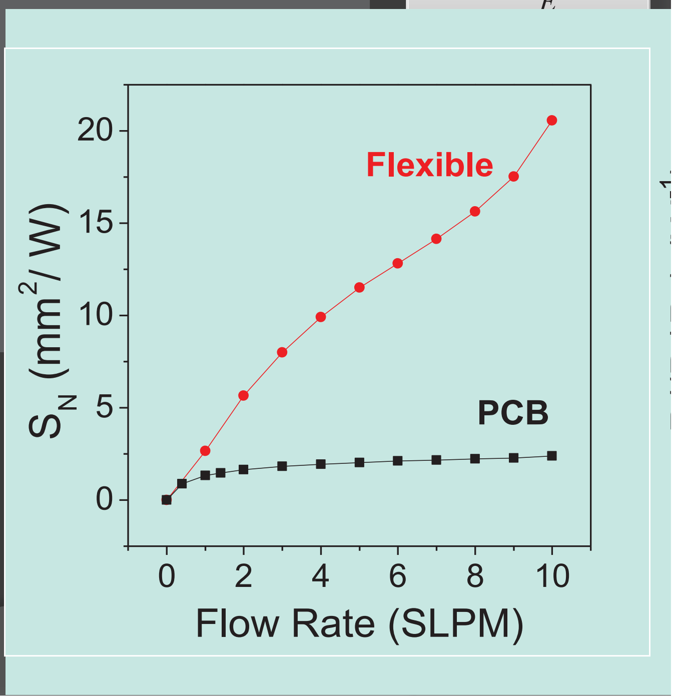
# Flexible Gas Flow Sensor Performances

**Sensor Operation in *Hot Wire Mode***




**Sensitivity Comparison**

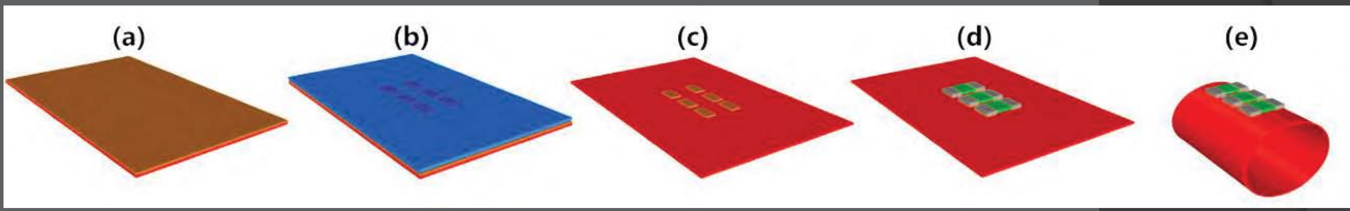
$$S_N = \frac{\Delta R / R_o}{\frac{P_i}{\frac{1}{F}}}$$

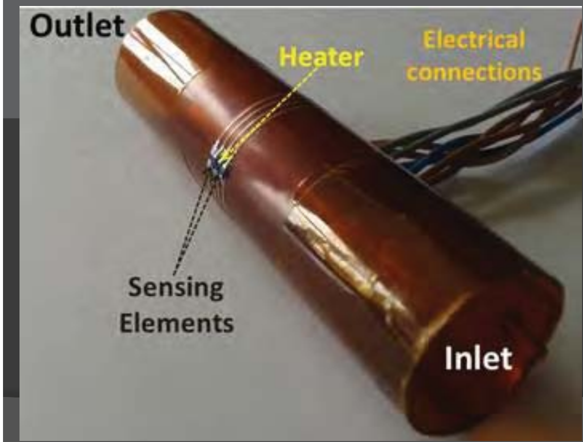



- Sensor Evaluation in the 0 – 10 SLPM region
- Performance comparison with a rigid PCB flow sensor

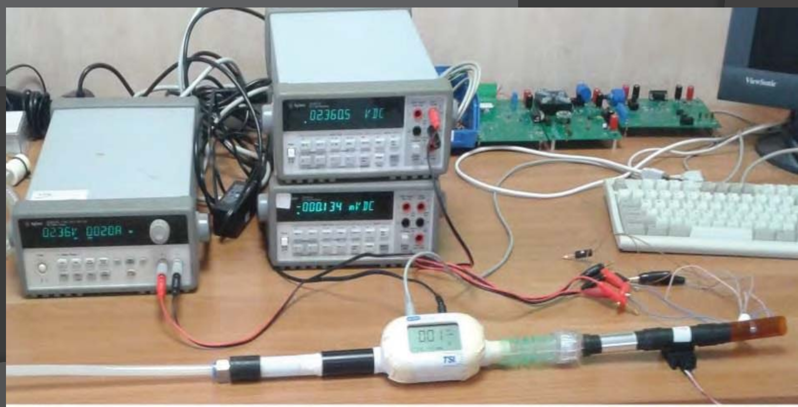
# Flexible sensor, with Discrete Elements implemented on the external surface of the flow channel

## Fabrication process




## Experimental setup



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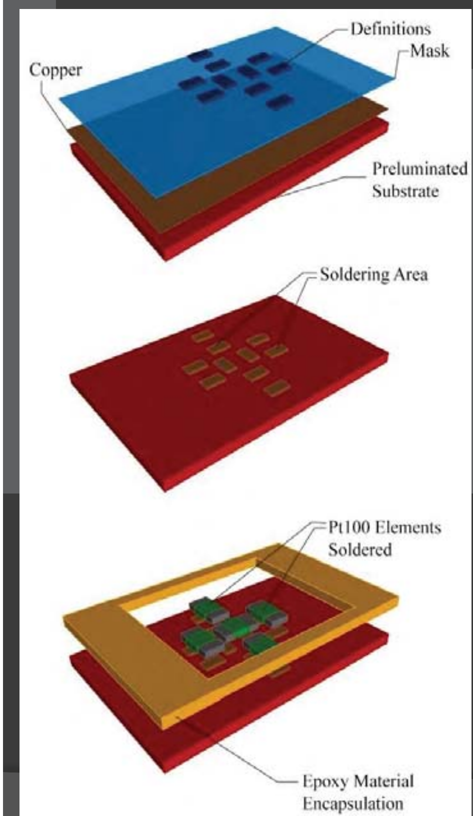
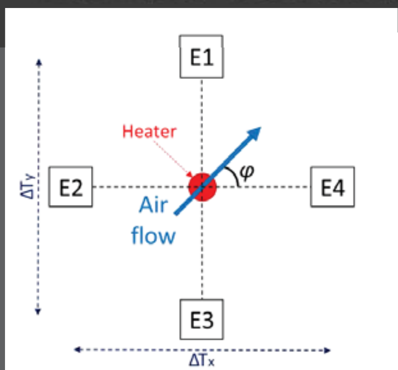
# A multi-directional thermal flow sensor fabricated on flexible substrate

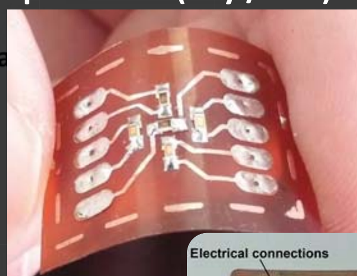


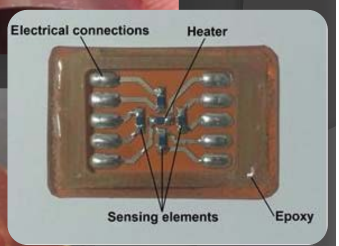




$\Delta Tx = \Delta T0 \cos\phi$

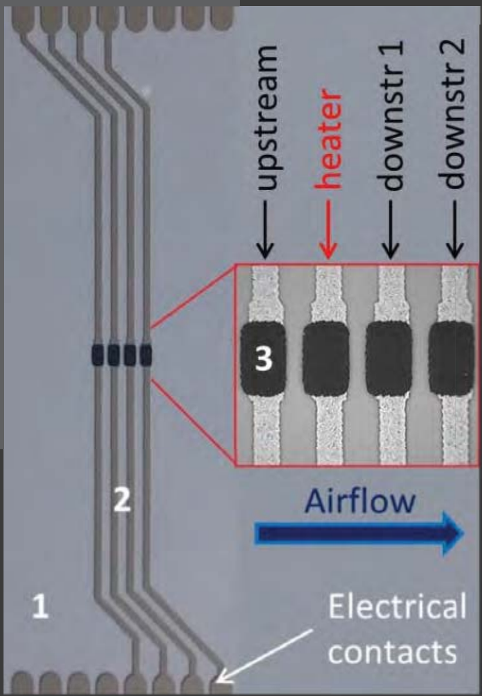
$\Delta Ty = \Delta T0 \sin\phi$

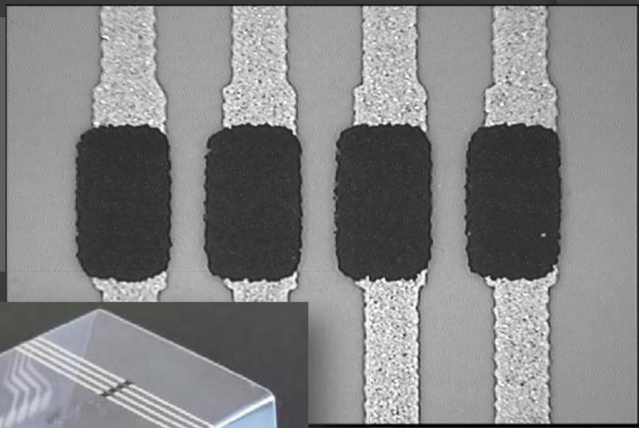
$\phi = \arctan(\Delta Ty / \Delta Tx)$

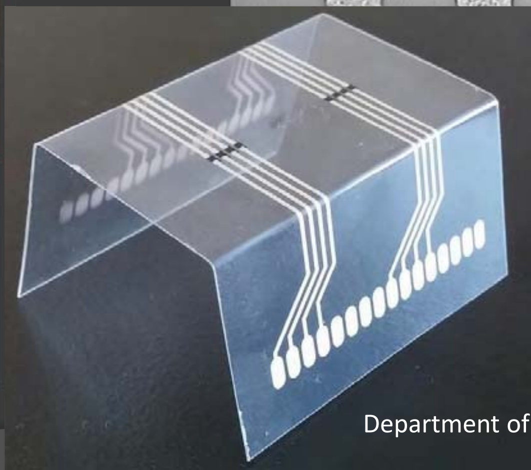





# Screen-printed thermistors for flexible flow sensing applications





In collaboration with:
University of Pardubice,
Faculty of Chemical Technology,
Department of Graphic Arts and Photophysics,
Pardubice, Czech Republic

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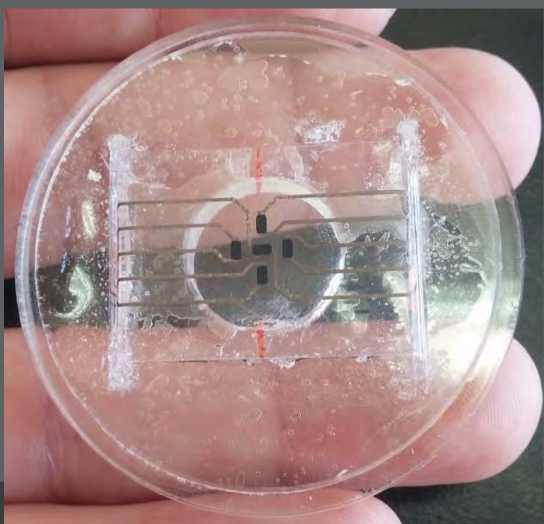
# 2D Screen-Printed Flow Sensor



- Sensing elements into flow channel
- Plexiglas packaging
- Interconnection through FPC connectors

T.E.I. of Athens
Department of Electronic Engineering
microSENSES Lab
Gr. Kaltsas
cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY
Acknowledgments ...
Faculty Staff
Grigoris Kaltsas
Professor (Head of the laboratory)
Evaggelos Valamontes
Professor
Ioannis Famelis
Associate Professor
Georgios Patsis
Associate Professor
Xenofon-Dionisios Kandris
Dimitris Pagonis
Assistant Professor
Odysseus Tsakiridis
Lecturer
Research Assistants
Georgia Paivana
PhD Candidate
Anastasios Moschos
MSc Student
Dimitris Barmpakos
MSc Student
Giannis Koutsis
MSc Student
Alexis Psiris
BSc Student
Damianos Marinatos
BSc Student
Kimon Mitrousias
BSc Student
microSENSES
Research Laboratory

## 4. 3D Printing

Tim Mortensen, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a

Swansea University
Prifysgol Abertawe

# 3D Printing: An Overview

WCPC Summer School

11th July 2016

Dr Tim Mortensen

Welsh Centre for Printing and Coating
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Canolfan Argraffu a Chaenu Cymru
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## What is 3D Printing?

- Additive Manufacturing which results in a three dimensional object
- 3D printing covers a large range of techniques: FDM, LOM, SLS, EBM, SLA, DLP
- Covers a large range of materials: PLA, ABS, PET, Nylon, Paper, Photopolymers, Metal Powders

# What can it be used for?

- Rapid Prototyping
- One off components
- Interlocked objects

- Lightweight parts
- Impossible (Or really hard to produce) Shapes



# What can't/shouldn't it be used for?

- High Volume Production
- High Speed production

- Certain high strength applications
- In vacuum operation

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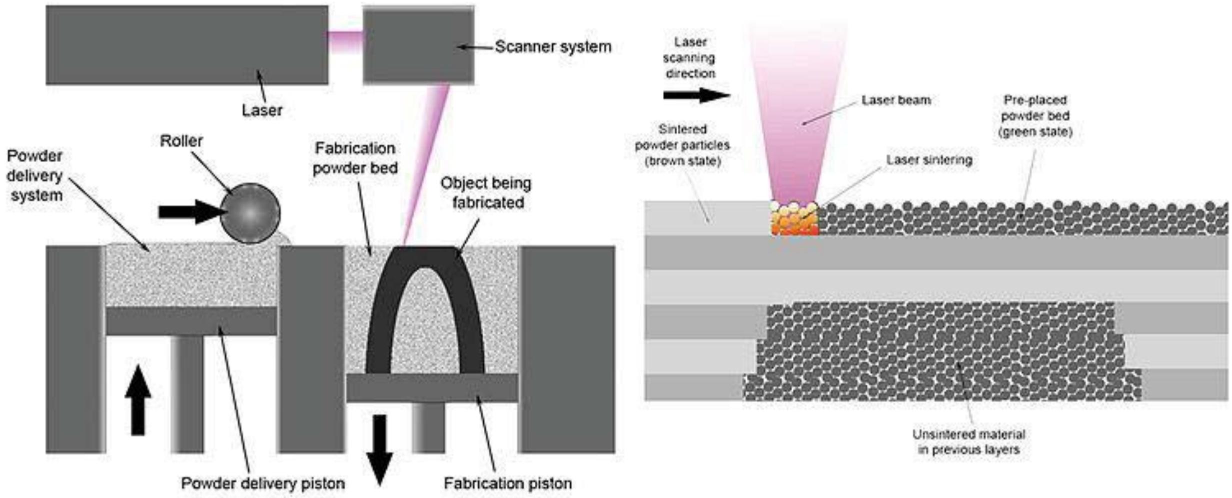
# Introduction to SLS/EBM






# Introduction to SLA/DLP

Note the differences:

- Support material required
- Material used must react and solidify upon exposure to light
- Parts are typically more sensitive to UV light once complete – not ideal for outdoor use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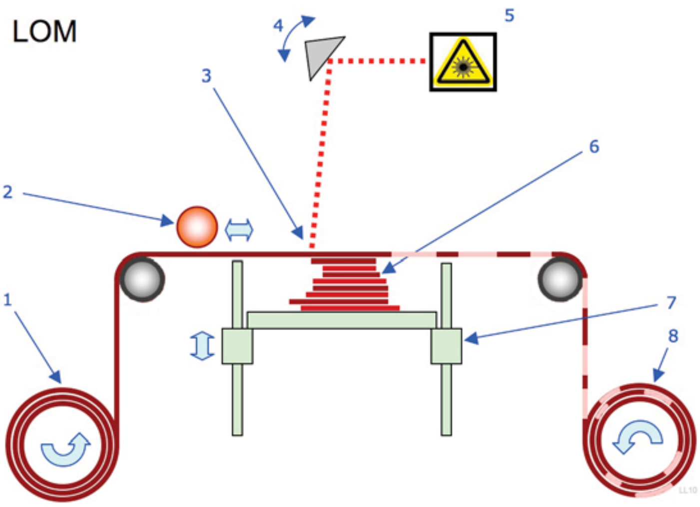
# Introduction to LOM

Sheets of materials are glued together and parts which are not required are cut away and discarded.

The objects can be made from sheets of paper, plastic or metal.

More wasteful than other methods because the cut material is wasted, but can work with very low cost materials that can't otherwise be used





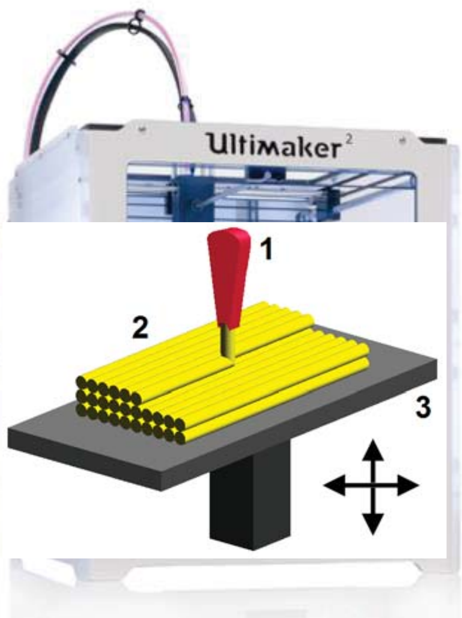

# Introduction to FDM

The type of device most people think of when they are asked to picture a 3D printer.

Plastic material, typically PLA or ABS, is forced through a small nozzle (~500um) at high temperatures (~200C).

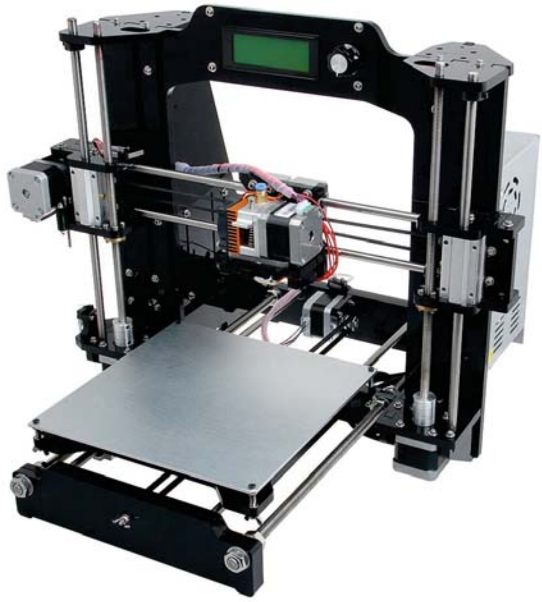
The nozzle is moved around as the material is extruded and the material sticks to the layer below.

Material can bridge a gap or overhang to a certain extent but must be supported in some way, printing in mid air is impossible.



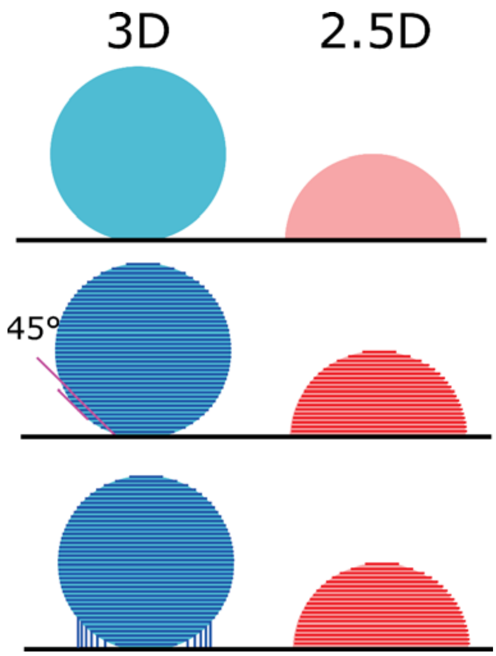
# Printer Parts: Overview

Nozzle
Hotend
Extruder
Heater Cartridge
Thermistor
Build Platform/Print Bed
Heated Bed
Bowden Tube
Motors
Lead Screw
Belt
Limit Switches
Inductive Sensor
Control Board





# 2.5D Objects




"2.5D" objects is a term which applies to 3D objects which have no undercuts or overhanging areas.

- Easy to print
- No need for support structures

If you are designing an object it is best to aim for a 2.5D type model where possible.

Although it is often possible to print an object in a range of orientations, selecting one that allows 2.5D printing is typically best.

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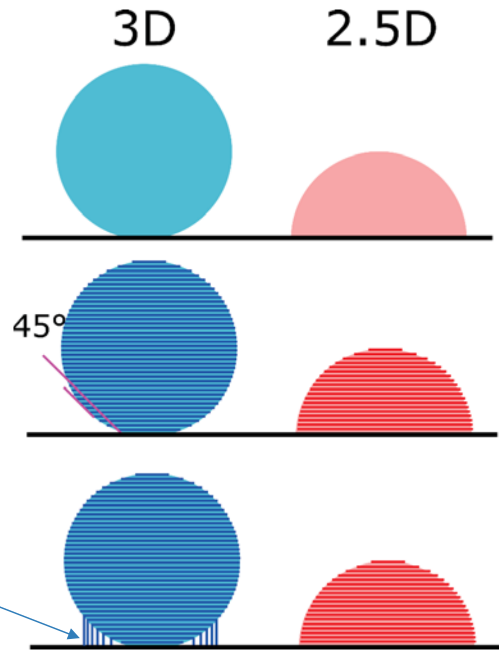
# 3D Objects




Often you'll want a shape which has overhangs. These can still be achieved, but will need a little more care.

- The model can be designed to have chamfered edges, gentle curves and extra features to reinforce hard to print sections
- The model can be oriented to minimise overhangs and reduce angles of features
- Support material can be generated.

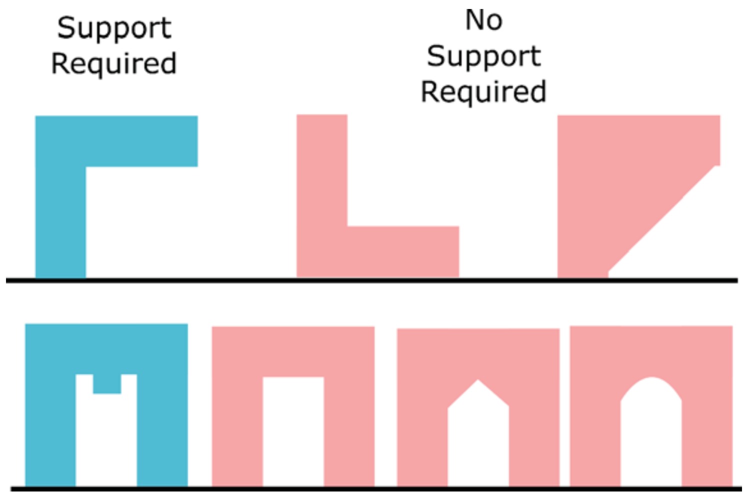


# Support Material

Avoid support material wherever doing so does not negatively impact your design.

It is possible to print over free air providing both the start and end of the overhang is supported.

"Bridging" varies in performance across machines and changes dramatically with parameters such as speed, temperature, cooling, nozzle size and extrusion multiplier.

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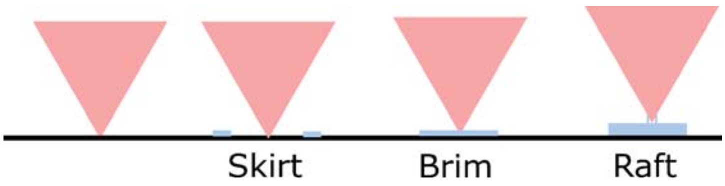
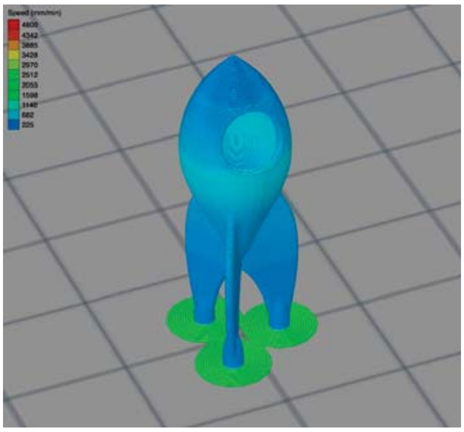
# Layer one objects: Skirt/Brim/Raft

A skirt does not touch the print, instead it draws a perimeters around the print ensuring the nozzle is full of plastic. Can also insulate or catch ooze.

A brim increases the contact area of the print with the bed this prevents to object falling over whilst printing

A raft is typically much larger than a brim and it prints before the first layer of the object. It pulls away like support material, but helps to object stick to the print bed.



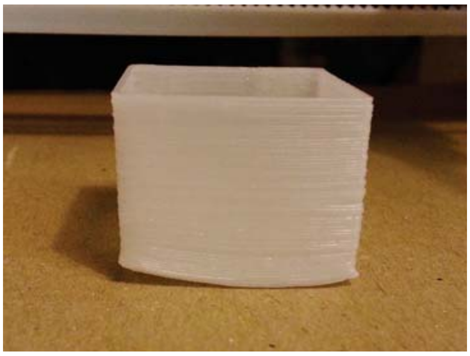


# Adhesion and avoiding warping

As plastic cools it contracts and if it is not stuck well to the surface it will lift from the print bed. This causes distortions to the object and even print failures.

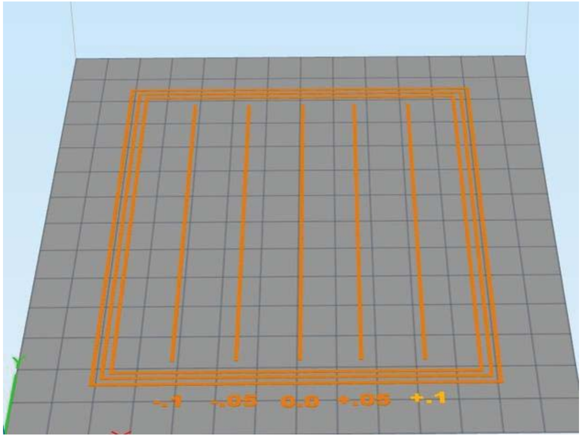
A few things you can do to prevent warping:

- Use a heated bed (Essential for ABS)
- Calibrate Z-Height
- Use stable cooling (No drafts or sudden temperature changes)
- Coat print bed in Bluetape/PVA/Glue Stick
- Print using a raft/brim
- Avoid long and thin designs
- Adjust print temperature
- Print slower
- Use less infill



# Checking Z Height Calibration and levelling

Z-Height calibration varies printer to printer. Follow your printer manufacturers guide to performing calibration.



To determine whether the calibration is correct print a large single layer square or circle near the perimeter of your build platform.

The shape should stick well to the build platform and when measured using callipers of a micrometre should give consistent readings.



# Automatic bed levelling/tramming

Some printers have automatic print height measuring and bed levelling built in.

A sensor near the print nozzle maps the surface of the build area and applies this offset to the print to ensure the print sticks well.

You can still have first layer issues if the Z-Offset, hotend temperature or surface coating are incorrect.

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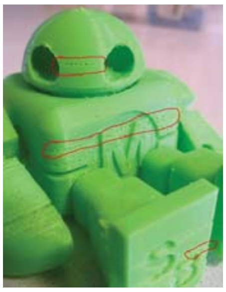
# More types of defects

There are a range of print defects that can reduce the quality of your print, including but not limited to:

- Under/over extrusion
- Too Hot/Cold
- Stringing
- Missing Layers
- Layer Splitting



Useful Guide: https://all3dp.com/common-3d-printing-problems-and-their-solutions/



# Removing the object and Supports/Brim/Raft

Once printed it is best to allow the model to fully cool before removing. If using a heated bed this can take some time. A thin putty knife, or other fine blade can be used to break the adhesion between model and print bed.

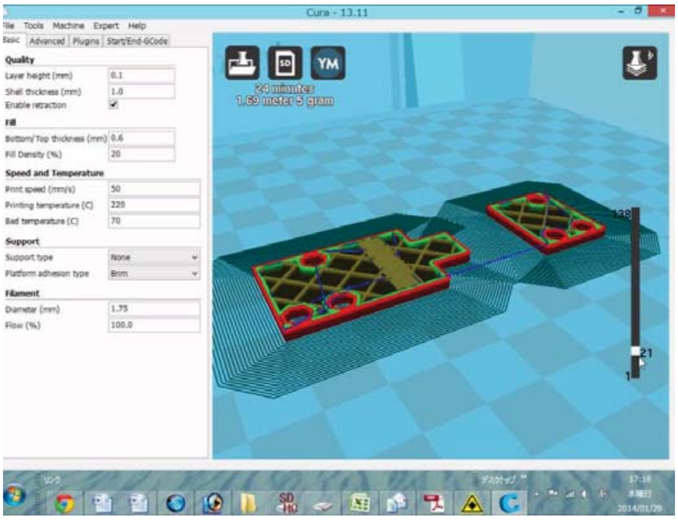
How easily support material comes away from your model depends on print parameters, material selection, support placement and the slicer you use.

Most supports should simply pull off from the model and require minimal clean up. A pair of pliers and a sharp knife are often useful.

# What is Gcode?

Gcode is the language that the printer speaks. Gcode contains all the information needed to print the object. Temperature, position, speed, retraction, etc etc.

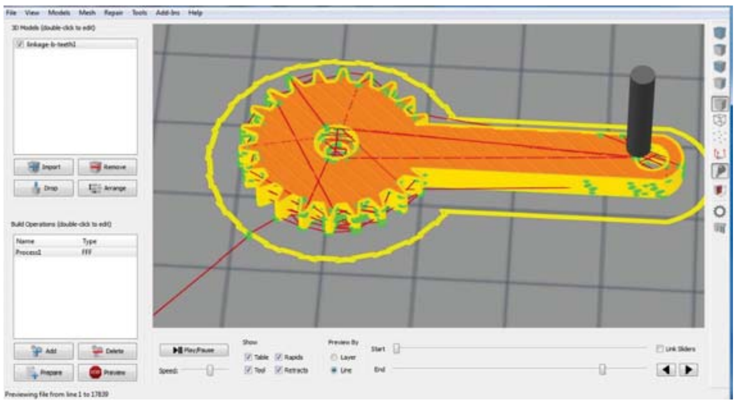
A printer can't understand a 3D model and instead a series of instructions must be made. These commands are generated by a piece of software called a Slicer. The slicer has to be told everything about your printer.






# Which Slicer to use?

If in doubt use the Slicer recommended by your printer manufacturer. Creating custom slicer settings is generally tough and time consuming.



Top Slicing Software:

Simplify3D – NOT FREE – Extremely Powerful

Craftware – Surprisingly Fast + Good Supports

Cura – Has a good range of built in printers

Slic3r - Basic

Repetier – Uses either Cura or Slic3r, but with a nice interface.

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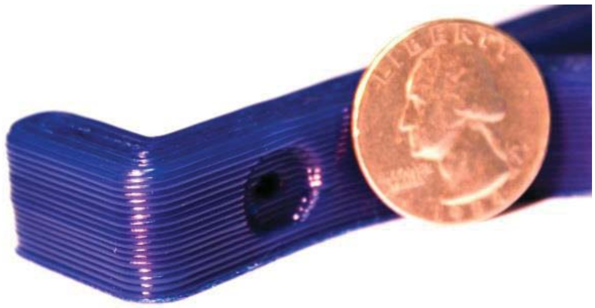
# Important Slicer Settings

Although fully calibrating printer settings is daunting there are a few settings in is important to check:

- Layer Height (Typically 0.2mm)
- Extruder Temperature
- Bed Temperature
- Extrusion Multiplier/Filament Diameter

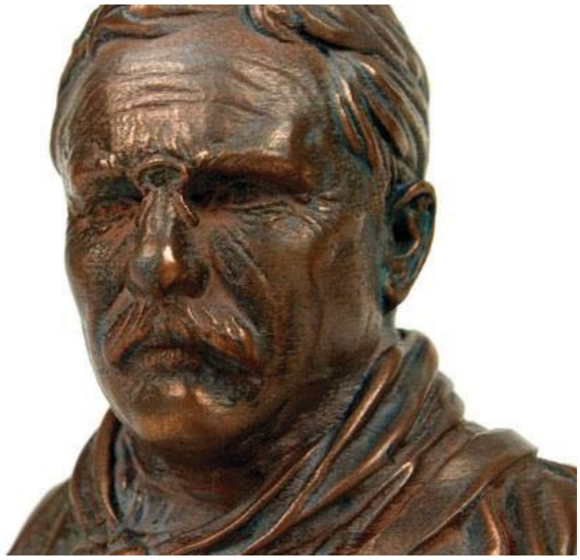


Smaller Layers aren't always better.



# Exotic Materials

Standard Filaments (PLA, ABS) can be combined with a range of interesting components to completely change the performance of the printed object.



- Bronze/Copper/Iron filled material
- Carbon Fibre
- Conductive Filaments

It's also possible to put different materials through some machines

- PET
- Nylon
- Flexible Materials

Though some materials require significantly higher temperatures which should not be attempted without an all-metal hotend.

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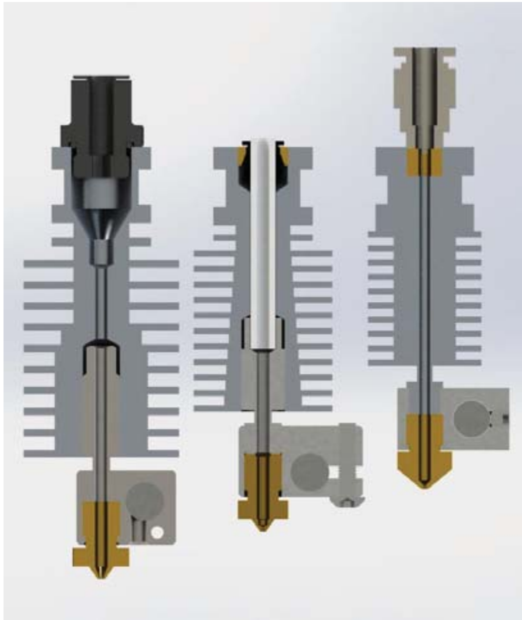
# All-metal hotends

Some plastics, such as Nylon (250-270C) require significantly hotter temperatures than PLA/ABS (190-230C).

At these temperatures any PTFE or PEEK components that feature in early hotend designs will be damaged and potentially produce toxic fumes.

All-metal hotends don't feature any of these components, but require higher machining tolerances and thus demand a higher price (£50 vs £20).





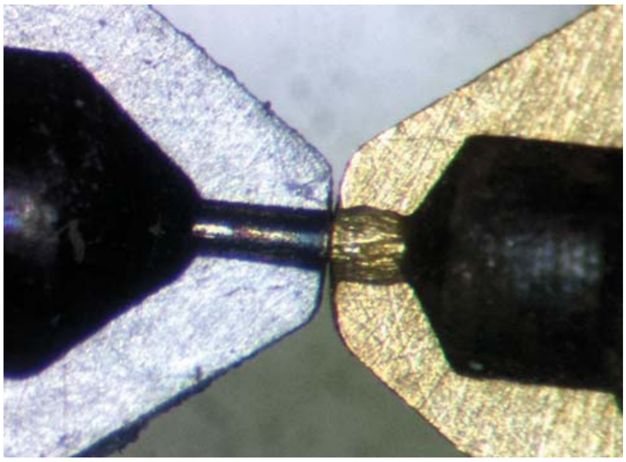
# Plated/Stainless Nozzles

Adding particles to a filament can make it significantly more abrasive to the nozzle of the printer.

Wear on the nozzle increase the apparent diameter and lead to under extrusion and oozing.

Plated nozzles increase the hardness compared to standard brass.

Stainless steel nozzles are much harder than brass but typically harder to machine so cost more (~£15 vs £5).



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# Dual Extrusion

The use of multiple extruders on a single printer can allow two different colours or materials to be combined in a print.

Multiple colours, mixing flexible and rigid materials or having dissolvable support structures can be achieved.

Downsides:

- Hard to do
- Clean separation requires rigorous calibration



# Delta vs Cartesian

Delta Printers do not have dedicated X,Y,Z motors and instead move in these directions by combining the motion of two or more motors.

Pros:

- Each axis is identical
- Tall printers are much simple to make
- Print bed doesn't move
- No motors on the printing stage
- Can achieve very high print speeds

Cons:

- Often use Bowden extruders (Discussed later)
- More demanding on control board
- Calibration can be challenging
- Resolution varies with radius

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# Delta vs Cartesian

Cartesian printers move in X,Y and Z. Often the head moves in X and Z and the bed moves in Y, but some do feature a static bed or other combinations.


Pros:

- Generally can handle a heavier extruder assembly
- Generally Direct Drive
- Resolution fixed across the print area
- More logical bed levelling

Cons:

- Heavier heads require slower speeds
- More expensive to increase size



# Direct Drive vs Bowden Extruder

Bowden extruders are located away from the hotend and the filament is pushed through a tube.


Pros:

- The weight of the hot end is reduced
- The size of the hotend is reduced
- The wiring is simplified
- The filament path is easier to control

Cons:

- Cannot print flexible filaments
- Additional drag on filament
- Uncertainty in amount of filament dispensed

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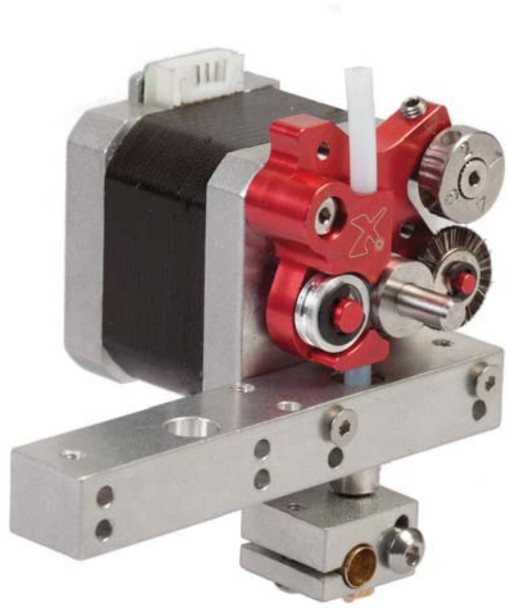
# Direct Drive vs Bowden Extruder

Direct drive requires the stepper motor to be attached to the print head.



Pros:
- Filament is fully constrained from the motor to the nozzle
- Can print flexible and tough to print filaments
- Less friction on the filament
- Potentially faster extrusion speeds

Cons:
- Slower head movement speed
- Bulkier assembly (smaller print area)

Ultimately both methods are a trade off and depend on the materials and printer you are planning to use.



# The future of 3D printing

There is no need for a 3D printer in every home, though they will become increasingly easy to access and use.

PHOTO: WARNER BROS./GETTY IMAGES

The biggest advances will be from the smallest changes. Automatic bed levelling, extrusion calibration, print recovery etc.

The exotic materials will play an interesting role. Added features such as conductivity, or strength will enable these parts to be used in new and different ways.

More tools available to make parts, slice parts into gcode and more ways to print.

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# Thank You For Listening

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## 5. Inkjet printing

### Dave Shaw, Welsh Centre for Printing and Coating

#### Biography

n/a

#### Abstract

n/a


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# Inkjet printing

# What is inkjet printing?

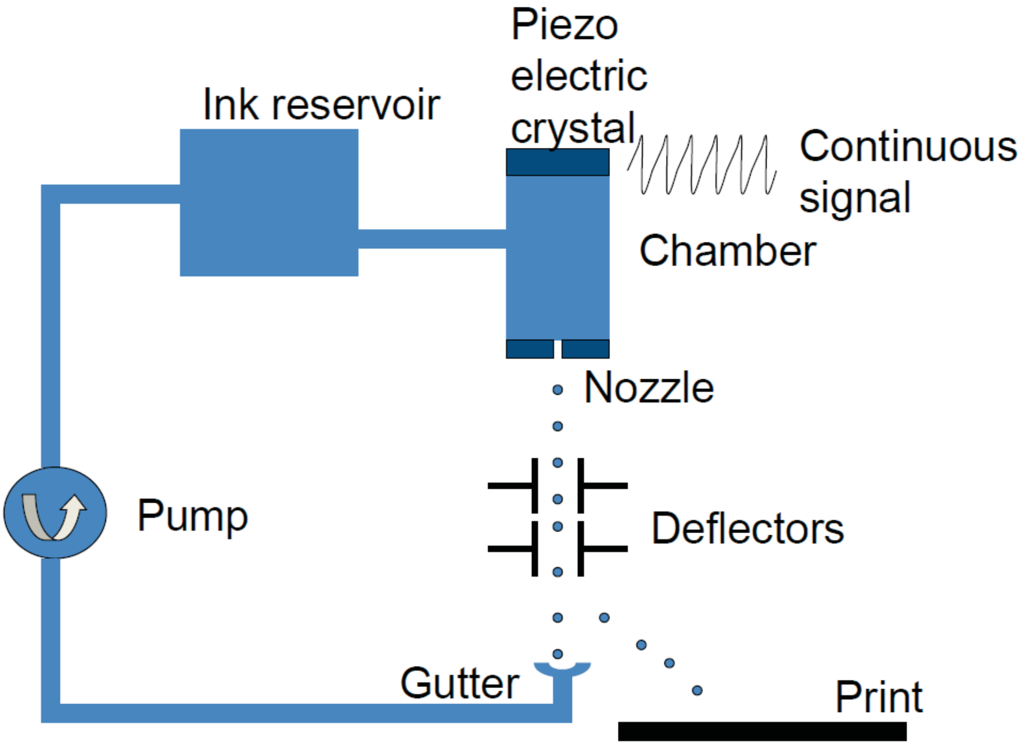
- Non-contact printing method
- Digital, master-less printing
- Image/pattern changes are viable in an extremely rapid time frame unlike more traditional printing techniques such as flexographic and screen printing
- Operates on a process of single droplet formation and deposition



# Types of inkjet printing

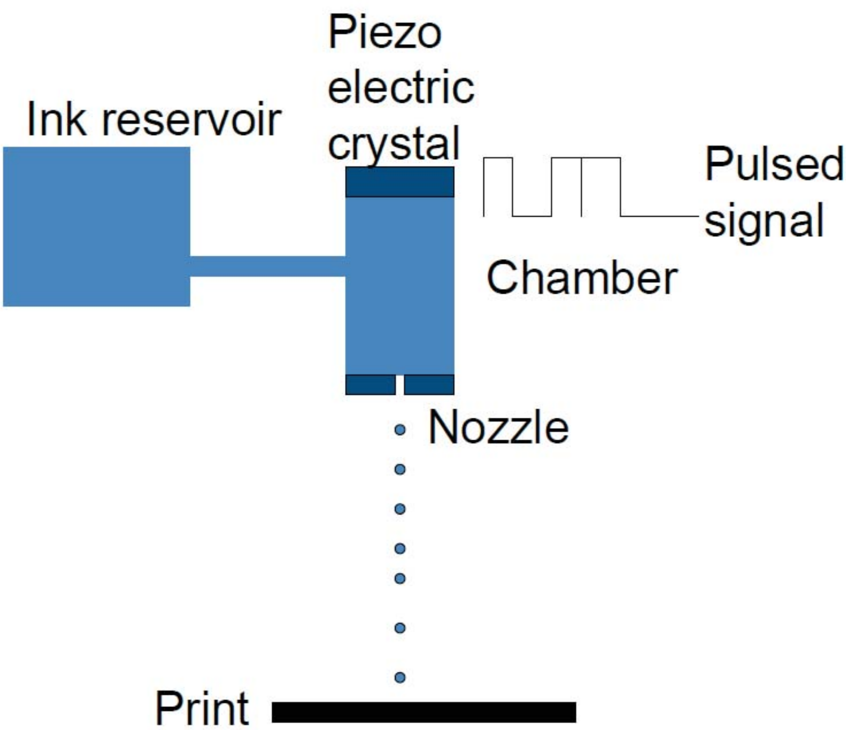
- Two umbrella categories:
- Continuous
- Drop on demand (DoD)
- Subdivisions of formation method (including):
- Thermal
- Piezo

# Continuous piezo

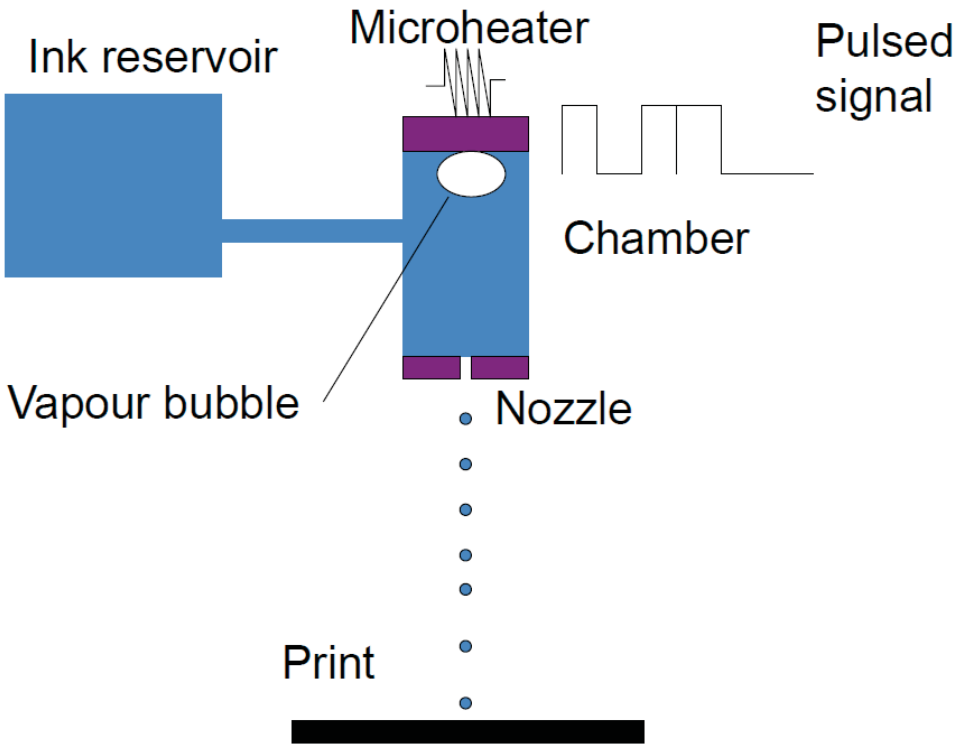





# DoD piezo



# Bubble jet

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# Ink property requirements

- Viscosity and surface tension critical
  - ➢ Surface tension too low
    - Ink will drip from nozzle
    - Non-uniform sized drops
  - ➢ Surface tension too high
    - Jet mechanism cannot be primed as cannot be removed
- Low viscosity
  - ➢ Typically 5 – 12 cP (mPa.s)
- Surface tension
  - ➢ Typically 30 – 45 dynes/cm
- Particles size
  - ➢ Typically <0.2 microns

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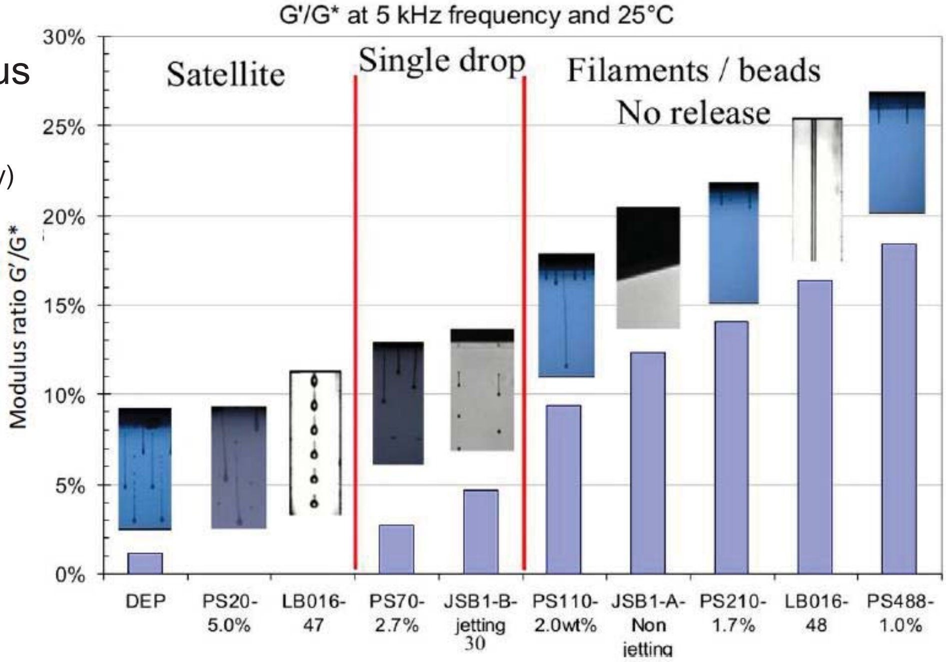
# Ink property requirements

- Careful control of ink properties is also required to prevent various drop formation issues
- G' = Elastic modulus
- G* = Complex modulus
  - ➢ $f_{(\text{shear viscosity, elasticity})}$

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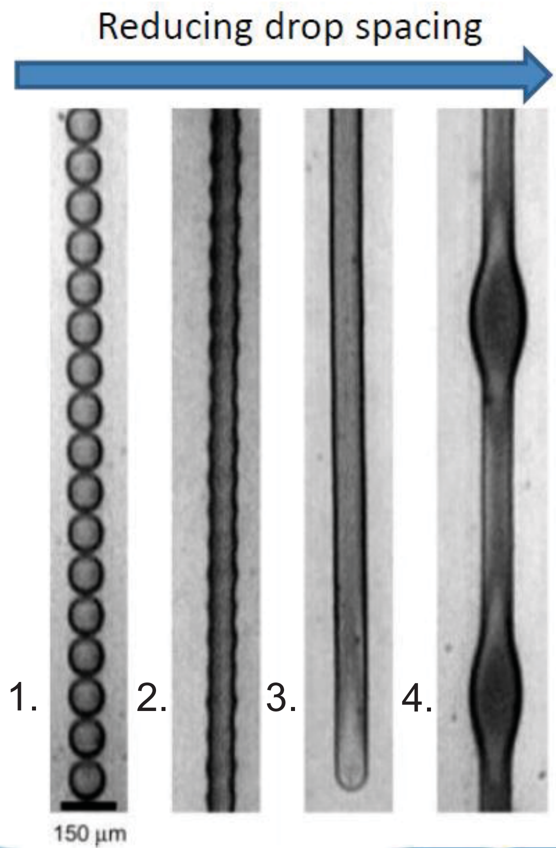
# Droplet formation boundaries

1. Individual drops
2. Scalloped
3. Uniform
4. Bulging

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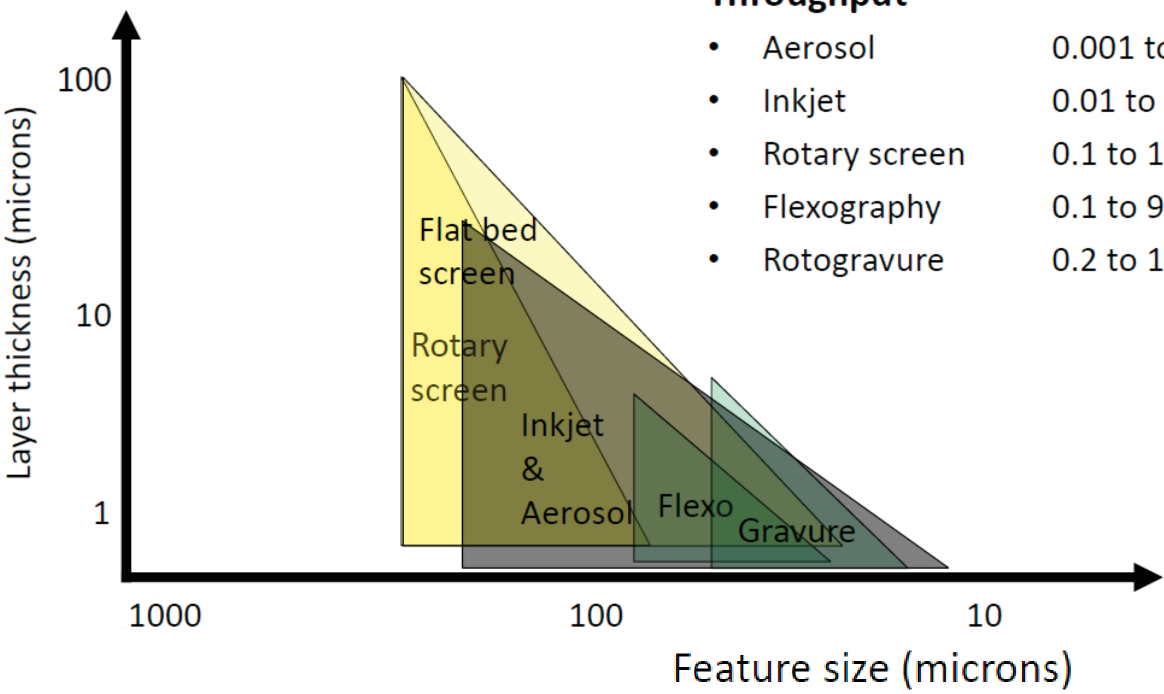
# Process capabilities




**Throughput**

| | |
|---|---|
| • Aerosol | 0.001 to 0.01 $m^2/s$ |
| • Inkjet | 0.01 to 0.5 $m^2/s$ |
| • Rotary screen | 0.1 to 1 $m^2/s$ |
| • Flexography | 0.1 to 9 $m^2/s$ |
| • Rotogravure | 0.2 to 15 $m^2/s$ |

# System option examples

- Dimatix
  - Made by Fujifilm
  - Standard research tool => used by many research groups
  - One head type
  - A4 sized print area
  - Lower initial cost
- Ceradrop
  - Newer research system
  - Multiple heads types
  - A4+ sized print area
  - Mid to high range initial cost
  - A range of scales available
- Pixdro
  - Made by Meyer Berger
  - Multiple heads types
  - A4+ sized print area
  - Mid to high range initial cost
  - Increased functionallity

# Conclusions

- Inkjet is an excellent research tool:
  - Small ink quantities
  - Digital process
- Process speed can be a controlling factor, but there are options to mediate this
- Careful control of ink properties and print settings are required for a successful deposition
- The process is scalable depending on product/industry requirements

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icmPrint

## 6. Pad printing

James Claypole, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a

## 7. Drying and sintering

Davide Deganello, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

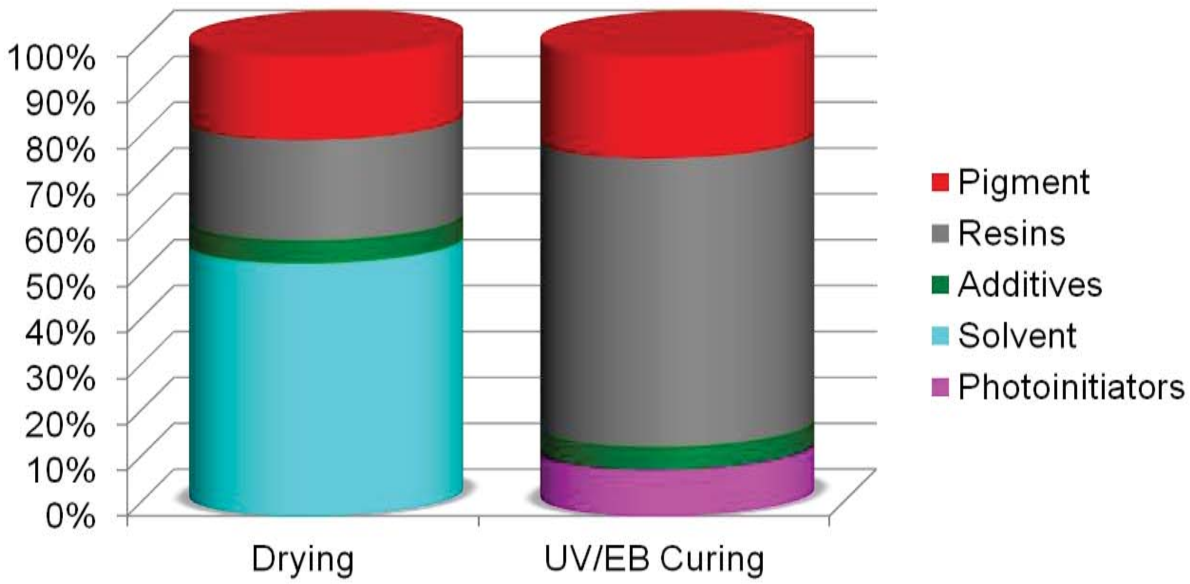
n/a

# Curing and drying

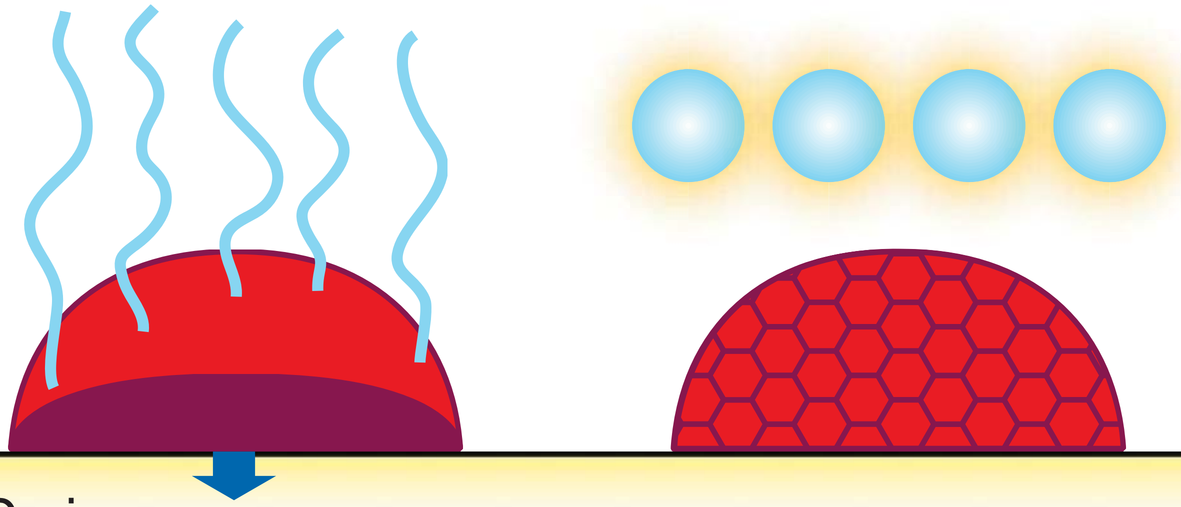
Presented by

D.Deganello

## Generic ink composition



## How inks reach the dry residue



- Drying
  - Water based
  - Solvent based
- Curing
  - UV
  - EB

## Why is drying or cure so important

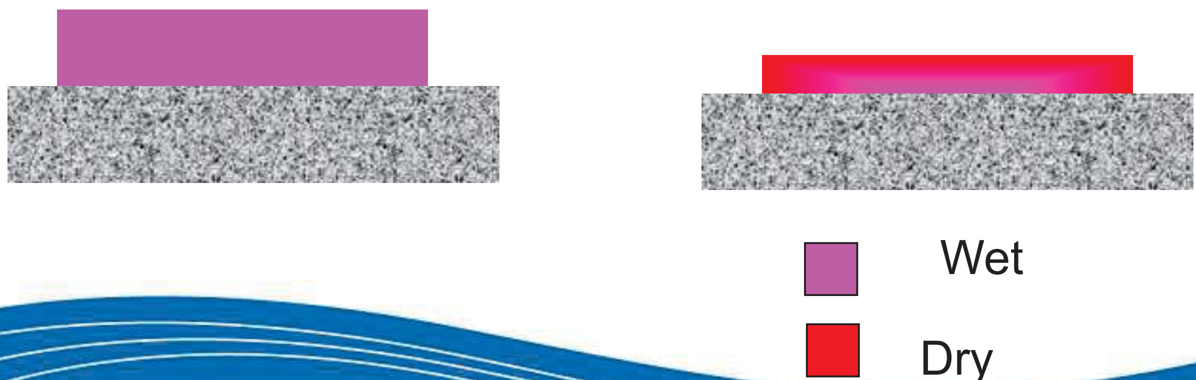
- Control is required to ensure the ink deposition cures, and cures completely, but at application stage only
- Correct dying or cure
  - Prevents premature failure of surface
    - Stops material being rubbed off.
  - Ensures correct properties of deposited materials.
    - Correct laydown of surface
    - Correct layer separation deposition and alignment of solids
      - El, Micro LED (so they can light up)
      - Carbon and metallic pigments conduct
  - Reduces downtime on the machine.
    - Build up of ink on rollers
    - Transport of ink to unwanted areas
    - Drying in on mesh/plate/cell

# Methods of drying

- Not only evaporation............
- Physical
  - Evaporation
  - Penetration
- Chemical
  - Polymerisation
  - (Oxidation)

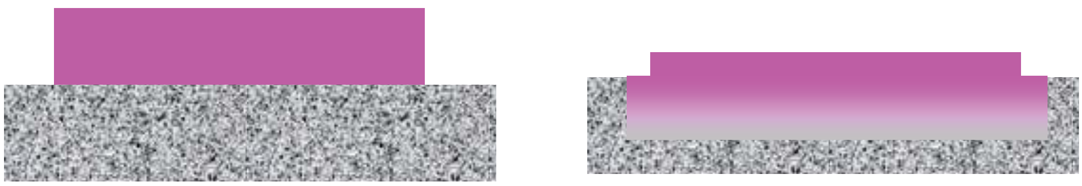
# Ink drying- Evaporation

- Evaporation- solvent loss
  - The vehicle carrying the pigment contains a low boiling point solvent which evaporates leaving behind the dry film
- Ink becomes more solid as liquid is lost as vapour
- Interlocking of resin: effect of chain length on rheology/performance



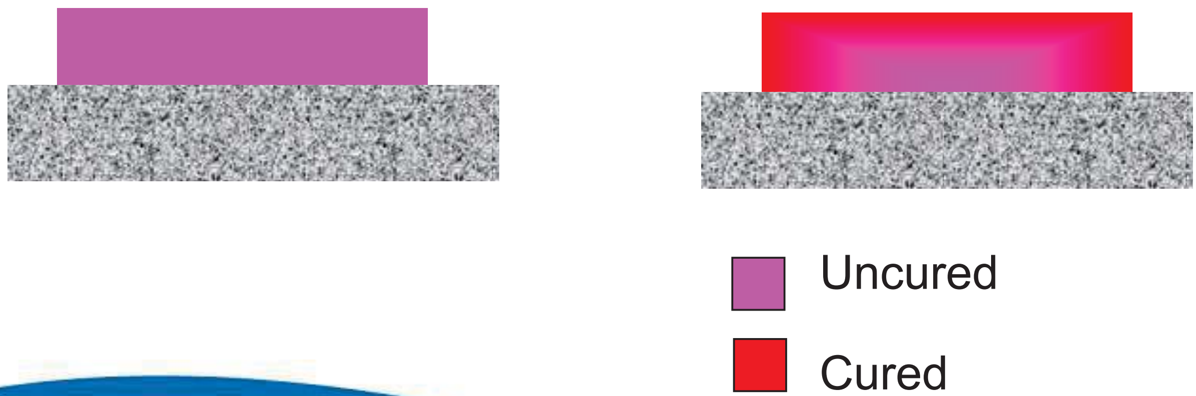
# Ink drying - Absorption

- Penetration - absorption
- The vehicle carrying the pigment is absorbed into the surface of the substrate concentrating the solid content (pigments and resin) at the surface.
- For some materials (oils)
  - Ink film never truly dries.... How ink can get harder?



# Ink drying - Oxidation

- Oxidation ( drying agents, i.e. Cobalt)
  - Is a chemical reaction of the vehicle. The oxygen from the air is absorbed into and reacts with elements within the vehicle causing the ink film to harden/polymerase
- High surface area of ink film and exposure to air results in hardening



# Evaporation

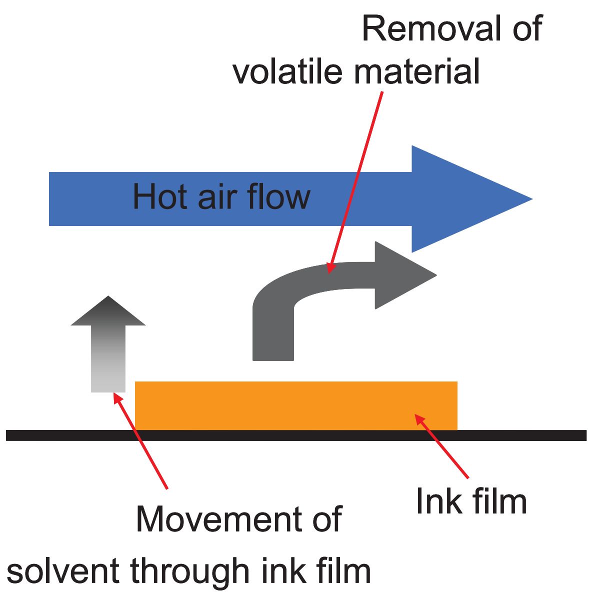
- Used for solvent based inks
- Key for plastic substrates/functional inks
- Removes solvent from ink
- Solidification occurs as solvent is lost, and polymers interlock
- Speed of drying dependent on
  - Ink film thickness
  - Press speed
  - Solvent properties

# Evaporation

To remove moisture from ink,

3 factors must be present:

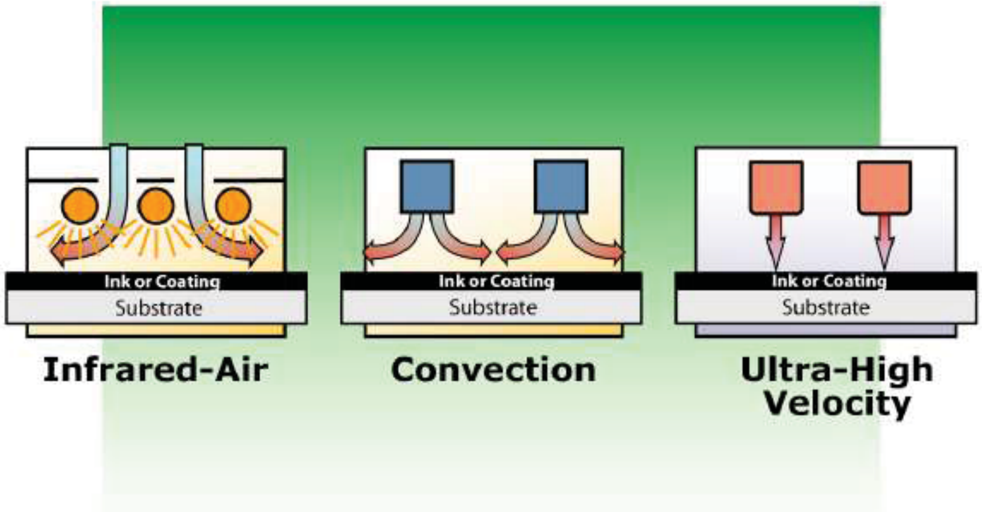
- Heat (energy)
- Air flow (Turbulence/speed)
- Low Humidity




- Flow of “dry” air on substrate to move vapour away from substrate
- Exhaust to remove vapour from within dryer

## Number of drying options available

### Dryer Types

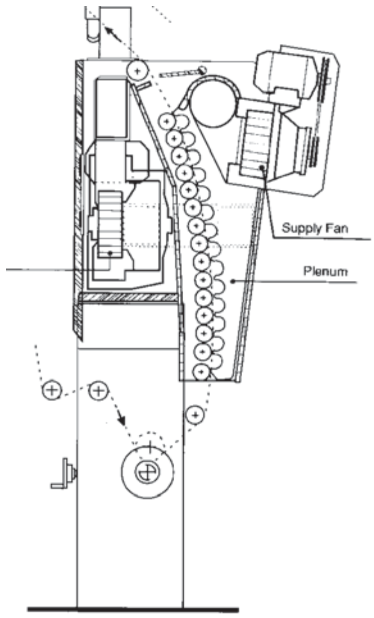



## Dryers

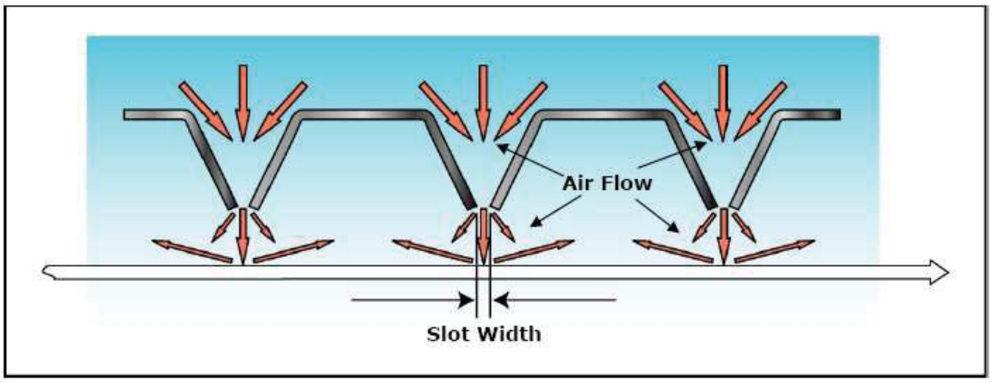
- Dryers designed to minimise explosion risk
    - Rugged construction
    - Known ‘weak point’
        - Control explosion if it occurs
- Pressure in dryer must be below air pressure in press room
    - No solvent migrates to press room
- Ducting / fans required to move air around press
    - High capital investment costs
    - Can take up a lot of space

# Convection "Warm air" drying

- Air jets impinge on surface
- High speed applications, e.g. Gravure
- Usually requires inter drying web control
- Usually gas / oil powered




# Convection




**Dryer Volume =**
**Air Velocity x Orifice Coeff. x Slot Width x Slot Length x Slot Quantity**

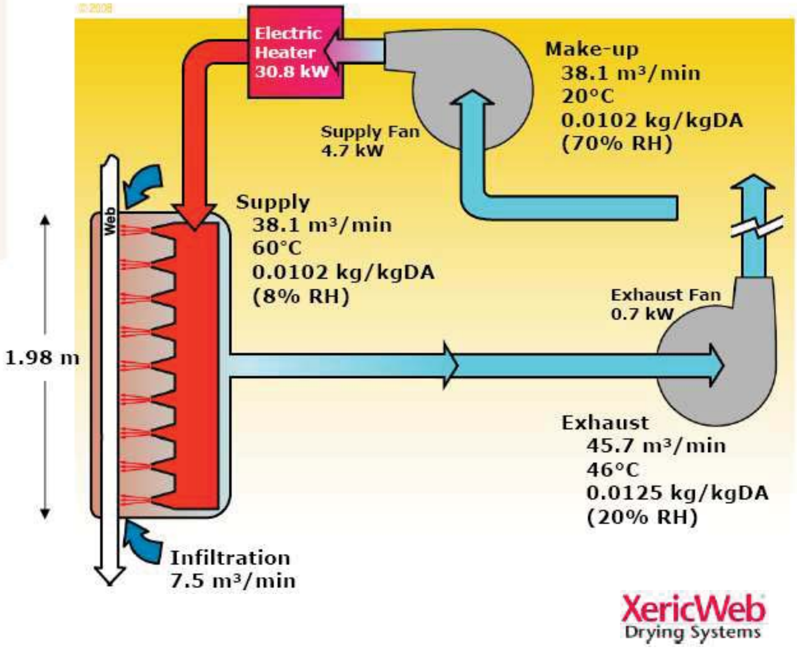
**Dryer Volume =**
**71.1 (m/sec) x 0.945 x 0.945 x 0.76 (mm) x 550 (mm) x 26 x 60/1000$^2$**

**Dryer Volume = 43.9 m$^3$/min**

XericWeb Drying Systems

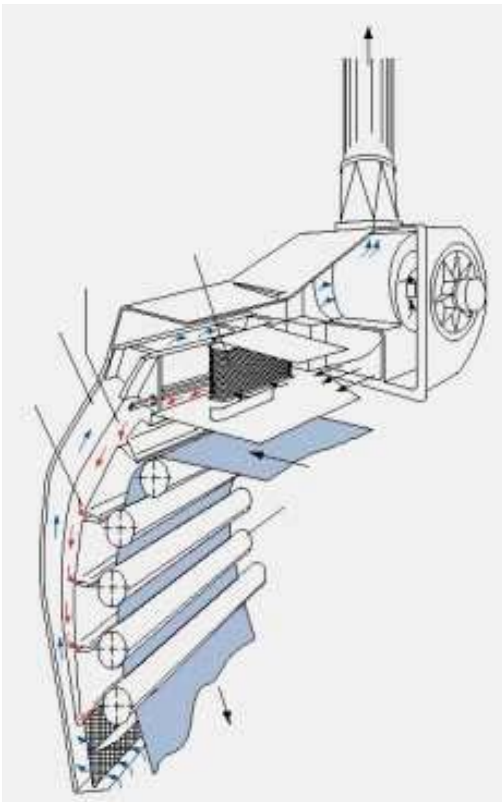
# Convection

Web:
- 150 m/min
- 500 mm wide
- 30 micron PET film
- 3 gsm wet coating weight – 40% water
- 20°C

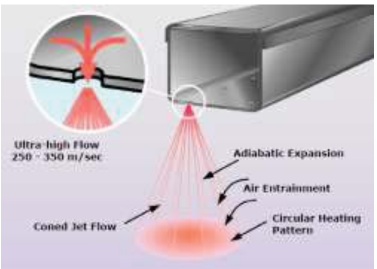


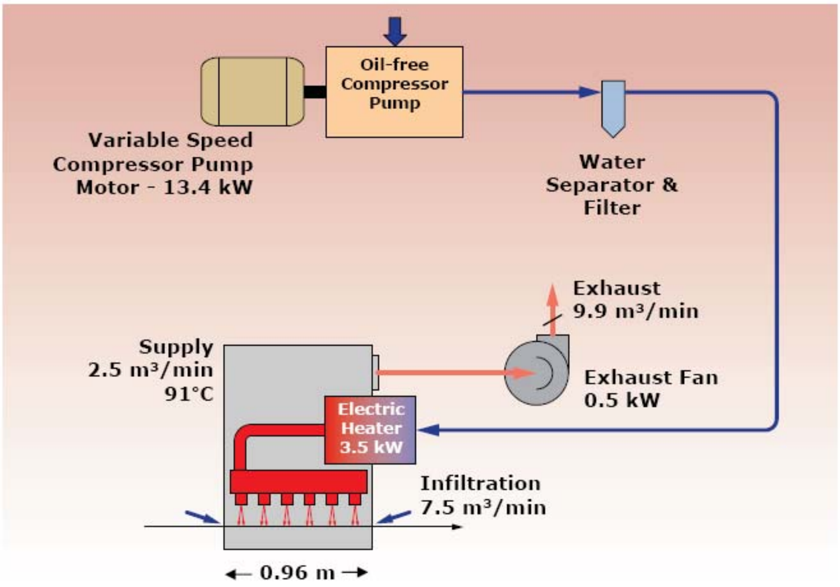

# Drying & cooling

- Hot air jet dries the substrate
- Cool air cools ink / substrate



# Ultra-High Velocity




**Web:**

150 m/min

500 mm wide

30 micron PET film

3 gsm wet coating weight – 40% water

20°C

# Air Dryers

- Large operational and installation cost
- Laminar flow stops substrate flap
- Turbulent flow increases mass transfer
- Air must be filtered
- High boiling point inks require more energy

# IR dryer

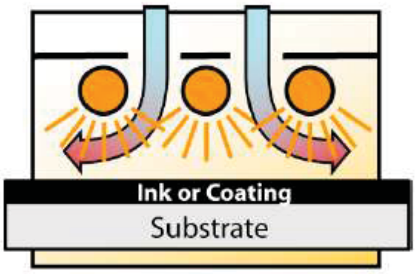
- Water-based inks require over 6 times more energy than solvent based inks
    - Often not efficient to use air dryers
        - Air flow rates
        - Limited speeds
- IR dryers can be used as alternative
- Not always suitable for solvent based inks
    - Risk of explosion

RA/Series
Electric Radiant-Air Heater
Shown with 90" heater mounted on movable stand

# IR dryers

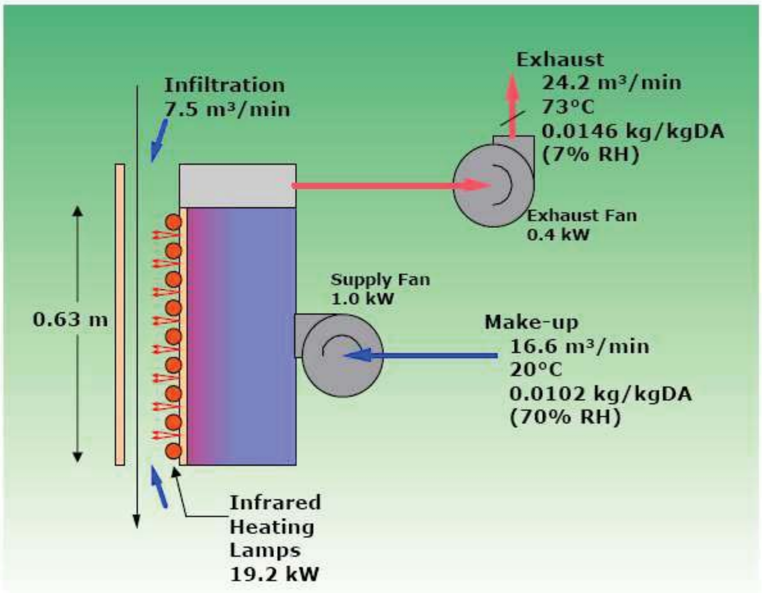
- IR dryers offer several advantages over air dryers
    - More compact in size
    - Lower initial capital investment
    - Easier to maintain
    - Provide greater control
    - More energy efficient
- Require extraction system to remove warm air
    - Water cooling may also be required

# Infrared - air




**Infrared-Air**

**Web:**
150 m/min
500 mm wide
30 micron PET film
3 gsm wet coating weight – 40% water
20°C




XericWeb Drying Systems

# Dryer comparison

| | Infrared Dryer | Convection Dryer (0% Recirculation) | Convection Dryer (72% Recirculation) | UHV Dryer |
|---|---|---|---|---|
| **Fans** | 1.4 kW | 5.4 kW | 5.0 kW | 0.5 kW |
| **Compressor** | - | - | - | 13.4 kW |
| **Heater** | 19.2 kW | 30.8 kW | 16.3 KW | 3.5 kW |
| **Total Power Use** | 20.6 kW | 36.3 kW | 21.2 kW | 17.4 kW |
| **Capital Cost Comparison** | 25-35% | 70-115% | 85-130% | 110-130% |

## Ink Curing- Polymerisation

- Polymerisation is the cross linking of mono/ short chain polymers forming a longer more ridged structure
- Normally polymerisation is accelerated in the presence of a catalyst, promoted by heat light or other high energy systems ( or 2 part system, mixed before printing)

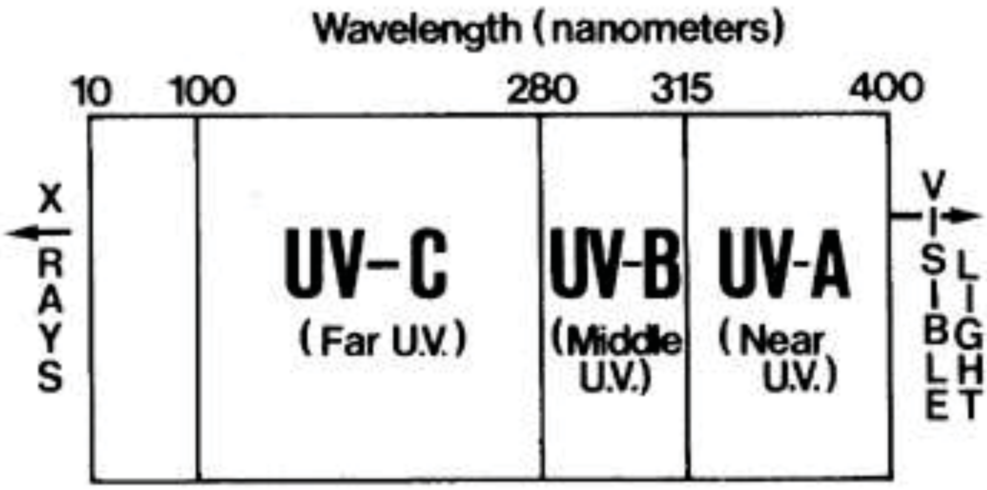
## UV Curing

- Zero solvent cure
- Ink film polymerisation started by UV exposure
- Can be instant cure
- Popular method for high speed curing
- Applicable to all processes
  - Speed and viscosity considerations

## UV - Lamps

- Emit radiation in UV part of spectrum
  - UVC (causes Ozone)
  - UVA and UVB
- Pure UV lamp would not be visible
  - Also emits other radiation
    - Visible light
    - IR
- Visible light also has safety function
  - So you know that lamp is on!
- LED UV Lights new format

## UV classification

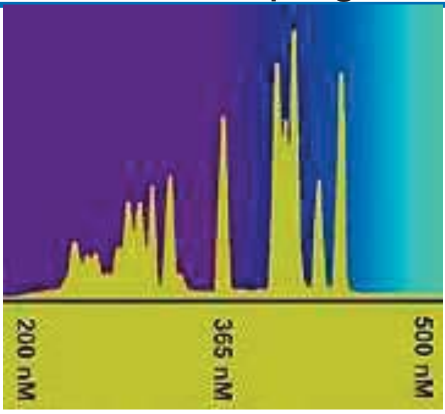


## UV Spectra

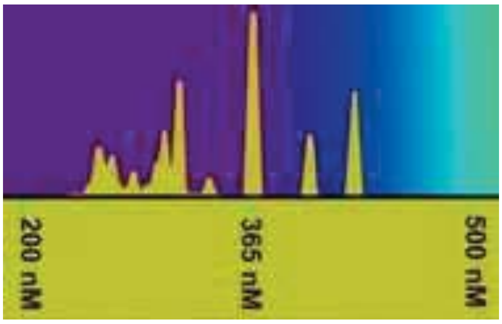
Doping improve UVA-UVB

(LED UV, Clearer peak, change in formulation)

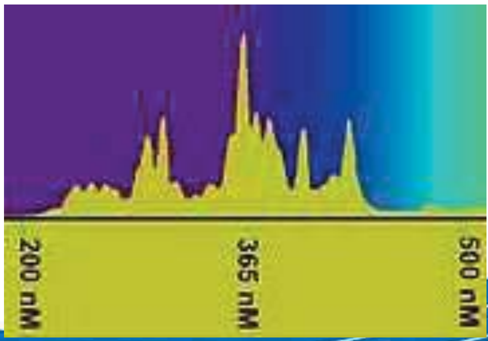
Gallium doping




Standard mercury




Iron doping




## UV operation

- Lower wavelength (higher frequency) gives higher energy, E=hf
- Higher energy gives higher cure speed
- UV - C produces low level ozone ($O_3$)
  - Respiratory problems

## UV curing

- Advantages
  - Rapid cure
  - Almost Zero VOC
  - Improved consistency through consistent viscosity
- Disadvantages
  - Lower limit of viscosity
  - Cured film is usually rigid with limited flexibility
  - Problems with recycling paper
  - **Unsure health and safety: food packaging**
    - Migration risk (back of substrate)

## UV inks - the curing process

- UV energy activates photo-initiator
  - Different mechanisms for Free-Radical and Cationic systems
- Photo-initiator causes the curing of the ink
  - Polymerisation
- Polymerisation is a chemical process
- TWO TYPES
  - Cationic (market dominant)
  - Free Radical

- Free radical:
  - Photopolymer initiator
    - Covalent bonding→ UV → split in free radicals ($Cl_2 \rightarrow Cl + Cl$)
    - Induce polymerisation
  - Requires energy to be supplied **throughout** curing process
    - They can recombine, inhibited by air (Oxygen)
- Cationic
  - Ionic bonding → UV → spilt in Cation and Anion $HCl \rightarrow Cl^- + H^+$
  - Polymerisation process continues until no monomer remains
    - Cations attack the monomers, New cation formed each time bond is broken
    - Not dependent on continuous supply of UV energy,(inhibited by amines, electron donor chemicals).

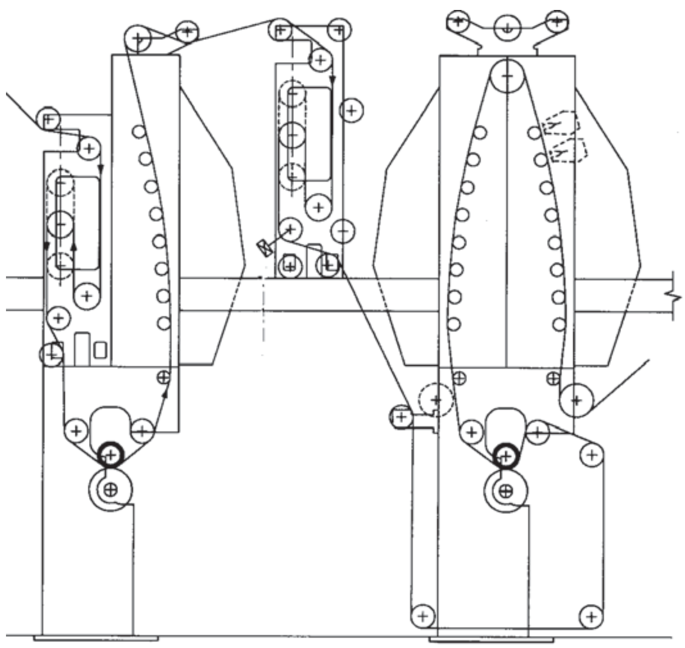
## UV bulbs - Life span

- Performance of bulbs deteriorates over time
- Above recommended life:
  - Shift in output towards IR
    - Greater lamp (and substrate temperature)
  - Less UV energy (reduced efficiency)
    - Could compensate with increased power to the lamp
      - Made temperature problems worse
      - Further decrease life of bulb
  - Cause of several UV problems observed by WCPC
- LED UV light (narrow band ... less energy....Change in optimum photoinitiator)

# Electron beam (& X – ray)

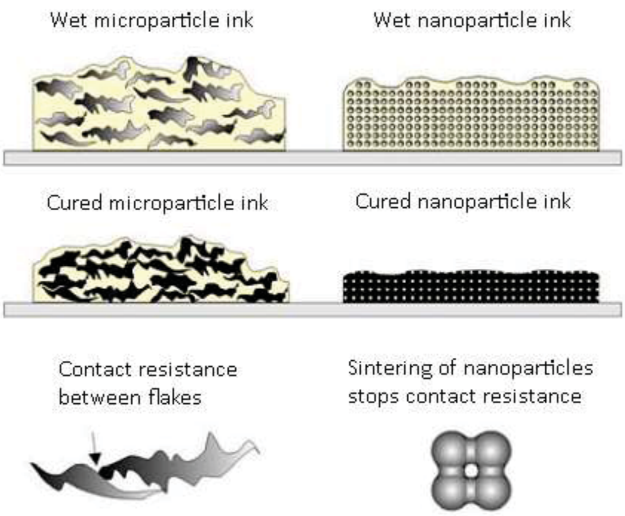
- Very high energy systems
- No requirement for other catalyst
- Highly specialised & potentially dangerous
- Increasing applications:
  - Ensure 100% curing of thick films (food packaging)
  - Kills 99.9999% bacteria (& virus)

# Extended path



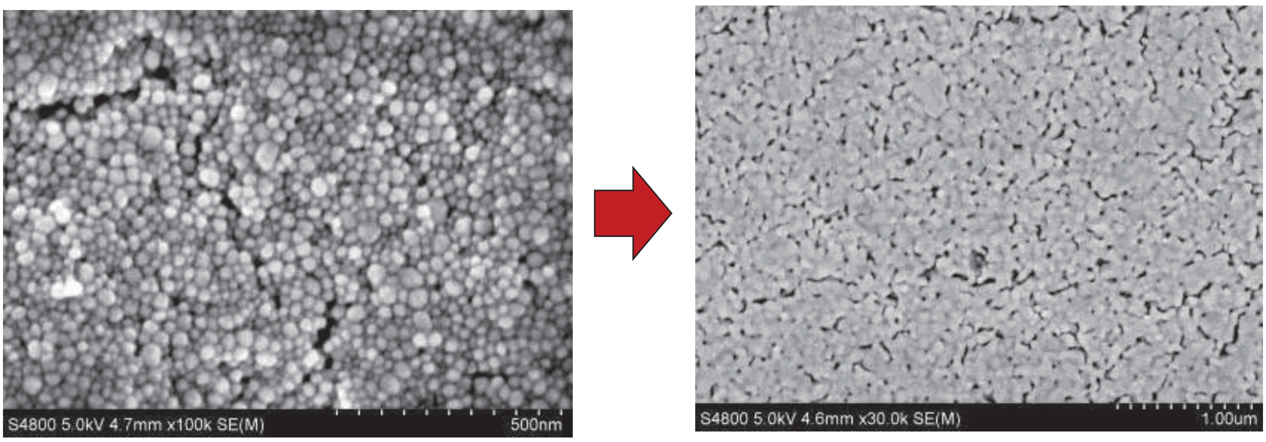
# Types of conductive inks

- Micro-particle
  - Metallic flakes in an organic matrix
  - Low temperature needed for solvent evaporation
  - High resistivity due to high contact resistance between particles
- Nano-particle
  - Small particle size (~40nm)
  - Increased ratio of surface area:volume results in lowered melting temperature (≤140°C)
  - Particles sinter together eliminating contact resistance
  - Low resistivity, best performing



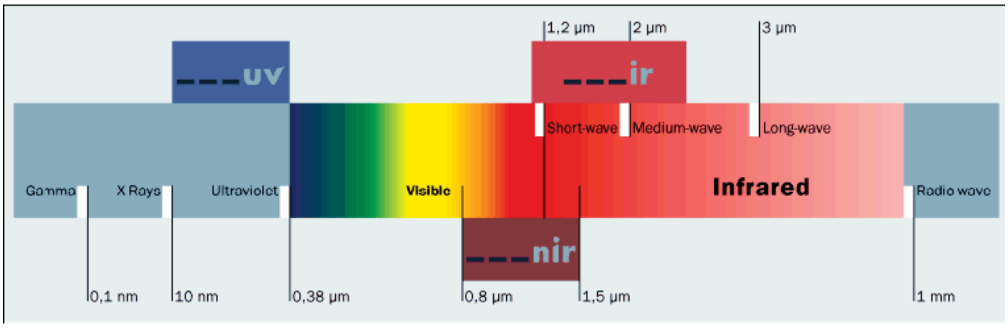

# Silver nano-particle sintering

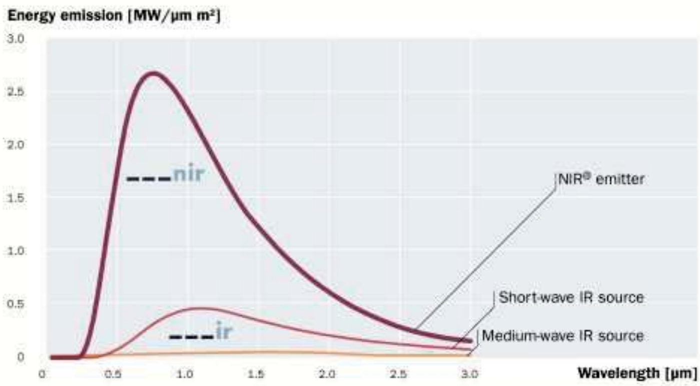
- Silver nanoparticles require sintering for optimum conductivity
  - Particles join forming a continuous highly conductive film
  - Conventional oven sintering : 130 °C for 10 minutes



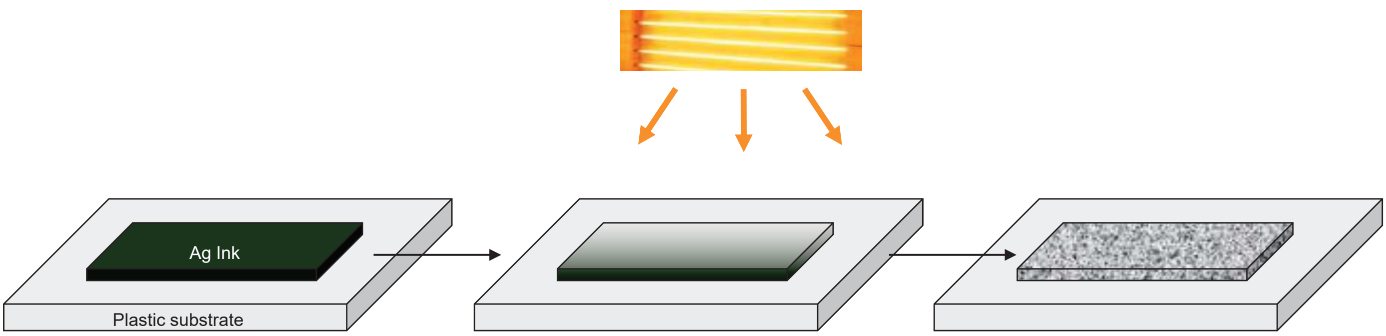

- If printing 50 m/min....500 m oven... not economically viable
  - Volume R2R production is prohibited

# Near Infrared in the EM spectrum



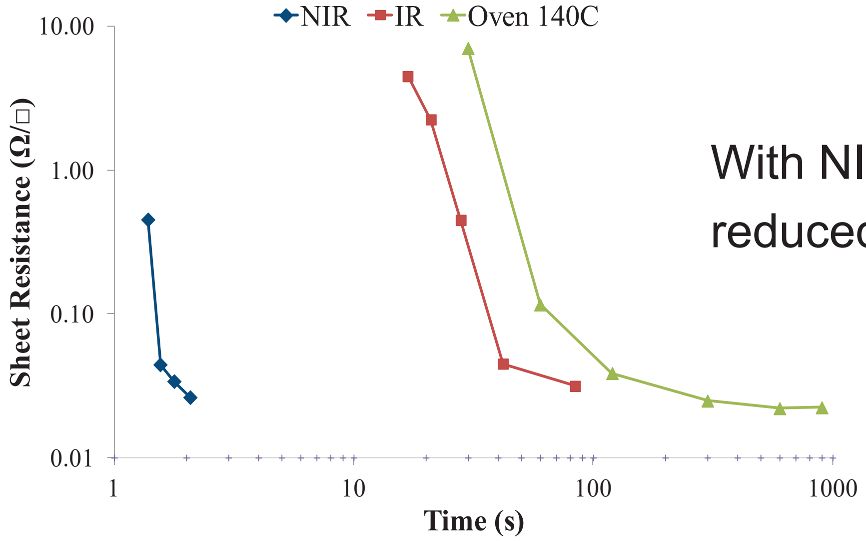

# NIR Sintering of a AgNP ink




*Ink is applied onto the plastic substrate*

*Energy from the NIR lamp is absorbed by the wet ink rapidly drying and sintering it*

# NIR Sintering of a AgNP ink



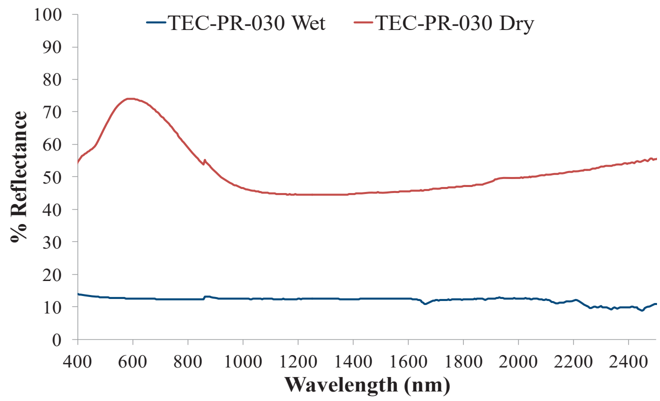

With NIR, sintering times reduced from 10 min to 2 s

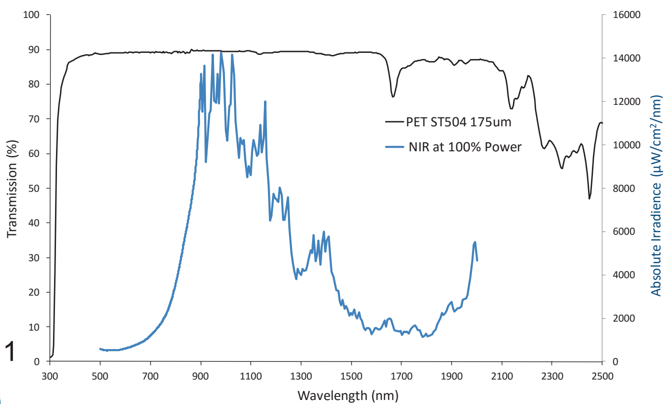
| Method | Sheet Resistance (Ω/□) | Resistive ratio to bulk silver | Time (s) |
|---|---|---|---|
| Oven (140°C) | 0.022 ± 0.0010 | 4.57 | 600 |
| IR | 0.032 ± 0.0013 | 6.65 | 84 |
| **NIR** | **0.026 ± 0.0029** | **5.41** | **2.1** |

# Why does NIR work so well?

- The ink absorbs ~90% of the NIR radiation when wet
- NIR penetrates the ink drying thick films
- Plastic substrate (PET,PEN) transparent to NIR spectrum : no substrate damage

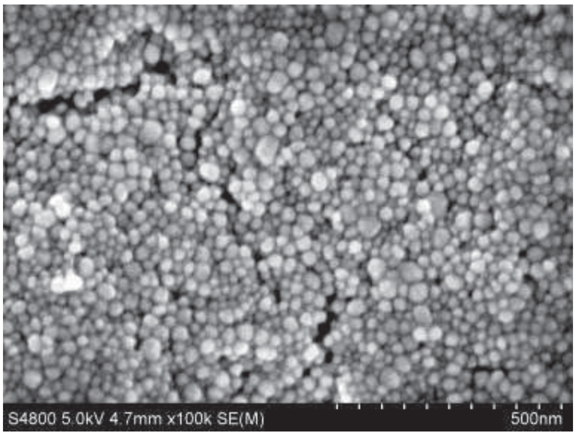
- Excellent ultrafast sintering method
- NIR Oven: 50 m/min... 1 m long

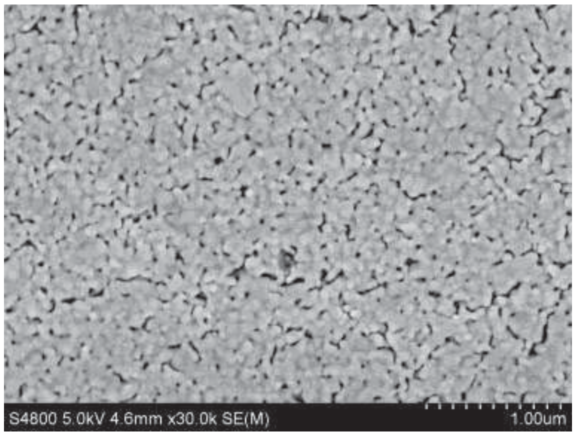



M. Cherrington et al., J. Mater. Chem., 21:7562-7564, 2011

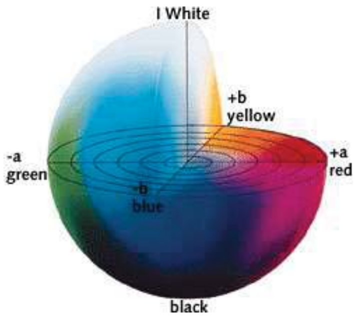
# Colour shift



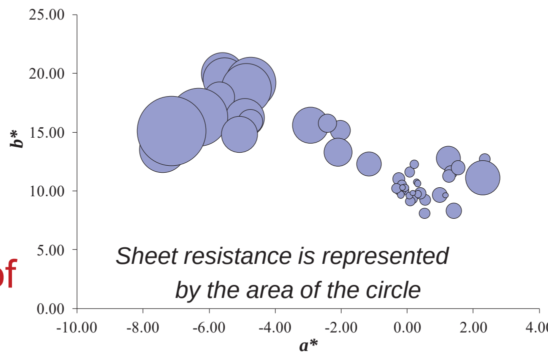

# New process: Online Monitoring of sintering

- Colorimetry for monitoring the sintering
- Contact-based measurements of electrical resistance inadequate for R2R: damage & slow

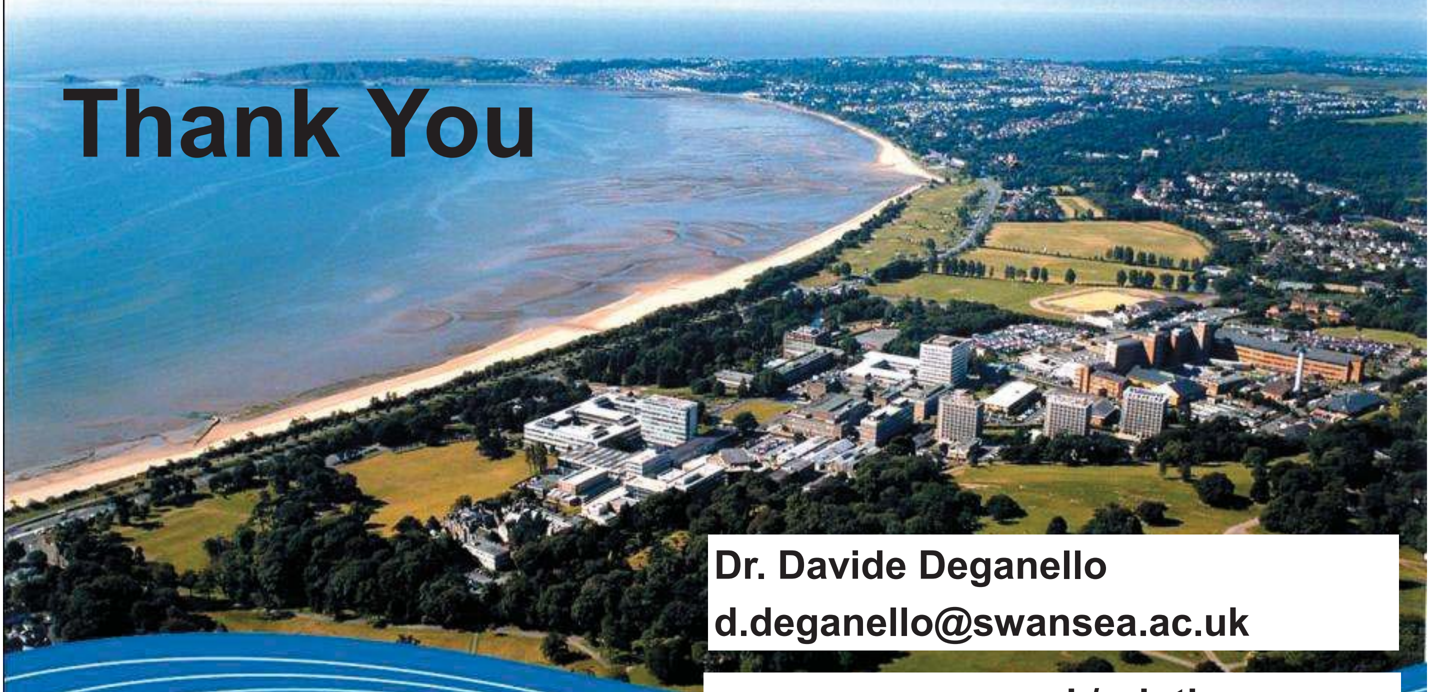



- La*b* Colour space
- Reliable shift in colour during sintering: Correlation with electrical performances
- Lorenz-Mie theory of electromagnetic (EM) scattering

- Non-contact fast online monitoring system of electrical performances & sintering



## Welsh Centre for Printing and Coating



# Thank You


Dr. Davide Deganello

d.deganello@swansea.ac.uk


www.swansea.ac.uk/printing

SWANSEA UNIVERSITY
PRIFYSGOL ABERTAWE

School of Engineering

## 8. Aerosol Jet printing

Chris Phillips, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

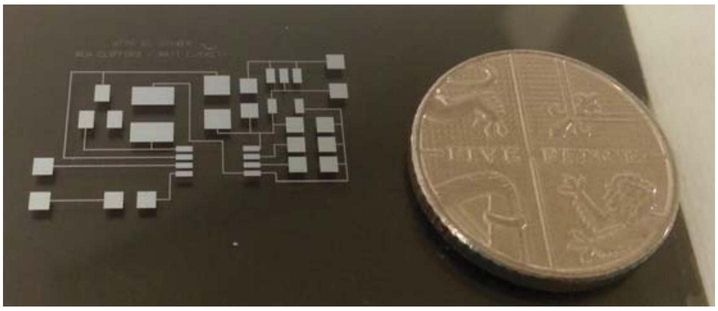
n/a


# Aerosol jet printing

Chris Phillips, Ben Clifford

## Content

- What is aerosol jet
- How it works
  - Comparison with other systems
  - Atomisation
  - Patterning and alignment
- What we have used it for
  - Some examples of prints

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## How aerosol jet works

- A mist of micron scale droplets is generated in the "ink" using ultrasonic or pneumatic atomisers
- This mist is carried by a flow of nitrogen and directed towards a nozzle
- An annular flow of clean nitrogen is used to channel and focus the flow into a collimated stream
- This is directed onto a substrate on a movable stage which is used to "draw" the image
  - Can use fixed substrate with movable print head
- Non-contact so can print on uneven surfaces

WCPC Swansea University Prifysgol Abertawe icmPrint

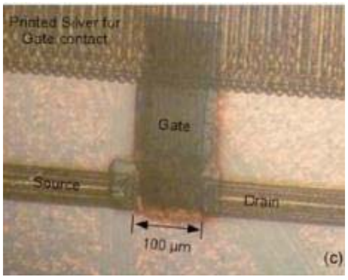
## What is the scale of the process?

- The printable area on our Optomec machine is 300 x 300 mm
    - Comparable with inkjet  machines such as Dimatix
- However like inkjet the process is scalable
- Potential for:
    - Multiple deposition heads
    - Larger stages
- Highly flexible ink film thickness range: 100 nanometers to  micron scale
    - Variable flow rate, stage speed and number of overprints etc.

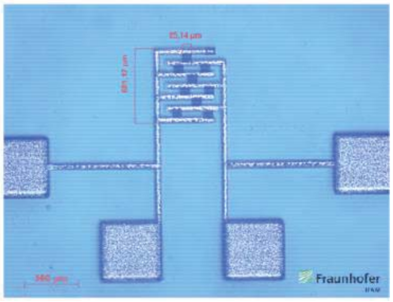
## Applications

- Operates in 10 to 100 micron features size range
- Occupies the niche between screen printing (100s of micron feature size) and silicon (nanometers)
- Well suited to printed electronics research
    - Evaluation of materials and device configurations
    - Low volume manufacture
- Solar Cells
- Printed antennae on non-flat surfaces
- Thin film transistors
- Interconnects

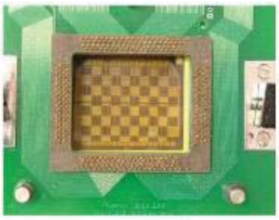
# Illustrations (Optomec website)



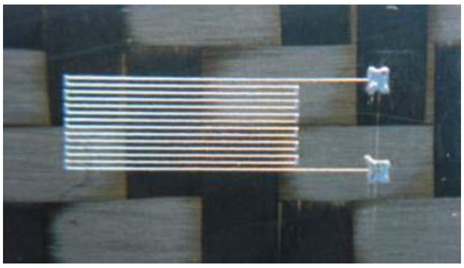

Thin film transistor using CNTs



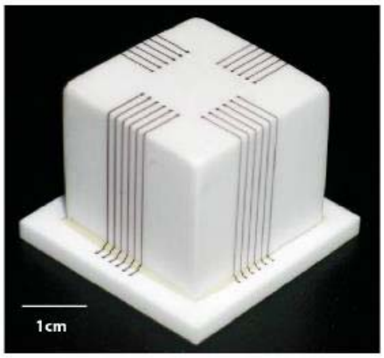

Gas sensor using silver circuitry with protein in between inter-digitated electrodes



TFT display



Strain gauge on carbon fibre composite




150 µm silver interconnects on alumina cube

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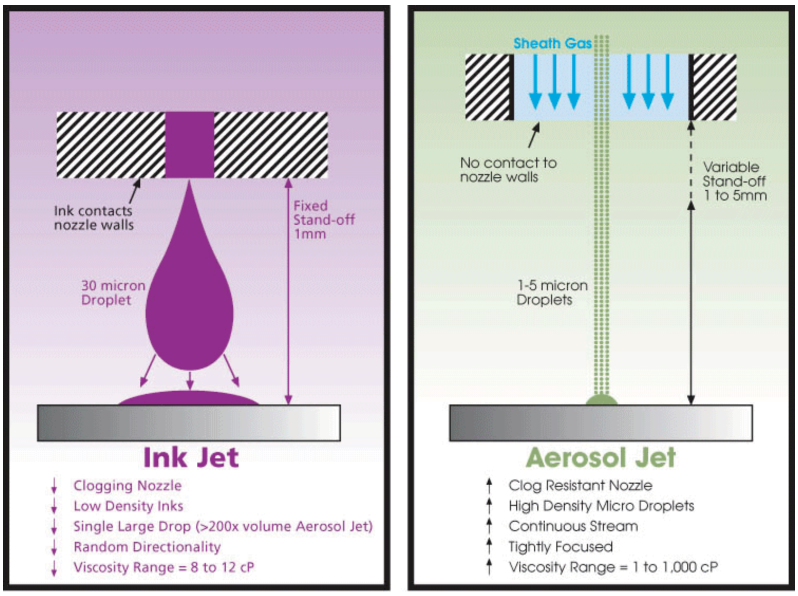
## Advantages over inkjet

- Larger viscosity range
- Higher solids content
- Continuous stream of tiny droplets
- Higher resolution and definition
  - Square edges
- Can deposit on to 3D or irregular substrates
- No clogging/contact with nozzle




Taken from Optomec website

- Far greater range of materials

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# Comparison with conventional printing

- Higher resolution
  - Better registration (around ±1-2 µm)
  - Fills the "features size gap" between screen printing and silicon
- Direct fabrication from a digital file
  - No image carrier required
- Good for prototyping
  - Rapid evaluation of design and materials
  - Minimal material usage
- Transfer is not limited by viscosity or wetting
  - Can simply dilute to get right viscosity for atomising
  - Coffee ring effect eliminated
    - Droplets are very small and evaporate rapidly

– Less suited to mass production – comparatively slow

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# Comparison with silicon electronics

- Tooling and masking are not required
  - Not reliant on designers, suppliers *etc.* for these
  - Faster development
- Additive rather than subtractive
  - Less waste
  - Fewer chemicals
- Economical for short runs
  - Silicon needs 100,000 +
- Changes in design can be rapidly evaluated

– Not well suited for large run lengths – scalability still an issue

WCPC Swansea University Prifysgol Abertawe icmPrint

# Our aerosol jet printer

- Produced by *Optomec*, Albuquerque, New Mexico
- Generates a fine mist which is highly focussed
  - Annular flow of sheath gas
  - 100 micron nozzle gives ≥ 10  micron stream
- Highly accurate movable platen
  - Temperature controlled to improve deposition detail and enable thermal curing
- Near infrared laser tracks the deposited print
  - Precise curing without thermally damaging substrate
- Precise registration for successive materials and over-printing multiple layers

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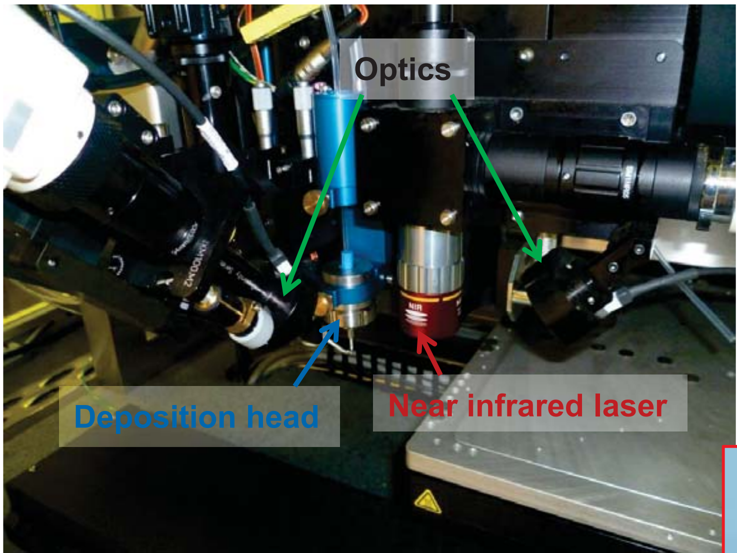
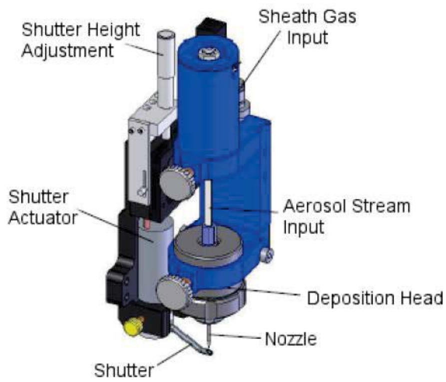
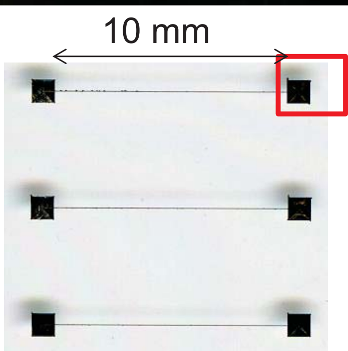
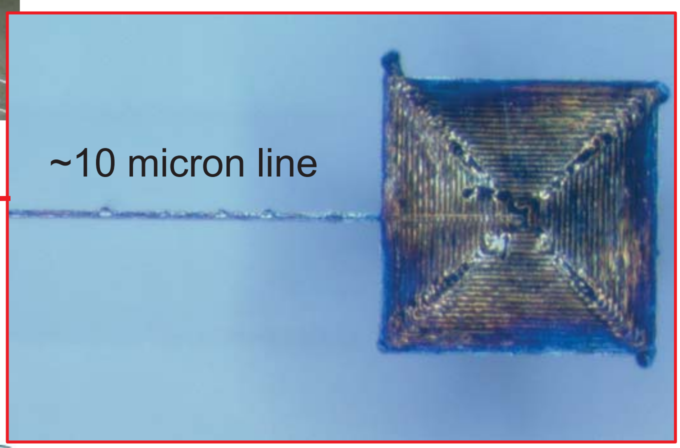
# Aerosol jet printer




WCPC Swansea University Prifysgol Abertawe icmPrint

## What can be deposited?

- Must be dispersible in a liquid carrier
- Can be diluted – no need to rely on viscosity or low surface tension to transfer
- Inorganic and organic materials:
    - Metals
    - Semiconductors
    - Organic polymers
    - Electro-optic materials: phosphors
    - Nano carbon: CNT, Graphene
    - Possibly biological materials: DNA, proteins, antibodies, cells

– Some limitations on solvent use in ultrasonic system

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## Atomisation systems

- The Optomec has two atomisation systems which have to run separately
- Pros and cons for each
- Ultrasonic
    - Best for low viscosity - <10s Cp
    - Can be used to deliver particles in solvent without any polymer
    - Can be primed with as little as 1 mL of dilute ink
    - Line width down to 10 μm (100 μm nozzle)
    - Atomisation sensitive to viscosity, surface tension and vapour pressure

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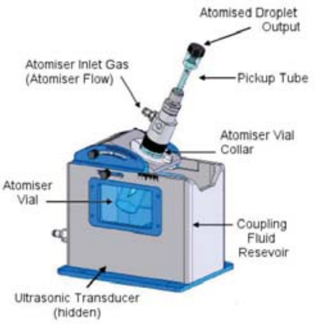
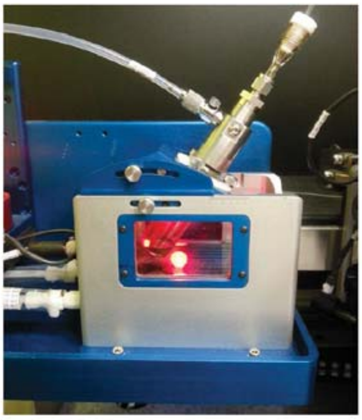
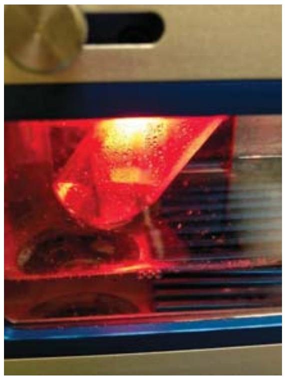
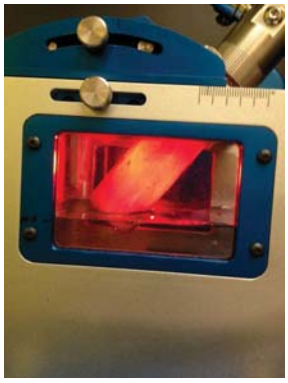
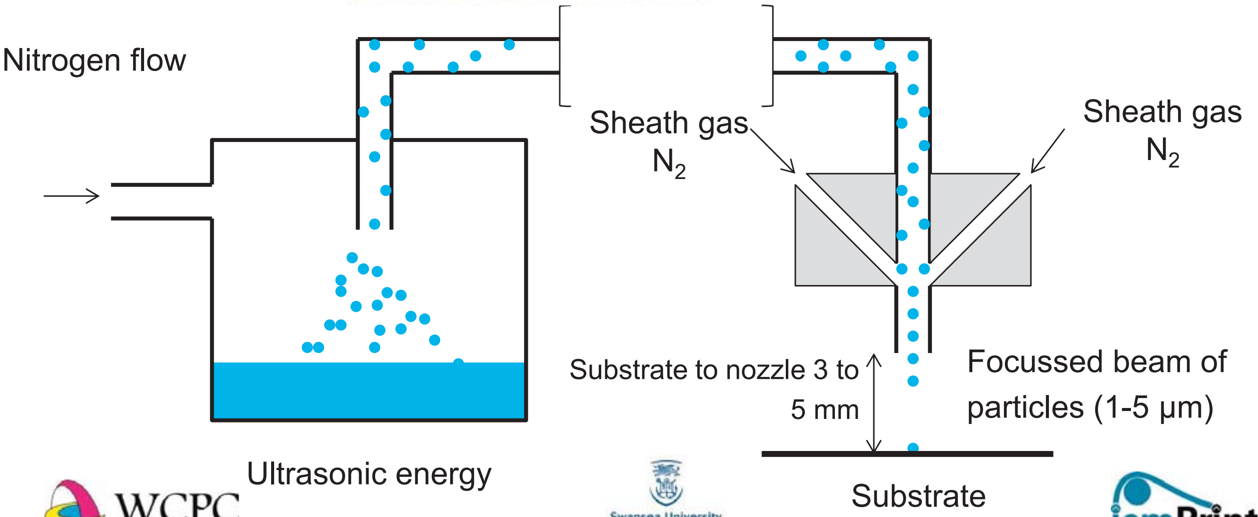
# Delivery of ink - ultrasonic







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# Theoretical drop diameter - ultrasonic

$$d = 0.34\left(\frac{8\pi\gamma}{\rho f^2}\right)^{1/3}$$

Where,
d = droplet diameter
γ = surface tension
ρ = density of solution
f = frequency of acoustic signal
Equation by *Lang*

Surface tension and density affected by temperature – can be modified by changing bath temperature

Typical drop sizes at 20°C:

Water 2.31 µm

Xylene 1.78 µm

Acetonitrile 1.85 µm

Particles need to be small to be carried in these droplets <100 nm works best

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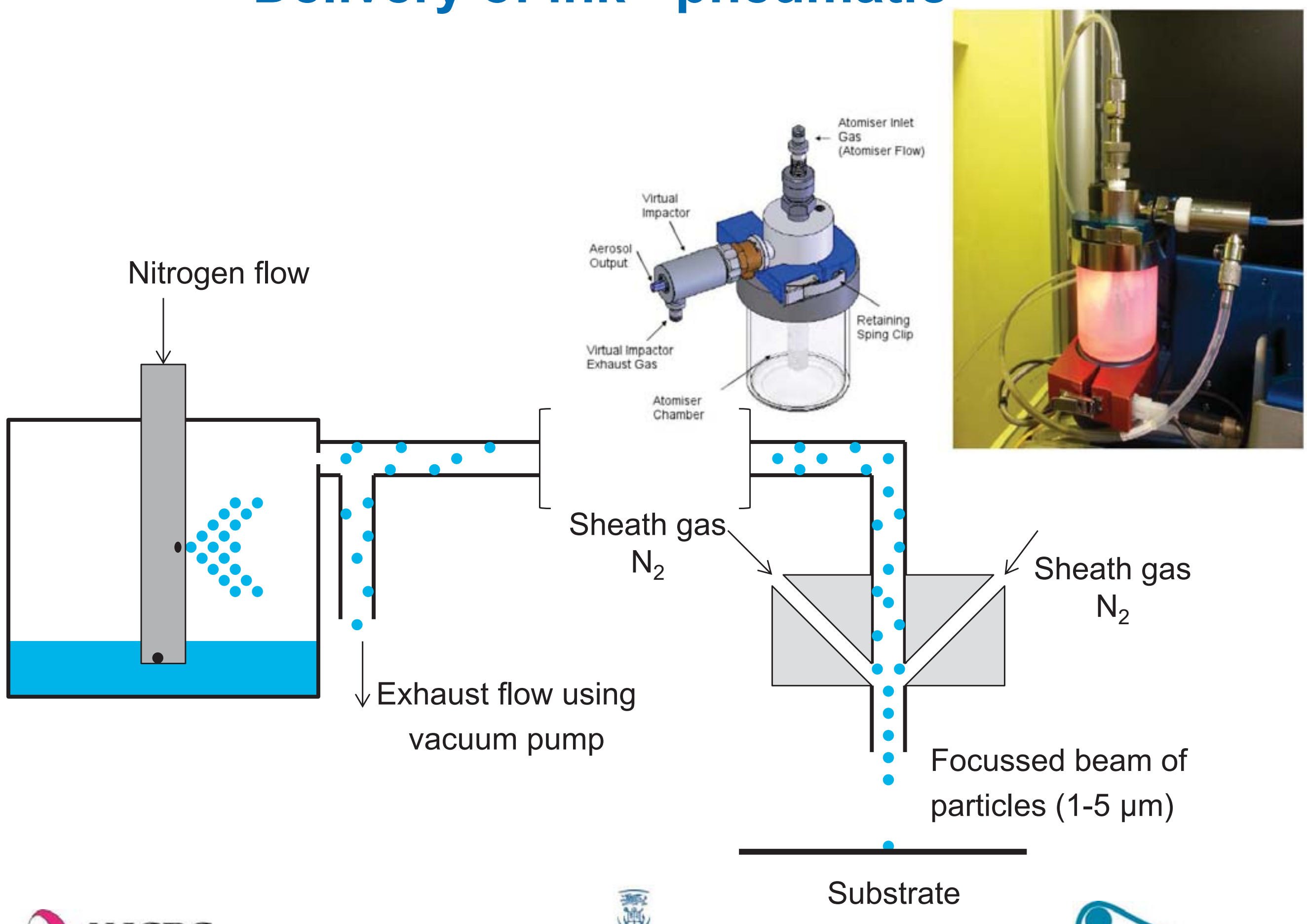
# Pneumatic atomisation

- Forces nitrogen into ink at high pressure to generate mist – "airbrush"
  - Requires 30 mL+ of ink
    - Wasteful for expensive inks
  - High gas flow required to atomise material
    - Generates higher material flow than nozzle can deliver so most is directed to a waste stream
- Better suited to volume production – process is inherently more scalable
- Line width down to 15 micron (150 micron nozzle)
- Wider range of materials
  - Higher viscosity range (up to 1000 Cp)
  - Higher solid content and particle size
  - Better suited to higher vapour pressure liquids (glycols)
    - But most materials will work



# Delivery of ink - pneumatic

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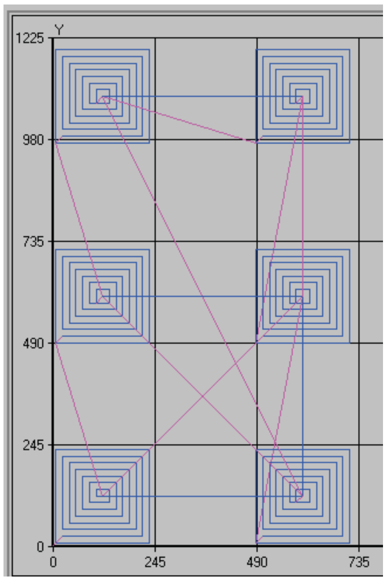
# How the image is "drawn"

- Platen moves in *x* and *y* at up to 200 mm/s
- Shutter diverts flow when print not required
- Solid areas composed of lines in a variety of fill patterns
  - Spiral fill
  - Serpentine fill
  - Circular fill
- Bit like an etch-a-sketch

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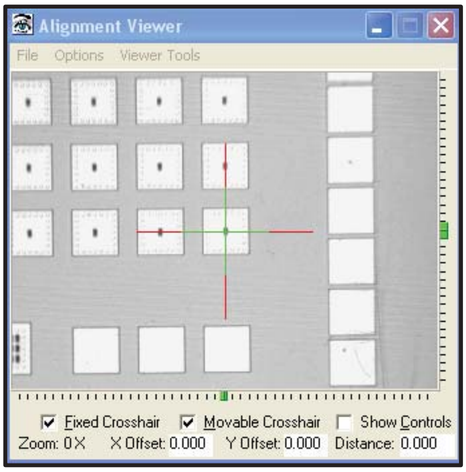
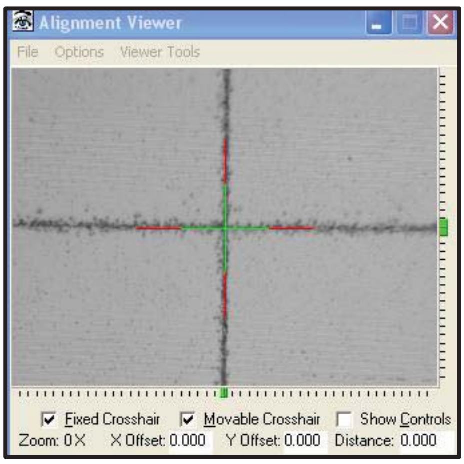
# Alignment

- Camera system allows alignment with features on a substrate (top) or registration marks on a previously printed layer (bottom)
- Registration accurate to approx 1-2 microns
  - Depending on ink and substrate
  - Software adjusts datum (0,0) and rotates design if needed
- Example: overlaying insulator over conductor

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## Some parameters which affect print quality

**Gas flows**: sheath, atomiser and waste flows (PA)

**Ink** viscosity, solid content, particle size, vapour pressure, surface tension, use of co-solvent, ink temperature

**Platen** velocity
Fill pattern
Platen temperature

**Nozzle** diameter and distance from substrate

**Substrate** type, roughness, angle

**Atomiser** power and positioning

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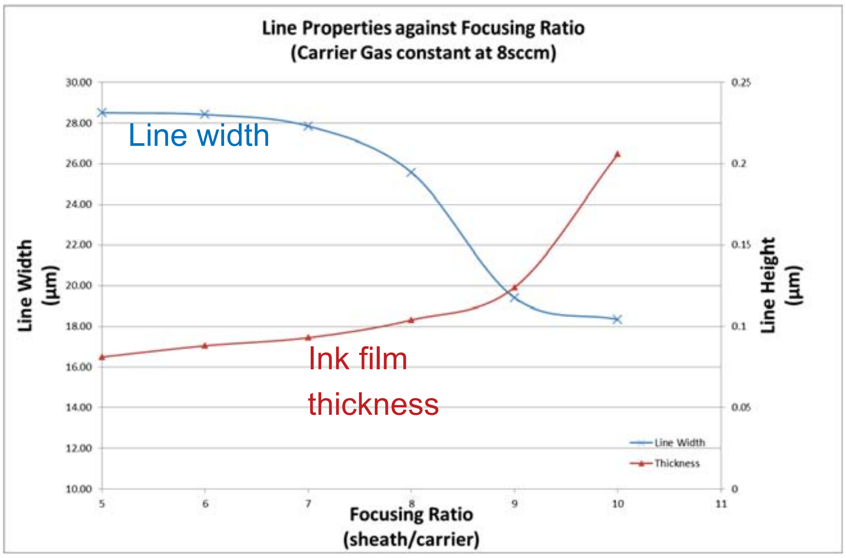
## Focussing

- The stream of material can be focussed by changing the gas flow
- + *sheath gas* – narrows "beam"
    - Too much causes turbulence and "overspray"
- + *atomiser flow* widens beam and increases material deposition

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## Challenges

- A large range of interacting parameters
  - Some very sensitive
  - Can be time consuming to optimise settings and material recipe
  - Atomisation can be finicky
    - Poor stability of some recipes
    - Short shelf life so need to make fresh batches
- Not all materials are suitable
  - Small number of commercially available inks
    - Many are adapted from inkjet inks – wrong vapour pressure
  - Especially for ultrasonic atomisation
  - **Still far less fussy than inkjet!**

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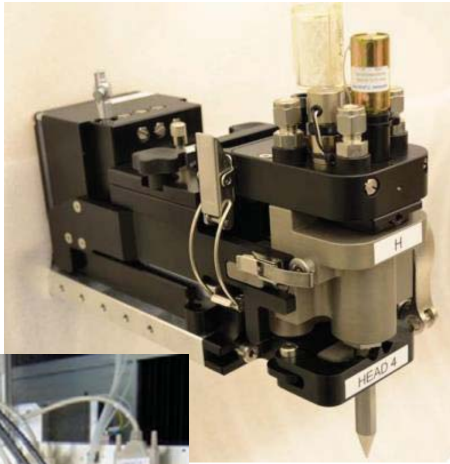
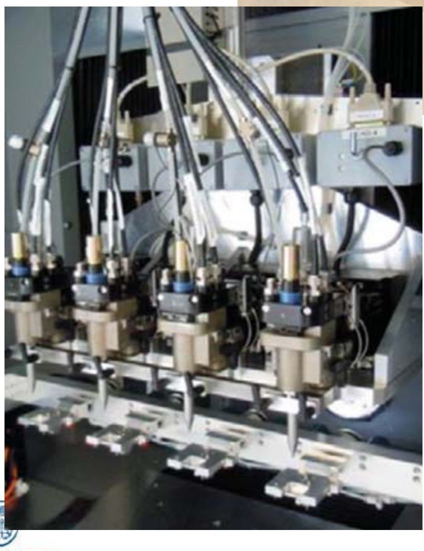
## Scale up and beyond R&D

- R&D systems only use single print head
  - Limited throughput
  - One material at a time
- Marathon Print Engine (Optomec)
  - Four pneumatic print modules
  - Quick release cassettes
  - Higher material output
- "6-axis" printing system
  - Sample can be moved in x, y and z, tilted and rotated



Images from Optomec website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# Our use of the aerosol jet

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## What have we been doing with the system?

- Testing a range of materials using different atomisation techniques
  - Optimising deposition
    - Understanding effects of process parameters
  - Coating and printing fine features
  - Evaluating registration capabilities
    - Aligning print onto electronic components
  - Developing new inks
- Printing over uneven surfaces and edges

## What have we been able to print

- Metallic conductors
  - Nano silver, platinum, copper in glycol and xylene bases
- Insulators
  - Polyimide – both atomisers
- Molecularly imprinted polymers
- Functional polymers
  - PEDOT:PSS, Nafion
- Salt solutions in water
  - Zinc acetate
- Carbon nano-materials in solvent

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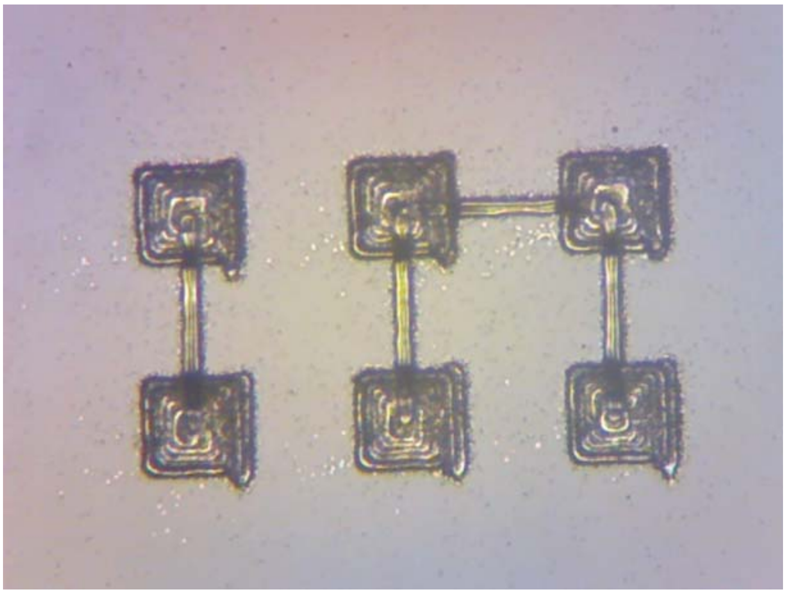
## Example prints for ultrasonic atomiser



- Cabot nano silver ink
- Slow platen speed
- Low deposition rate
- 65 micron contact pads
  - Filled with square spiral
  - Can be reduced in size
- 10 micron line width
  - Consistent , unbroken and well defined

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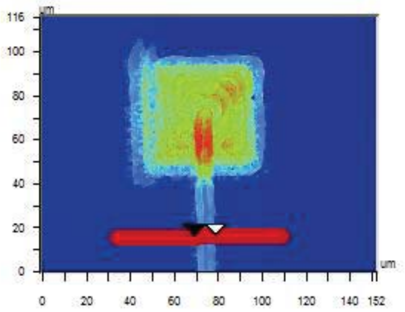
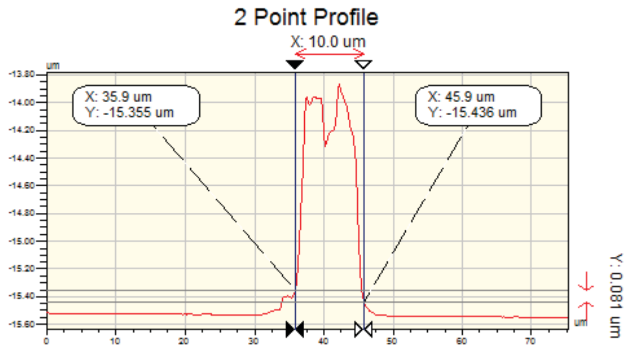
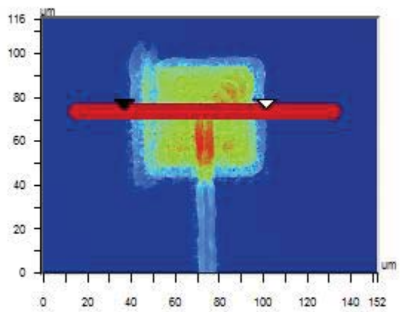
# Feature measurement – white light

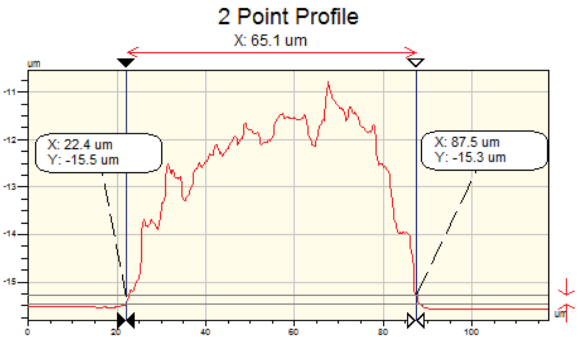



40 x magnification 152x116 μm




10 μm line width, ink film thickness is 1.5 μm




Pad profile shows 65 μm width

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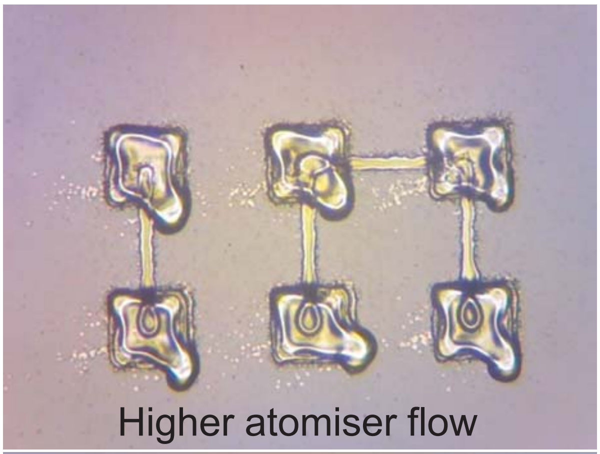
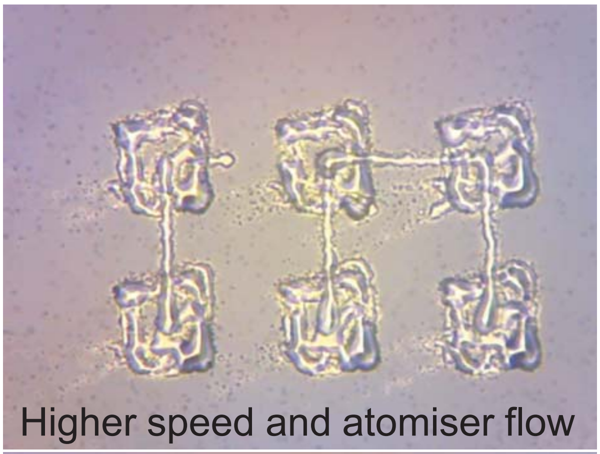
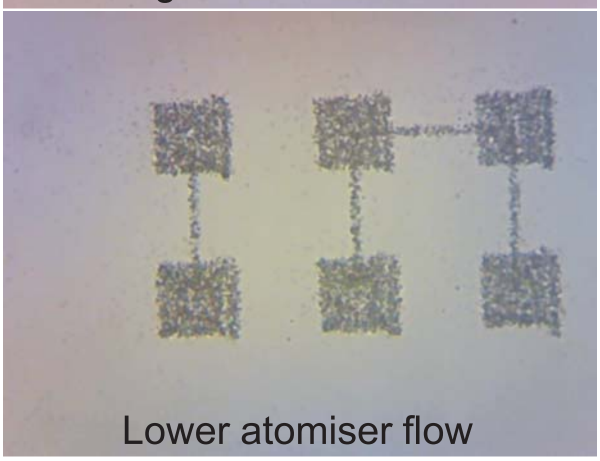
# Effect of process parameters (examples)



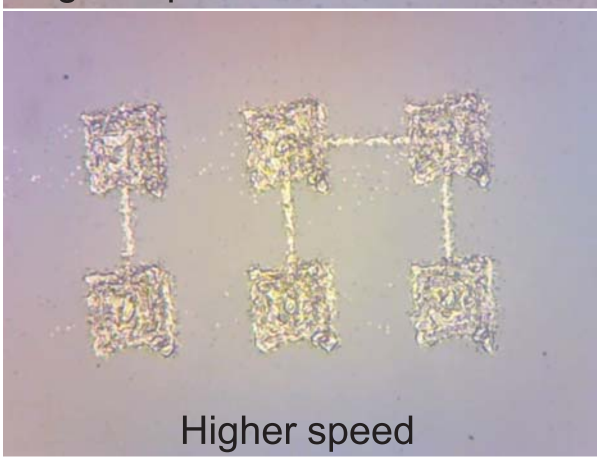
Higher atomiser flow



Higher speed and atomiser flow



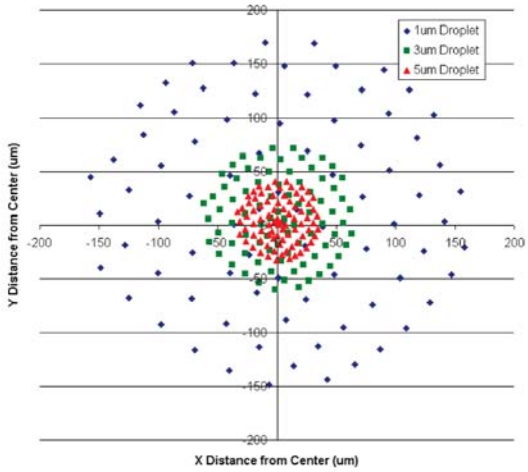
Lower atomiser flow

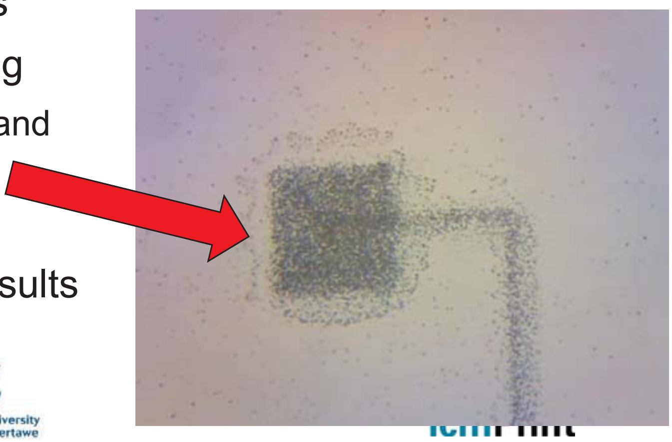


Higher speed

# Deposition for high volatility

- Ultrasonic atomisation works well with high volatility materials
- E.g. silver nanoparticles in xylene
  - Highly volatile
  - Low surface tension
  - Needs 10°C atomisation temperature to sustain droplets
  - Cannot heat platen to aid drying
    - Evaporation = smaller drops and deposition further from target
    - Fuzzy print
  - Print optimised to give good results



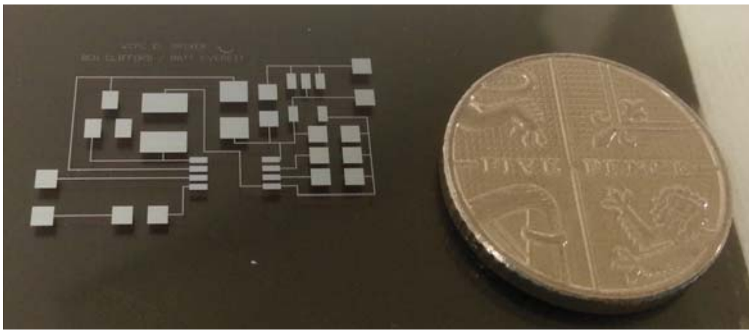



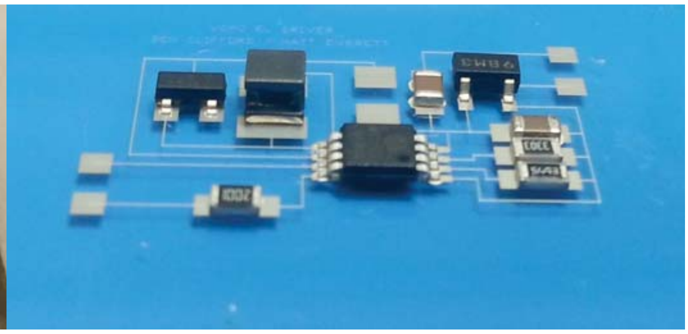


# Example projects

# Electroluminescent lamp driver

- Nano silver ink
  - 5V DC supply to 210V AC at 1.2KHz.
  - 2 x resistor, 3 x capacitor, 1 x voltage regulator IC, 1 x diode, 1 x inductor and 1 x high voltage translator IC





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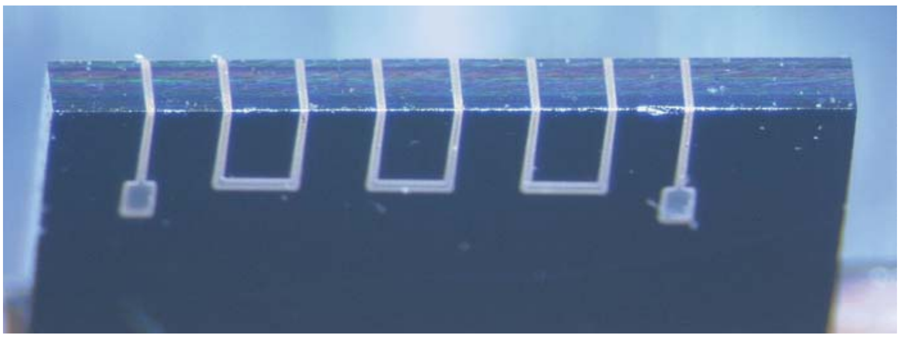
# Over edge printing on silicon

- Nano silver ink
  - Front-to-back contacts
  - Sample mounted at 45°
  - 5 mm wide wafer, 0.53 mm thickness



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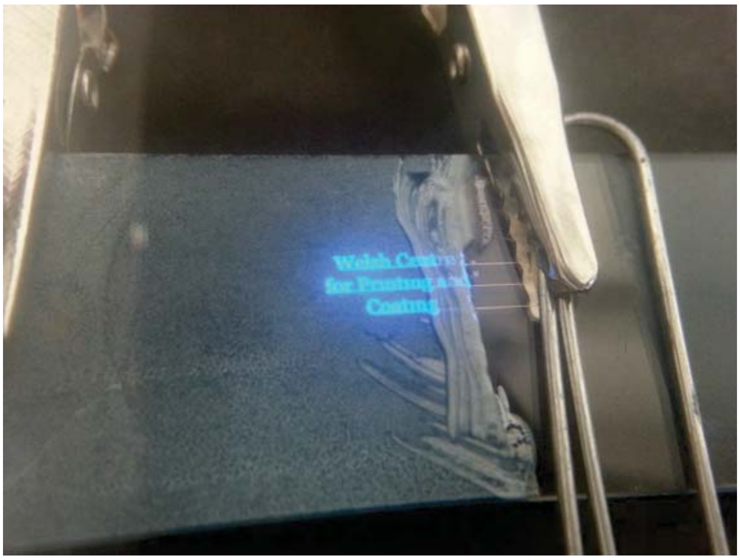
# Miniature EL lamp

- Intricate text printed in silver
- Bar coated dielectric and PEDOT:PSS layers



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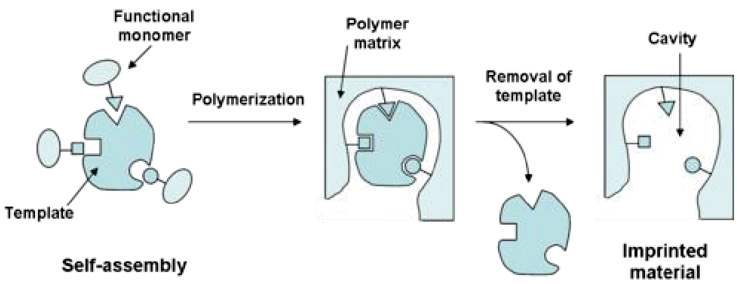
# Tuning forks as sensors

- Coating of molecularly imprinted polymers onto tuning forks
  - Collaboration with **Waterford Institute of Technology**
  - Polymers receptive to certain molecules
  - Binding of molecule with polymer causes change in resonant frequency in tuning fork
  - This can therefore be used to measure the levels of that molecule




Taken from Wikipedia

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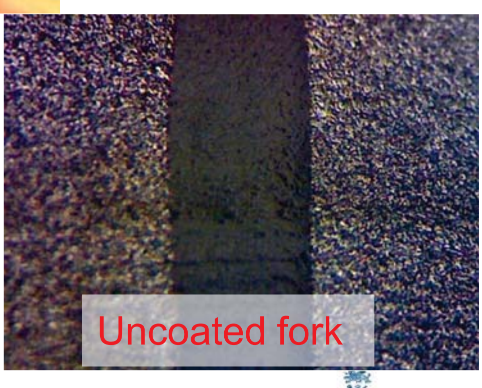
# Why aerosol jet

- Waterford have been using dip coating
  - Unpredictable process
- Aerosol jet can deposit in a controlled fashion
  - Vary flow rates or speed to change the amount of deposition
  - Can register to the position of the forks

Forks approx 1.3 mm x 3.3.mm (prongs ~0.5 mm)





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# Closure

- The Aerosol jet enables more precise electronic fabrication than other printing technologies
  - Fairly rapid and master less
  - Requires small sample volumes
    - Good for R&D and small volume manufacture
- Most comparable process is inkjet
  - Aerosol jet is more flexible
  - Better definition and higher solid loading
- Fabrication of a wider a range of materials in 2 and 3 dimensions

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## 9. PHOTONIC FABRICATION WITH PULSEFORGE

ROB HENDRIKS, NOVACENTRIX

### BIOGRAPHY

After his studies, Rob Hendriks started working at the Holst Centre in 2011, where he became the expert on photonic curing and the characterization of conductive inks. In 2013 he started the PhATT Project (Photonic Ablation & Transfer Technology), which focusses on the development of new technologies using high intensity light pulses. Driven by the idea of commercialization of these new technologies, in 2014 he started working for NovaCentrix, the company which produces state-of-the-art photonic curing equipment.

### ABSTRACT

As the demand for printed electronics is increasing, faster and cheaper processes are required to reduce production costs. In contrast to time consuming oven post-treatment steps, curing of conductive inks and soldering of components can be done within a fraction of a second by means of highly intense light pulses (photonic curing). This short processing time allows for high volume, cost-effective and energy efficient production of flexible electronics in a roll-to-roll manner. Photonic fabrication enables high temperature processing on temperature sensitive substrates such as PET and paper.

## 10. Gravure printing

## Gunter Hubner, HdM

### Biography

Since 1999 Prof. Huebner teaches at the University of Applied Science, Stuttgart Media University "Hochschule der Medien" (HdM) in Stuttgart, Germany.

From 2004 till 2014 he was the leader of the HdM study program "Print and Media Technology". Besides the entire printing technologies and printing processes his specialties in teaching are digital, screen and functional printing.

In 2006 the Institute for Applied Research (Institut für angewandte Forschung - IAF) was founded at the HdM. He took over the leadership of the IAF which is an umbrella organization over meanwhile about 30 research groups within the HdM. His own research group is called "Institute for Innovative Applications of the Printing Technologies" (IAD) and mainly deals with functional and fine line printing. Recent successful developments are printed antennae for automotive applications and screen printing of rechargeable batteries.

Before joining the HdM he worked for about 11 years with the companies AGFA Gevaert AG and DuPont de Nemours as a research and process engineer or system specialist, thus, combining mechanical and process expertise with a well-grounded knowledge in information technologies.

With his PhD-thesis about numerical simulation of ink-splitting processes in printing he 1991 obtained the Dr.-Ing.-title at the Technical University, Darmstadt, the place where he had passed his diploma in mechanical engineering, before.

### Abstract

n/a

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# Innovative Applications of the Printing Technologies (IAD) Media University Hochschule der Medien, Stuttgart

July 12th 2016

HdM Campus Stuttgart-Vaihingen

photo: D. Seydel

Prof. Dr.-Ing. Gunter Hübner

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## Overview of Projects @IAD

- “PrintEnergy” printed rechargeable zinc-air batteries
  governmental funding (main partner: VARTA)
- “Haptic Feedback Signal”
  governmental funding
- KoSiF complex systems in foil
  governmental funding

Recently finished:

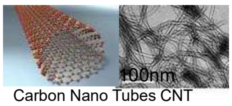
- “BatMat”
  printed rechargeable Ni/MH batteries
  governmental funding (main partner: VARTA)
- Printed antennae for automotives
  Hirschmann Car Communication GmbH
- Printed Thermoelements
  governmental funding
- Demonstrators for Heraeus (H.C. Starck)
  Microstructures with Clevios (OE-A), Touchpads, Sensors
- Carbo-TCF Transparent and Conductive Films based on CNT-Hybrids
  governmental funding

Bionic gripper with „smart skin“ containing flexible sensors, chips, displays, radio link and batteries

Rolled up battery in F-type housing

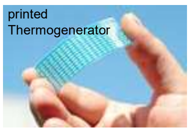
Antenna integrated in rear mirror

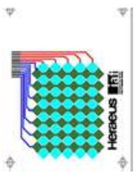
Printed NiMH rechargeable thin film battery



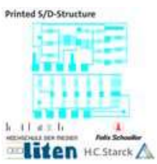

Carbon Nano Tubes CNT

Bildquelle: http://technokaksha.blogspot.com/



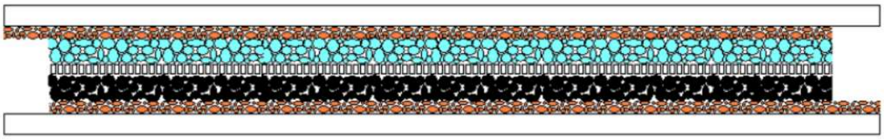

OE-A Demonstrator kapazitives Touchpad Printed with Clevios (PEDOT/PSS)

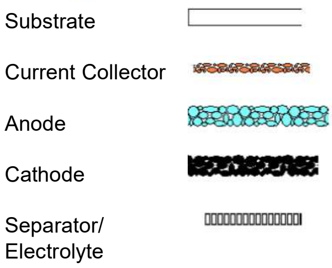



OE-A Demonstrator Source-Drain-Structure Printed with Clevios (PEDOT/PSS)

Example: Printed Batteries

# "Stack"-Type Battery

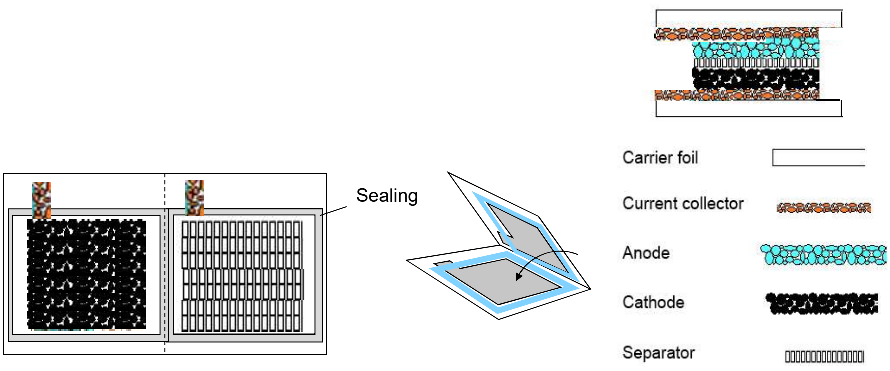





For zinc/manganese-dioxide cell:

- Current Collector: Carbon Black
- Anode: Zinc (Zn)-Paste
- Cathode: Manganese-Dioxide ($MnO_2$)-Paste
- Separator: fleece soaked in zinc chloride or printable electrolyte

# Assembly




BatMat Video

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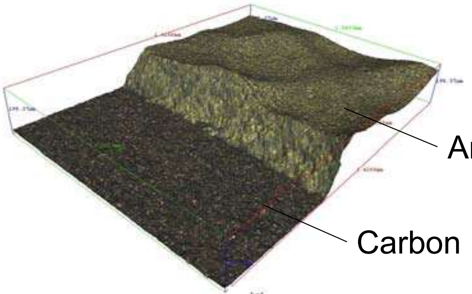
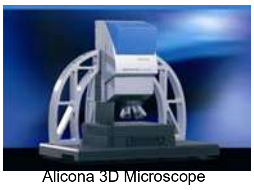
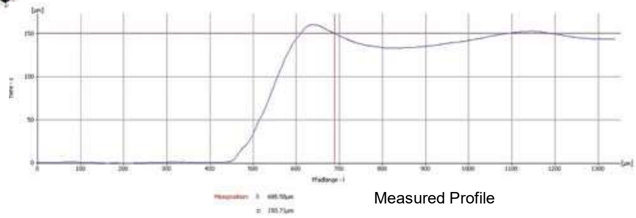
## High layer thicknesses (150µm in one stroke)



Alicona 3D Microscope



Measured Profile

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## Demonstrator - 1st price @LOPE-C 2014

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## Thank you for your attention!

http://www.creepygif.com/images/full/812.gif

Hochschule der Medien
Nobelstraße 10
70569 Stuttgart / Germany
phone: +49 711 8923 2144
fax: +49 711 8932 2180

huebner@hdm-stuttgart.de
www.hdm-stuttgart.de

Prof. Dr.-Ing. Gunter Hübner

HOCHSCHULE DER MEDIEN

# Gravure Printing

Image: 4color Roto-Gravure press at HdM

COST Summer School Swansea July 2016

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# Agenda Gravure Printing

1) Introduction
2) Applications
3) Principles of Gravure Printing Presses
4) Cylinder Preparation
5) Resolution
6) Printing Process

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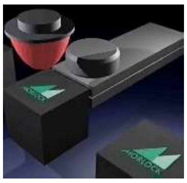
# Gravure Classification

- Rotogravure (web-fed, very seldom sheet-fed)
  - Blade gravure
    - Direct
    - Indirect
      - Rotational Pad Printing
        video: https://www.youtube.com/watch?v=OBhG0QU8IkE
  - Intaglio

Rotational pad printing product
www.tampoprint.com

- Flatbed
  - Lab presses
  - Pad Printing (indirect)



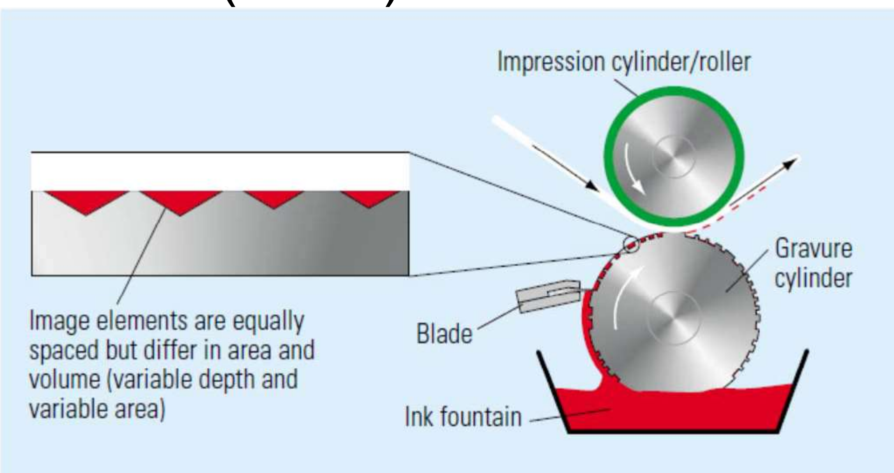
Ink cup with circle-shaped blade
source
http://www.tampoprint.de/de/download/pdf_de/brochuren/farb_rakeltoepfe_2008_de_web.pdf





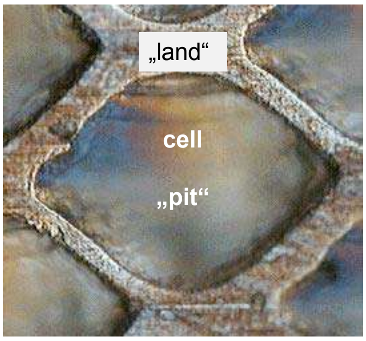


# Blade (Roto-)Gravure Process

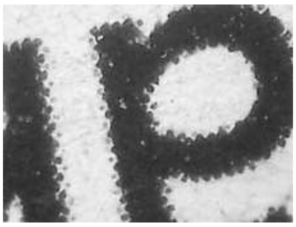



Source: Kipphan „Handbook of Printmedia“

# Printing Form and Printing Result




„land“ needed to support blade
Solid tone ≠100% cell



Typical print result: tiny „sawtooth“ at edges

Image source: Kipphan „Handbook of Printmedia“ and Google images





# Gravure Applications

- Commercial
  - Magazines, catalogues, directories, white papers
- Packaging
  - Flexible packaging, cardboard, paper, multi layer films, metal laminated films
- Technical applications
  - functional varnish, adhesive (cold seal, hot melt)
- Security
  - RFID, stock paper, bank notes, stamps
- Decor
  - Wood laminate, gift wrap paper, inlays, wall paper




Image source: Google images

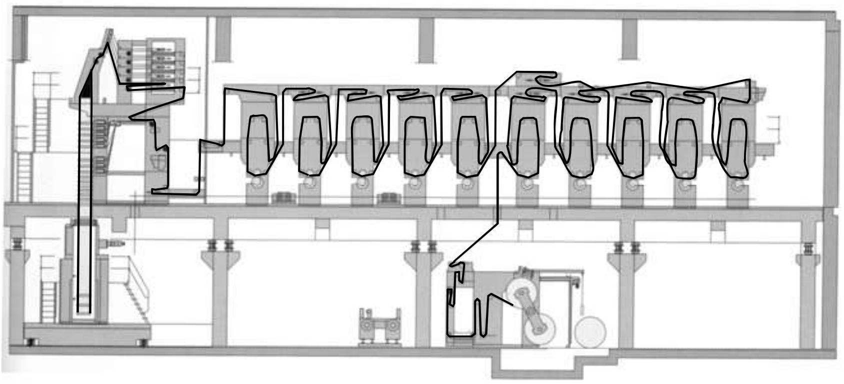
# Examples Decor

Source: http://de.wikipedia.org/wiki/S%C3%BCddekor





# KBATR7B 5/5 Rotogravure Press



Inking from below web, only:
special web transport for printing on backside

Gravure Printing Press Configuration

HOCHSCHULE DER MEDIEN

# Commercial Rotogravure Press Schematic

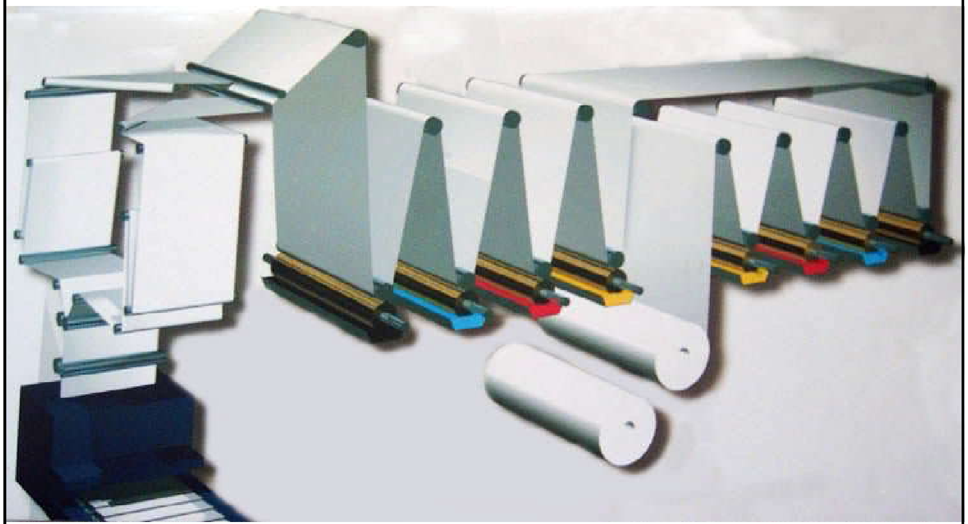


Photo: G. Hübner Overview Chart at tour in swiss print shop Rignier

Gravure Printing Press Configuration

Prof. Dr.-Ing. Gunter Hübner

HOCHSCHULE DER MEDIEN

# Commercial Press

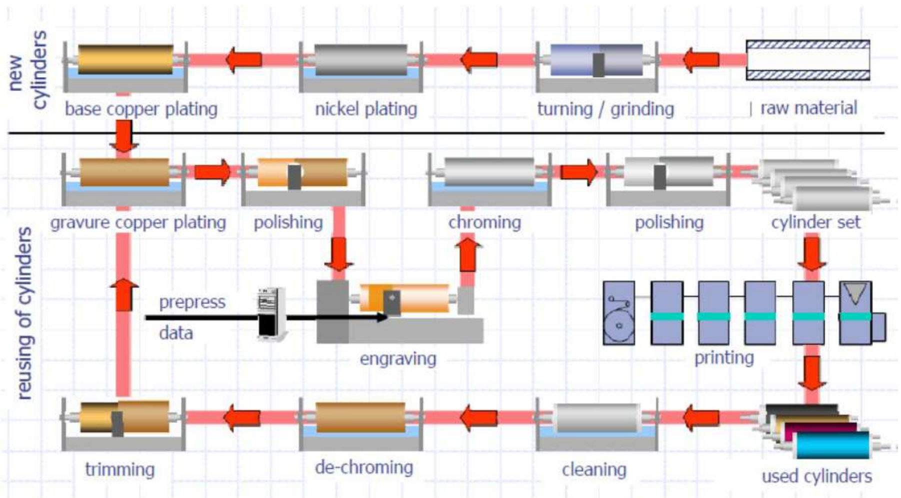
Source: Kipphan, "Handbook of Printmeda"

# Packaging press single sided 8 colors +

Source: Kipphan, "Handbook of Printmeda"

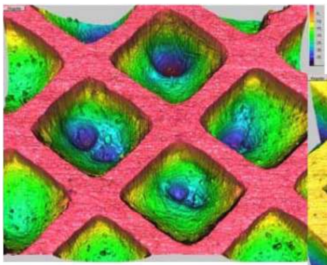


# Process steps of gravure cylinder making

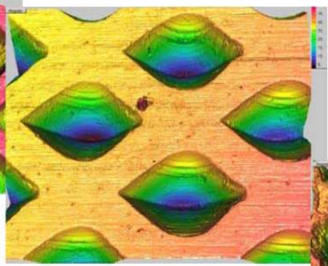



Source: A. Weichmann lecture on gravure printing HdM, Stuttgart

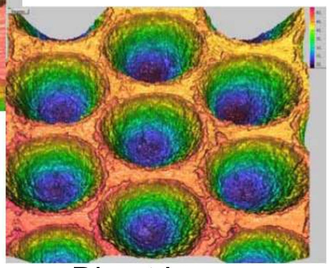
# Printing Form Preparation Techniques



Etching



Electromechanical Engraving



Direct Laser

Source: A. Weichmann lecture on gravure printing HdM, Stuttgart





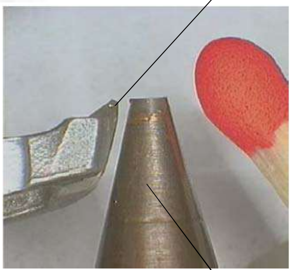
# Electromechanical Engraving

Mechanical Engraver at HdM

Source: A. Weichmann lecture on gravure printing HdM, Stuttgart

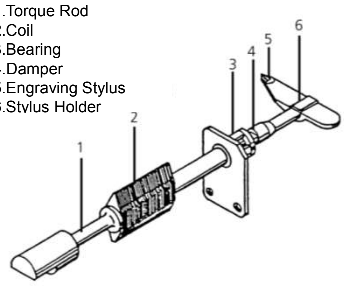
# Electromechanical Engraving

Diamond tip



Gliding foot

1.Torque Rod
2.Coil
3.Bearing
4.Damper
5.Engraving Stylus
6.Stylus Holder




Source: A. Weichmann lecture on gravure printing HdM, Stuttgart

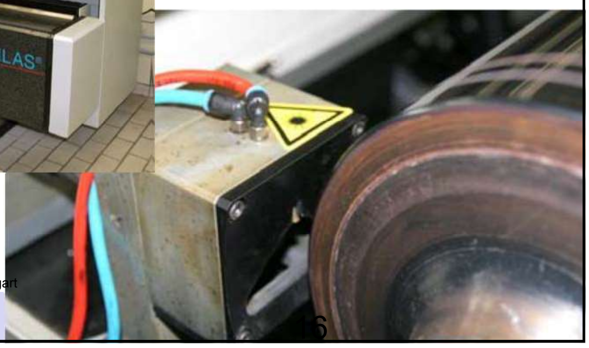




# Masking and Etching Technique Using a High Resolution Laser

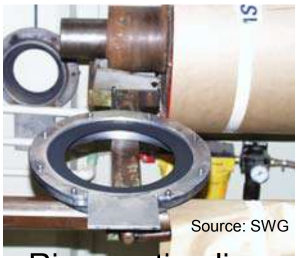
Direct engraving of copper almost impossible. Apply black mask, then ablation of the black mask, followed by etching and removal of black mask laquer


Schepers Digilas



Source: A. Weichmann lecture on gravure printing HdM, Stuttgart

# Masking and Etching-Technique


Source: SWG
Ring coating lip


Photoresist Coating
Source: SWG

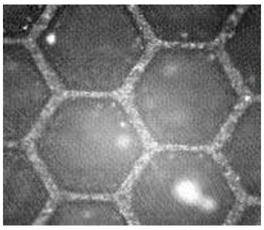

Laser Ablation
Source: www.saueressig.de

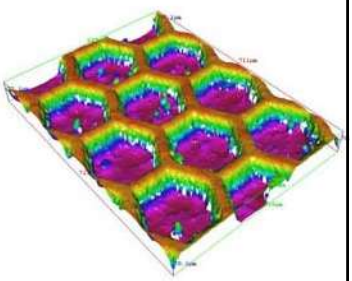

Spray etching
Source: SWG



# Engraving in Rubber (EPDM)

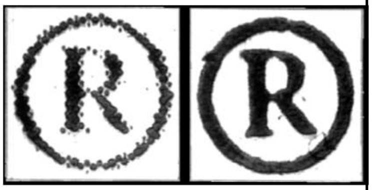

Rubber Cylinder for Lab Press


Honeycomb Structure


3D Image of Honeycomb Structure

# Resolution

- Electromechanical Engraving
  - Standard: 20µm
  - Xtreme Gravure 10µm
- Masking techniques, direct Laser
  - Depending on Laser spot diameter and repeatability of machine bed, down to 3µm



Example: left conventional gravure Raster 70, angle 4 (Reff 100 lpi), right Xtreme Engraving 200 lpi





Prof. Dr.-Ing. Gunter Hübner
HOCHSCHULE DER MEDIEN

# Solvents for gravure inks

| Solvents | evaporation number | boiling point | Viscosity mPa·s | usage |
|---|---|---|---|---|
| Ethyl acetate | 2,9 | 77,0 °C | 0,44 | packaging |
| Toluene | 6,1 | 110,0 °C | 0,59 | commercial |
| Ethanol | 8,3 | 84,7 °C | 1,19 | packaging |
| Ethoxy propanol | 34,0 | 88,4 °C | 2,6 | packaging |
| Water | 80 | 100,0 °C | 1,0 | packaging, decor |

# Gravure Printing


My colleague,
Armin Weichmann,
presenting new light weight
Aluminum-Cylinders

Thanks and hope I could attract your attention for gravure

## 11. Flexographic printing

Davide Deganello, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a

Welsh Centre for Printing and Coating

SWANSEA UNIVERSITY
PRIFYSGOL ABERTAWE

School of Engineering

Welsh Centre for Printing and Coating

# Printing for the future: Flexography

Davide Deganello

Contact email: d.deganello@swansea.ac.uk

Thank you to Stefano D'Andrea &

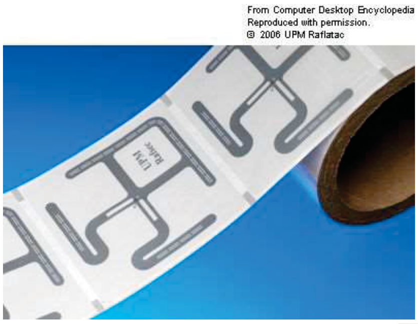
2016

SWANSEA UNIVERSITY
PRIFYSGOL ABERTAWE

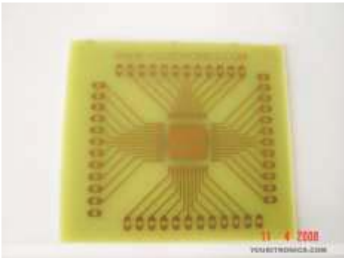
School of Engineering

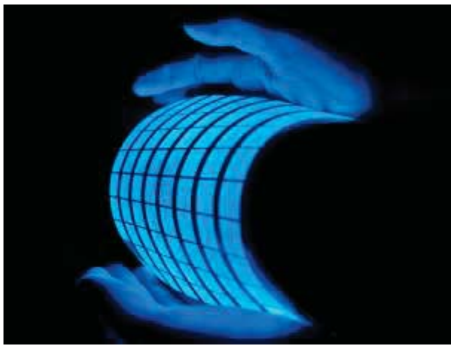
## Electronics & Printing

- Printing has an important role for the future of flexible thin-film devices for electronic and biomedical applications




RFID





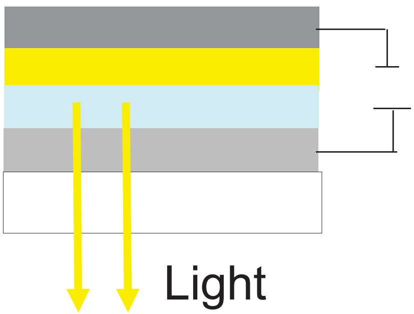
OLED Lighting

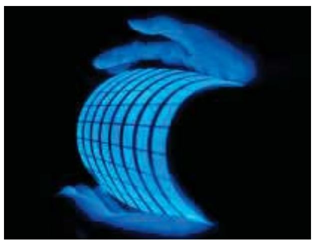
Circuit board

## Thin-film technology

- Thin film technologies:
  - Consist in the deposition of thin layers of special functional materials that work together creating a device:
  - Example: OLED
    - Light-emitting diode (LED) whose emissive electroluminescent layer is composed of a film of organic compounds

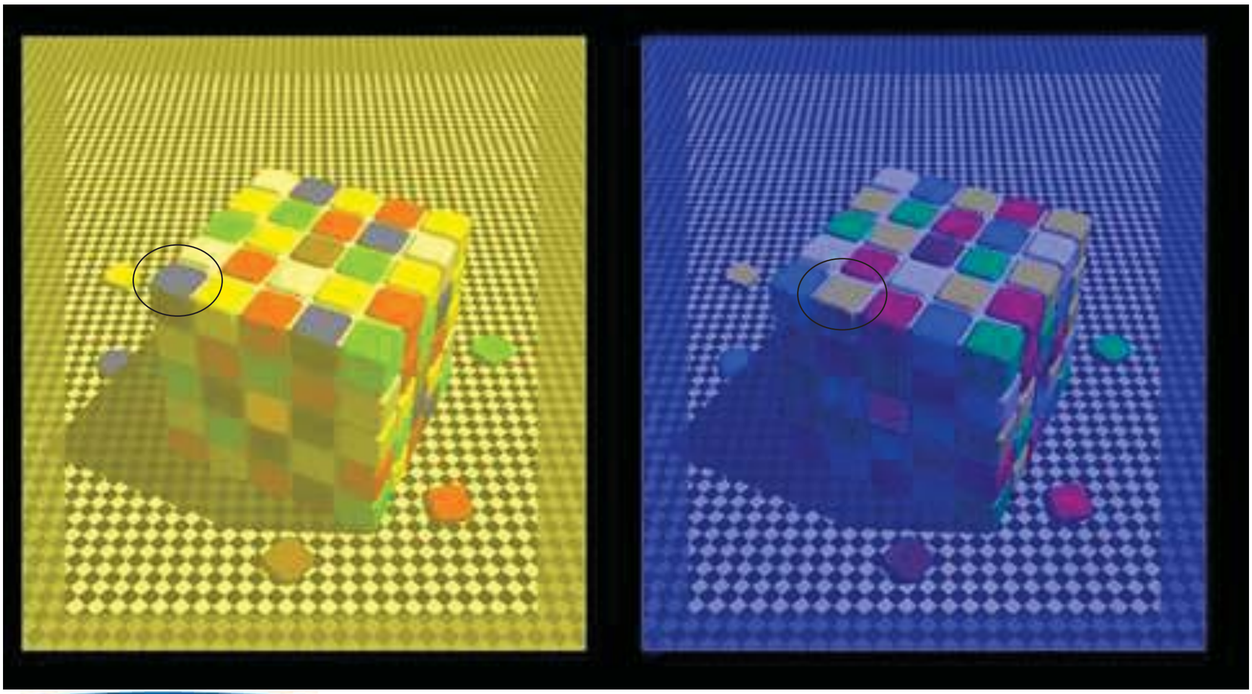
Cathode
Light-emitting polymer
Hole-injector layer
Transparent conductive anode
Transparent substrate



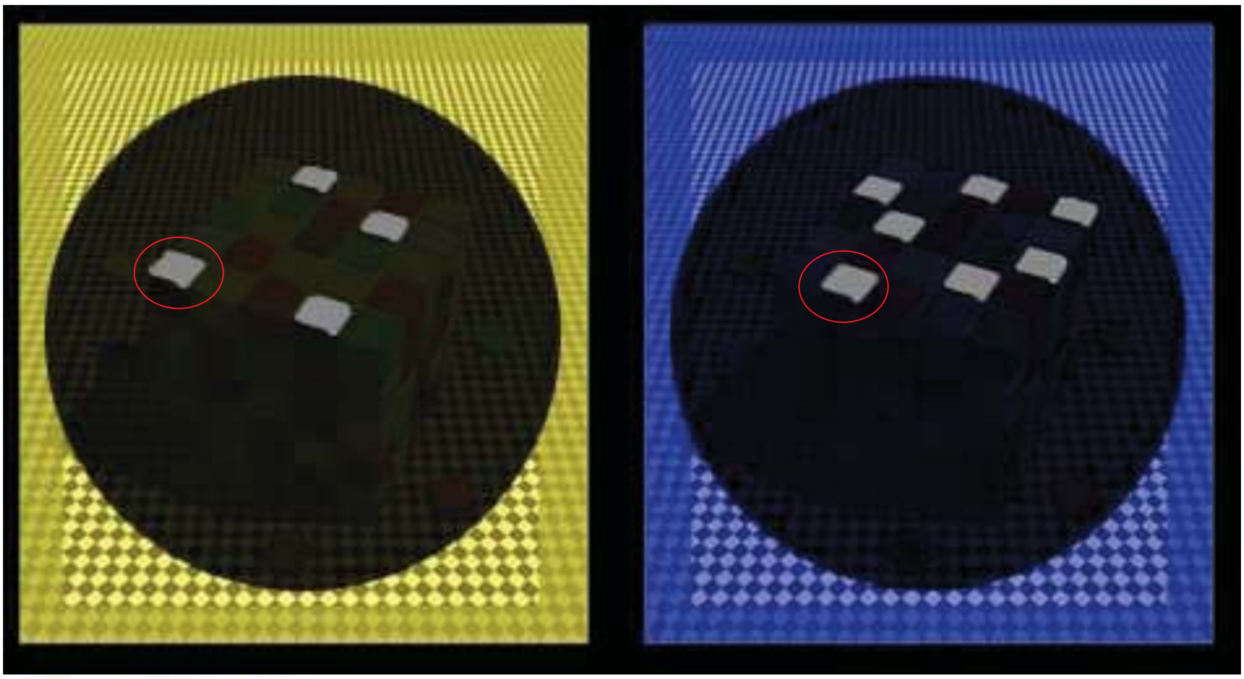
## Graphic to printed electronics: the challenges?

- What colour are the tiles?



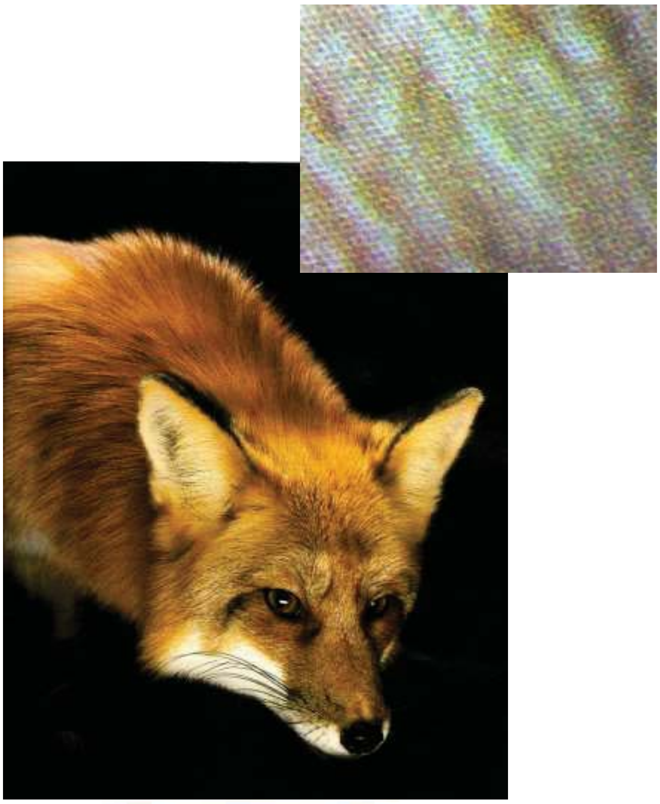
## What is a colour?

- Masking the surrounding....



Images by R.Beau Lotto
http://www.lottolab.org

## Printing challenges



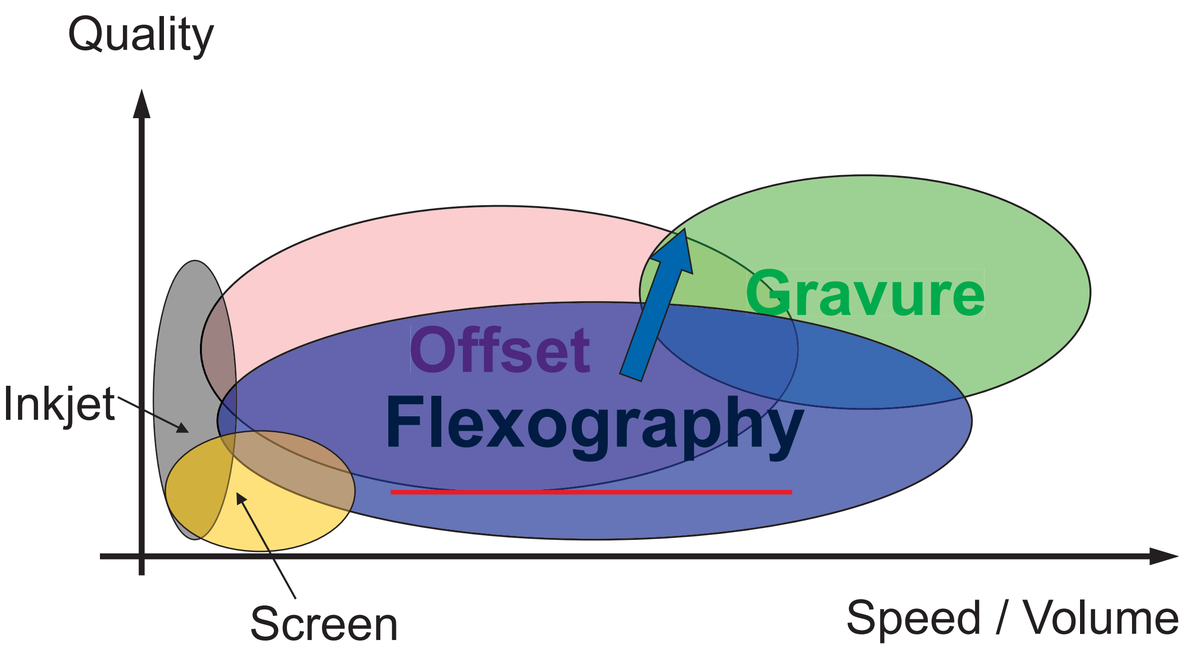
*Graphic Printing*

- Eye "compensates"

*Printed Electronics*

- New level of accuracy / understanding required

## Printing technologies



## Printing technologies: origin

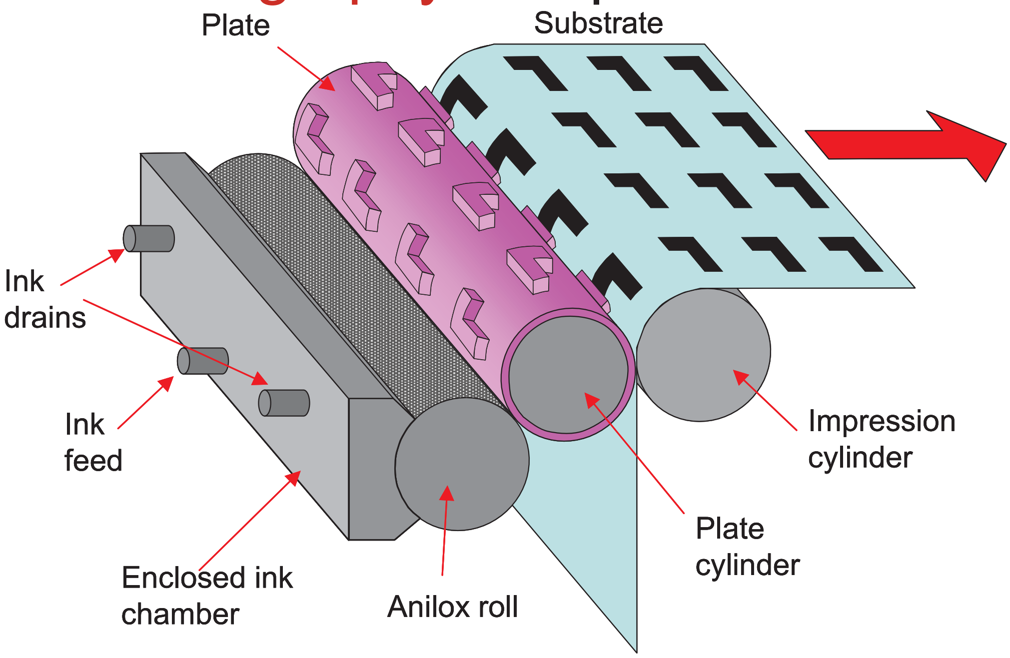
- Gutenberg Printing: Letterpress
  - A raised hard surface plate is inked and then pressed against a sheet of paper
  - Gutenberg “invention”: movable and reusable lead metal types

## Printing technologies for accurate patterning

- Flexography
  - Evolution of letterpress
  - Image on a soft plate
  - Graphic Applications:
    - Packaging
    - Publication (magazines)
  - Improved quality over last 25 years:
    - Press
    - Plate
    - Anilox

## Flexography

- **Flexography:** the process




- A raised image on polymer plate pick up the ink from an engraved cylinder (anilox) and deposit it over the substrate

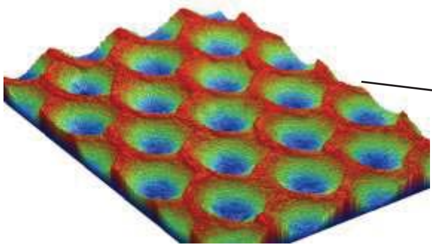
## Flexography: advantages

- Flexographic inks:
  - Flexible formulation
  - Wide viscosity range (0.05-3 Pas)
  - Can process big particles (up to 10-20 µm)
  - High and flexible functional content possible
- High deposition rate
  - All the image in one “go”: roll-to-roll
  - Speed up to 500-800 m/min
- High commercial & industrial interest

# Flexography the components

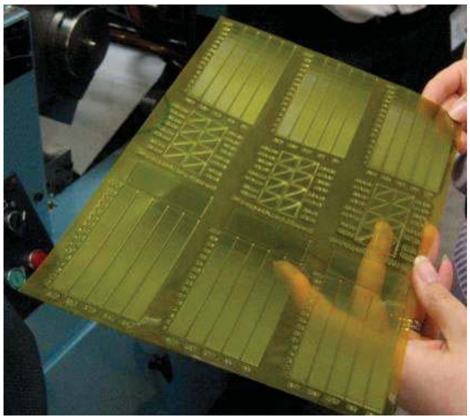
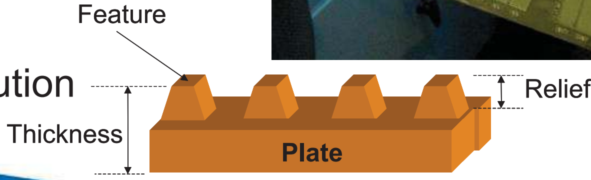
## The Anilox:

- Metering system
- Ceramic cylinder
- 100% engraved




## The plate:

- Image carrier
- Soft Photopolymer
- UV exposure creates a raised surface from which to print
- Taped around cylinder
- Improvements in plate resolution


# Flexographic press

- Bench tester

- Industrial press

- Industrial press offers mechanical stability/ controls for accurate printing
- Medium-high initial capital cost (the press): a limit to research

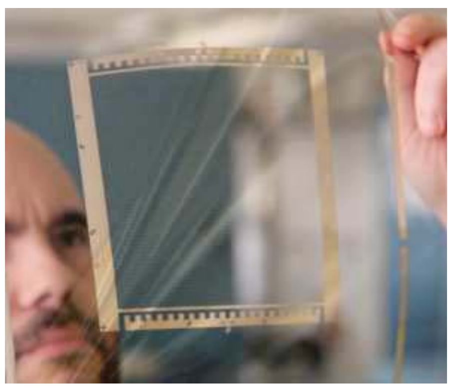
## Continuous development

- Central drum

- In line

## Flexography for electronics: case study

- Flexography for accurate micro-scale conductive networks for roll-to-roll large-area flexible OLEDs



## Fast2Light

- Project for development of mass-produced OLED lighting technologies on flexible film for replacement of traditional room lighting
  - 26m€ FP7 Integrated Project (2008-12)
  - 13 partners


## Large area OLEDs issue

- Large-area flexible OLEDs require an excellent conductance and transparent layer for light uniformity
- Current standard ITO: expensive and limited flexibility
- A replacement with improved sheet resistance is needed

## The solution

- Integrating micro-scale highly conductive networks with transparent conductive layers

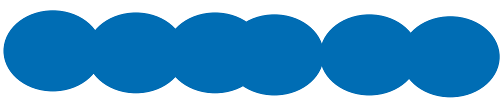
  - Consistency is critical : no break-up allowed

  - Excellent patterning is required
    - Photolithography capable but too slow and expensive
    - Compatibility with large-area, high speed

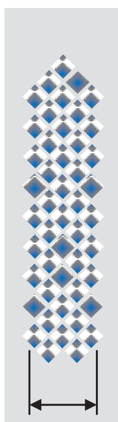
    - Flexographic printing ?

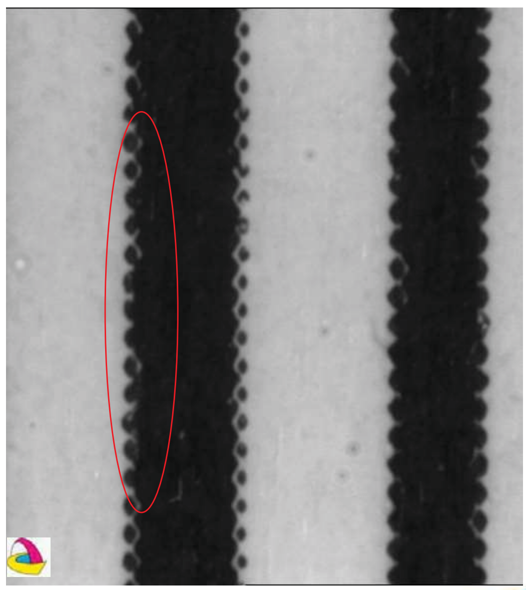
## Printing Technologies

- Which Printing for tracks?
- Inkjet, screen printing, conventional rotogravure
  - Lines are generated by combination of printed dots
  - Limits in line resolution
  - Break-ups



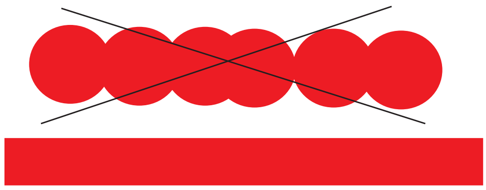
Flexography





# Why Flexography?

- Relief plate allows the deposition of ink as a continuous lines, instead of a series of joining dots (eg. Inkjet)



- WCPC: research in improved plate resolution/chemical resilience

- Testing accurate patterning by flexography

# Experimental trial

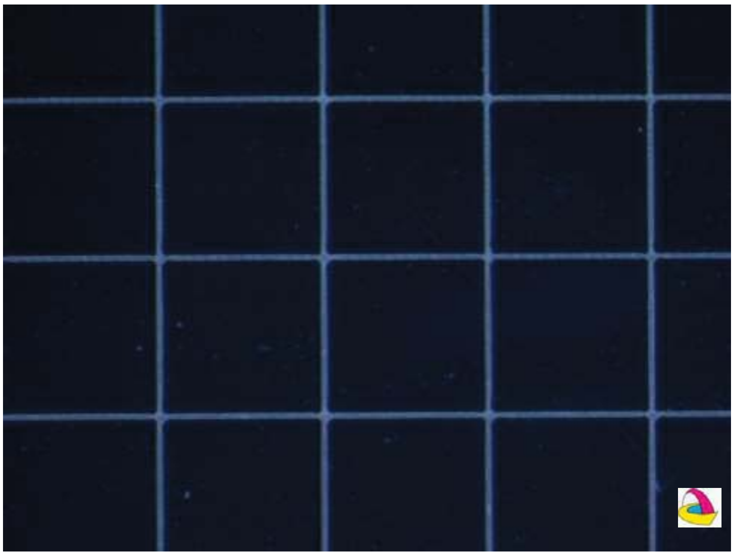
- Roll-to-roll print trial on industrial press with accurate control of substrate-plate pressure
- Ink: Silver nanoparticle ink
- Speed 5 m/min, >100 m printed
- Sintering of prints at 130°C, 10 minutes

Timson T-Flex 508

# Results

- Flexoprinted silver network over PET

  - Line width (SD): 70 ± 2 µm
  - Over 100 m produced
  - Low sheet resistance: 3 Ω/□ at 7% area coverage
  - Excellent accuracy, deposition rates & consistency

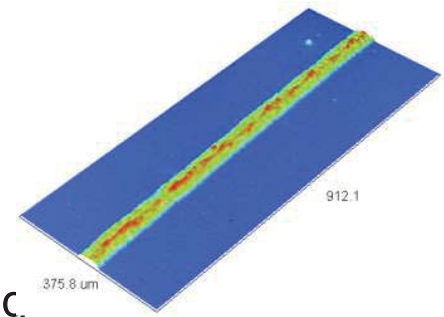


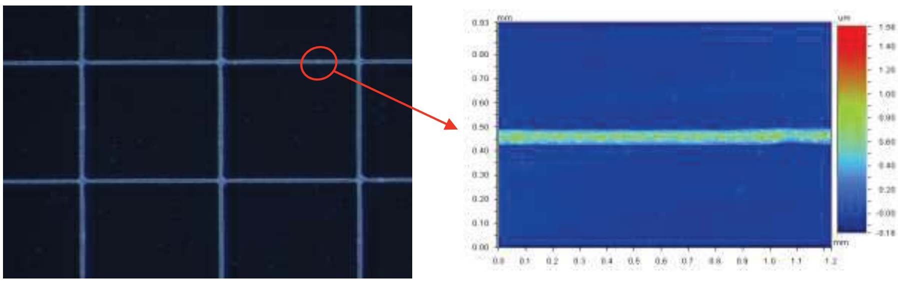
2 mm

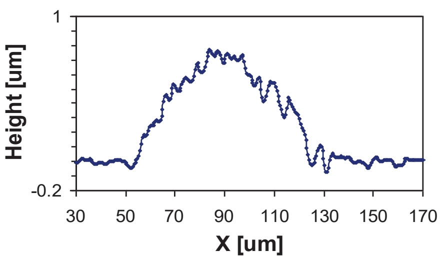
# Results

- Printed tracks are smooth

  - Smooth edges and surface
  - Resistivity: 2.5x bulk silver
  - Ideal for overcoating, multilayer structuring

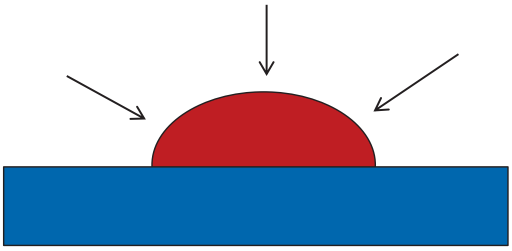


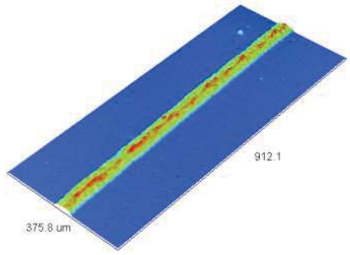





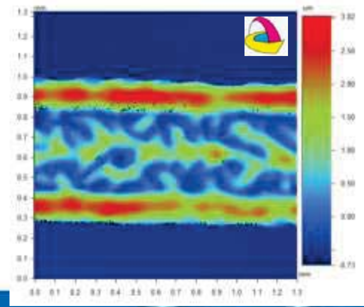
# Results

- Flexography: Why dome-shaped?
  - Surface tension (hypothesis): lines are < 200um range, surface tension is a dominant force; thanks to quality of starting deposit, line structure is kept avoiding inconsistencies



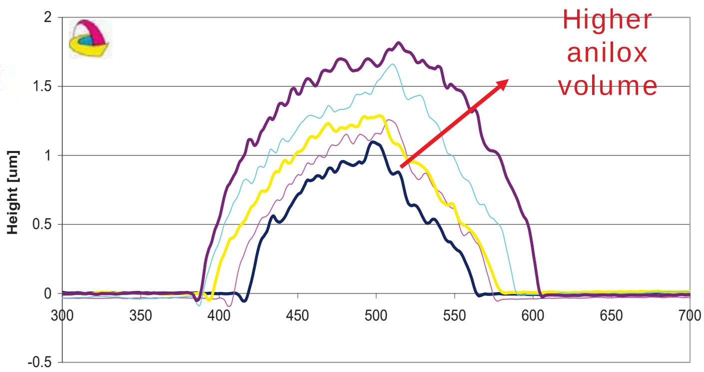



  - Attention to engagement plate/substrate:
    - Too high pressure, squeezing the ink out



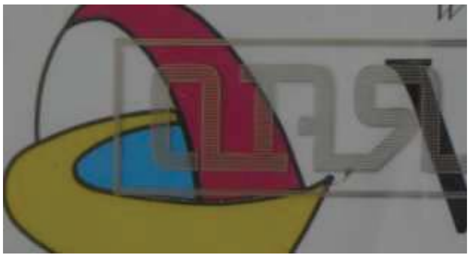
# Flexography: control thickness

- Flexography: flexibility in control of deposit thickness
  - Anilox roll is metering system, independent from plate image
  - Increasing anilox volume: tracks with similar width , > cross area

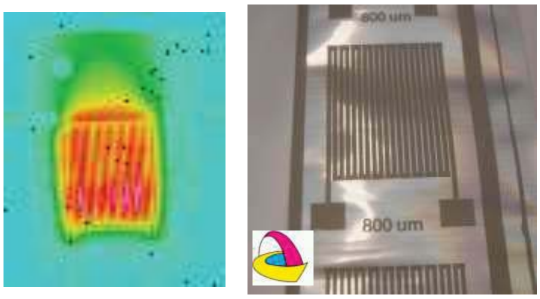


# Printed micro-networks

- Packaging Applications of printed micro-networks on flexible films



R2R printed see-through RFID



R2R printed micro-heaters

R2R Strain gauges

# Patterning by flexography

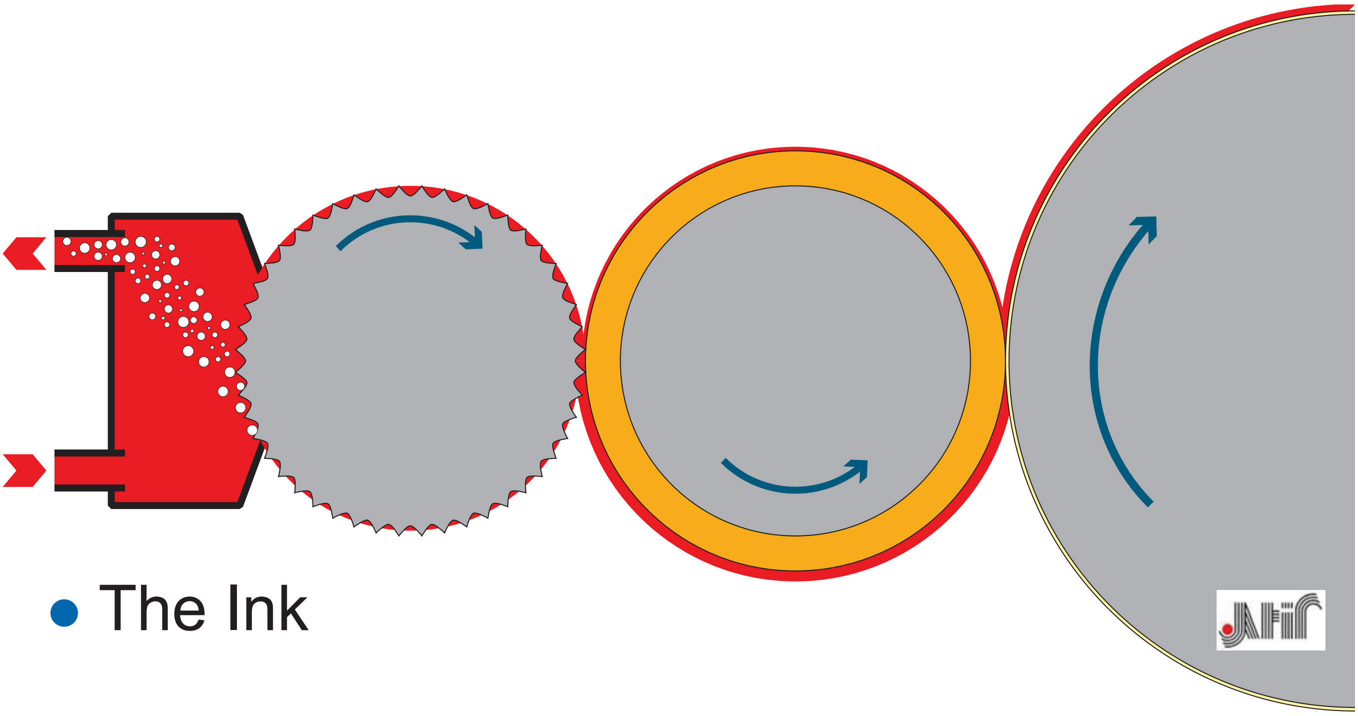
- Flexography:
- Ideal R2R patterning for functional materials
- High resolution
- Excellent accuracy
- Good deposition rate, smooth texture
- Fast & cheap process

- Flexography: understanding its components


• D. Deganello et al. *Thin Solid Films*, 518: 6113–6116, 2010

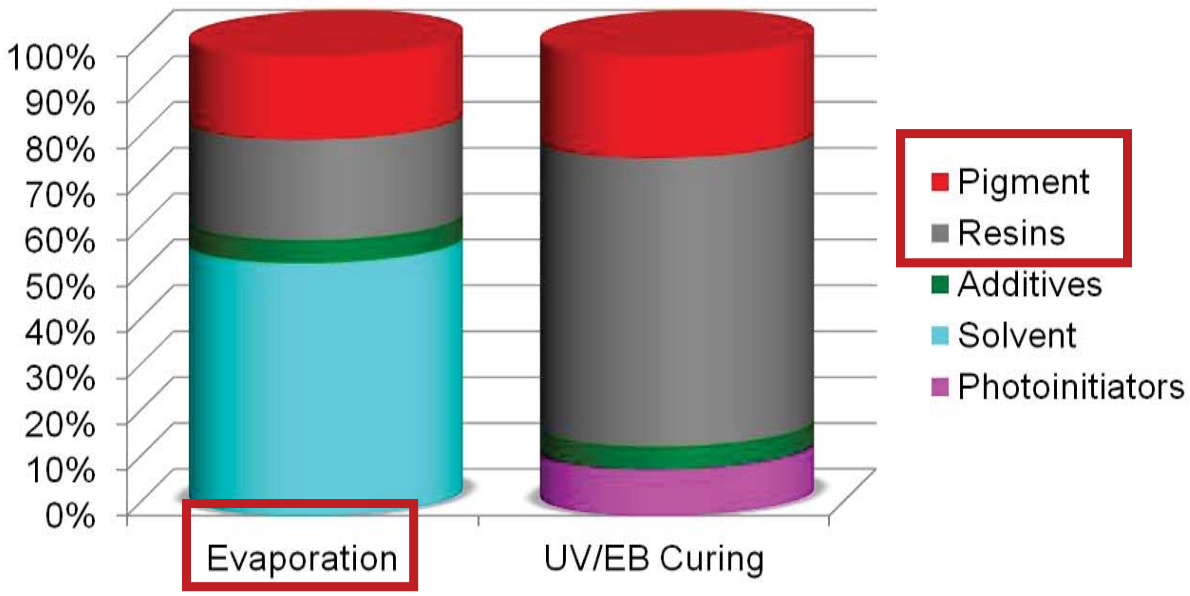
• D. Deganello et al. *Thin Solid Films* , 520:2233-2237, 2012

## Flexography: the components



- The Ink

## Generic ink composition

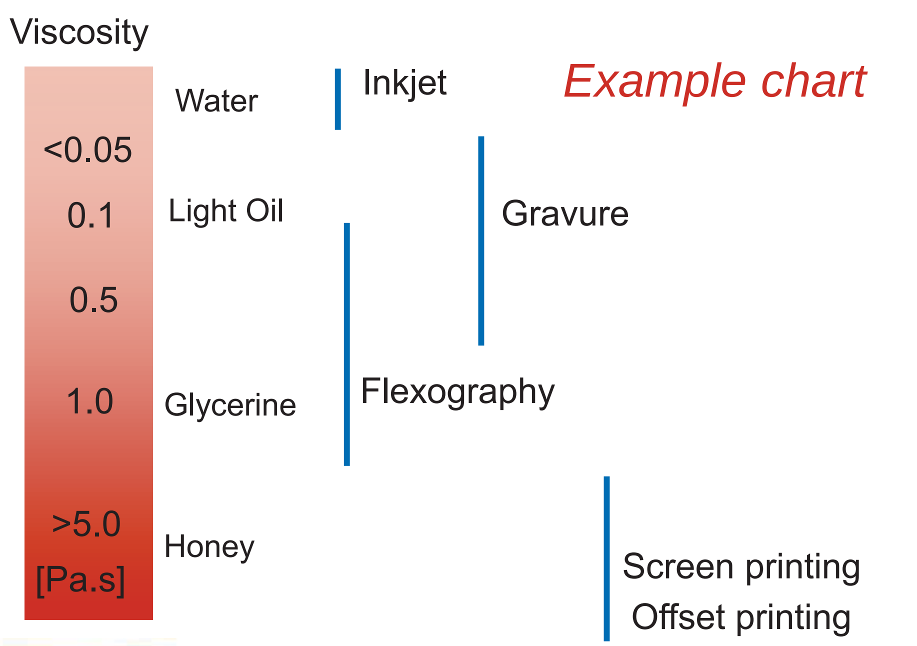



- Functional inks are typically evaporation based
- Evaporation limited during transfer

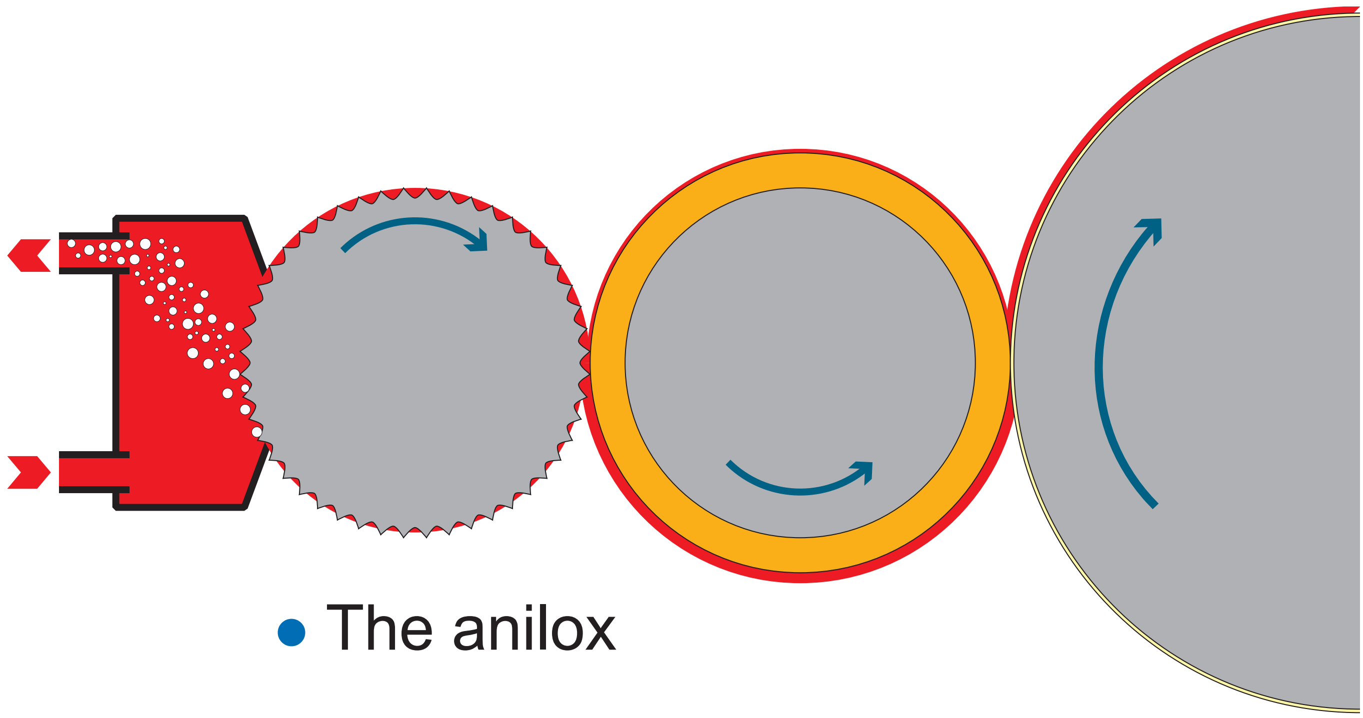
# Viscosity and Processes

## Which Viscosity for which process ?

- Each printing process works within an ideal viscosity range

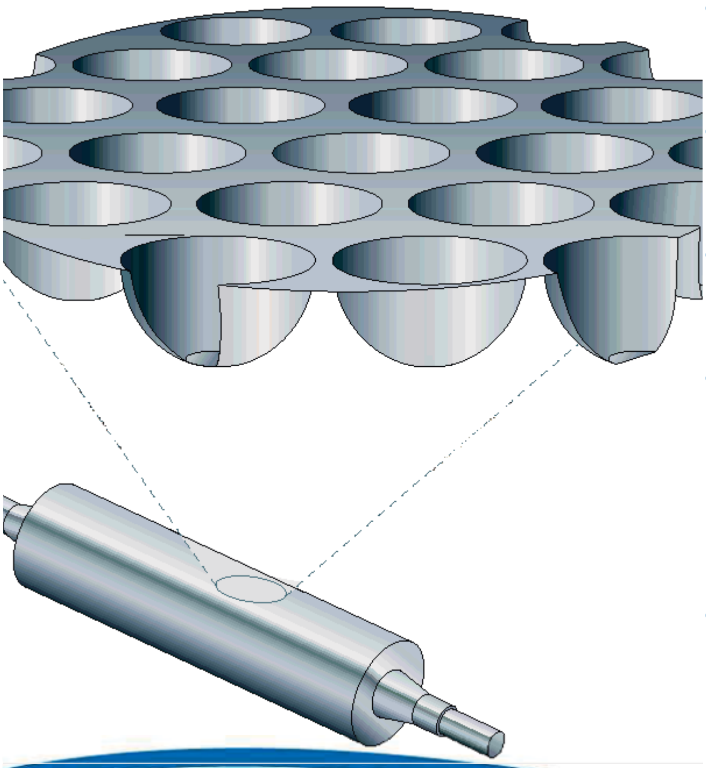



# Flexography: the components



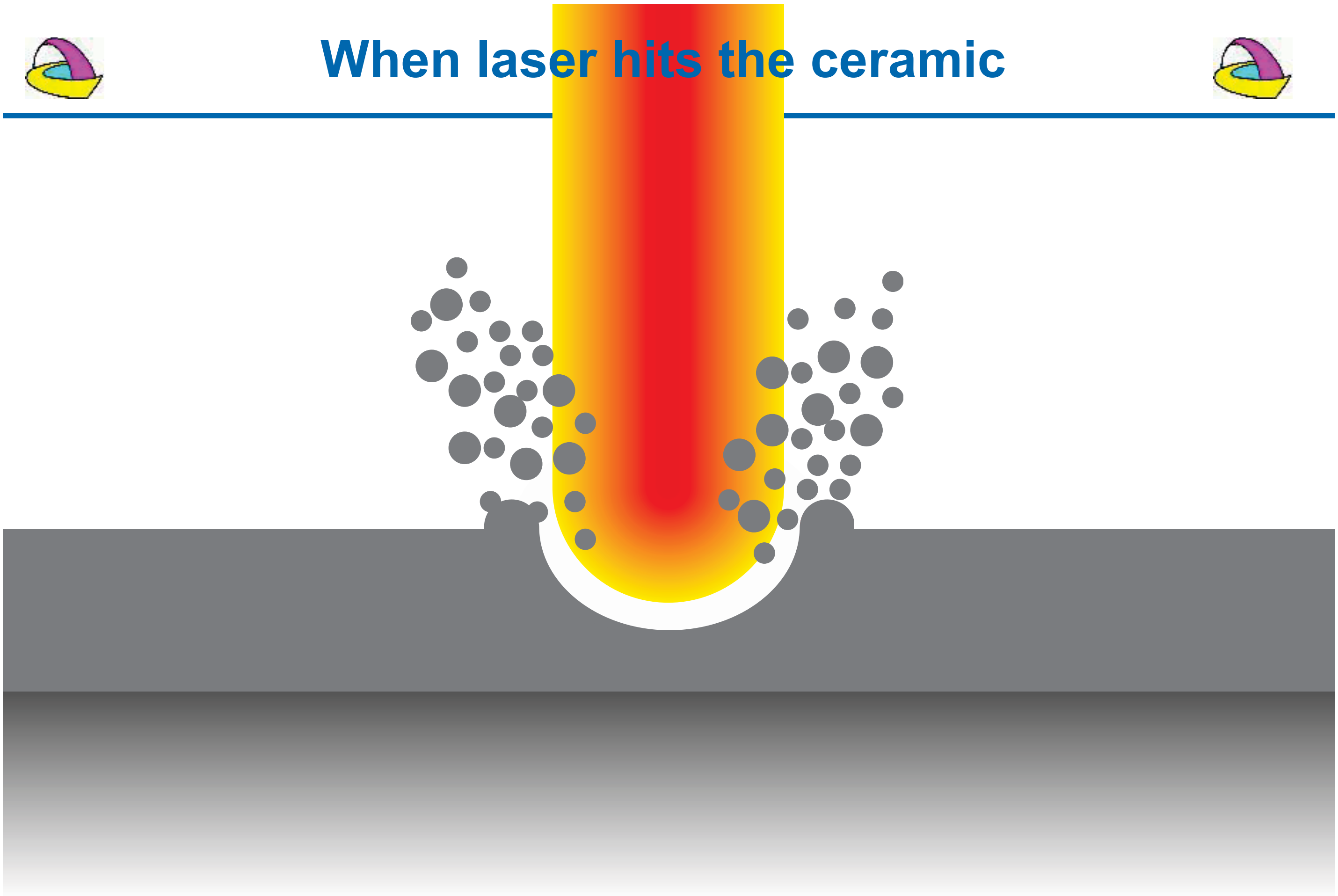
- The anilox

## The importance of anilox roll

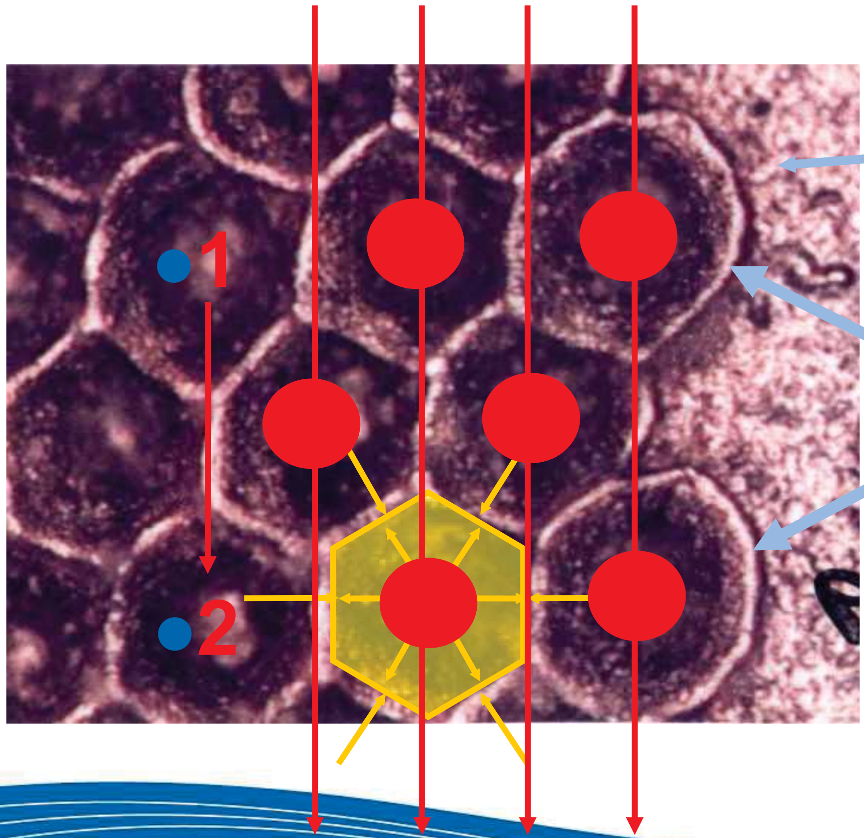


- It is considered the heart of the flexo printing system
- It is the most critical component to be optimized
- It is the most sophisticated component in the printing group
- **It is the only component able to determine the quantity of ink that is transferred onto the printing plate**
- Laser engraved ceramic cylinder

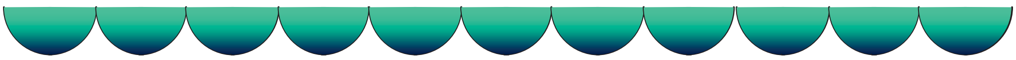
## When laser hits the ceramic



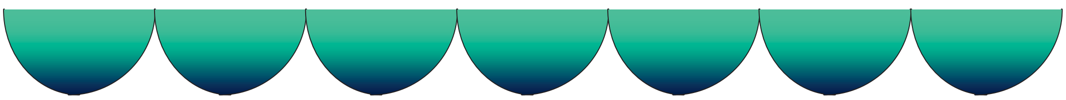
## Laser engraving on ceramic




## What is line count?



- 250 lines

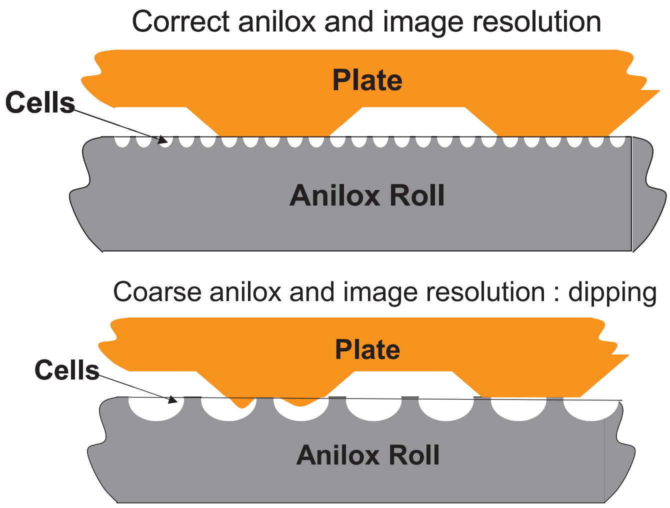


- 150 lines

- Number of cells per linear measure
- l/cm (lpcm), lpi

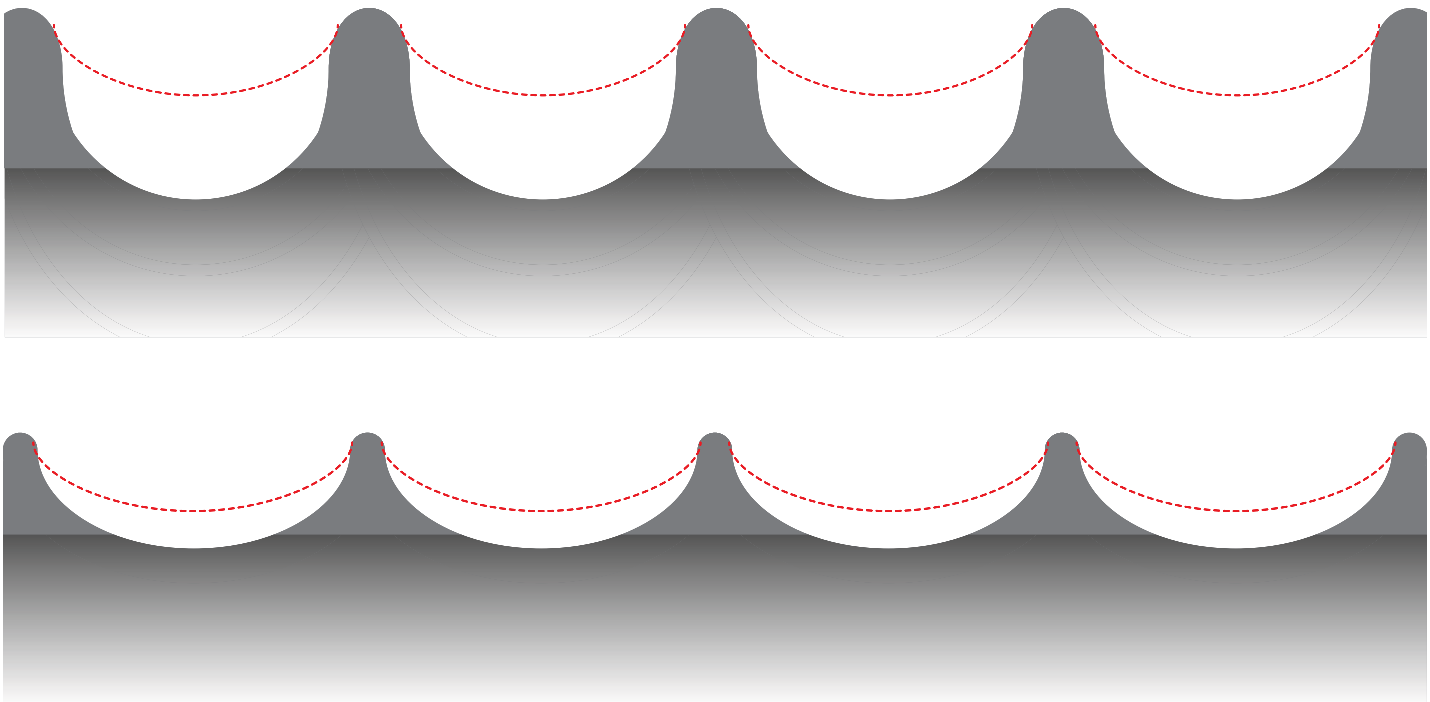
# Anilox

## Cell dipping - 5 to 1 ratio



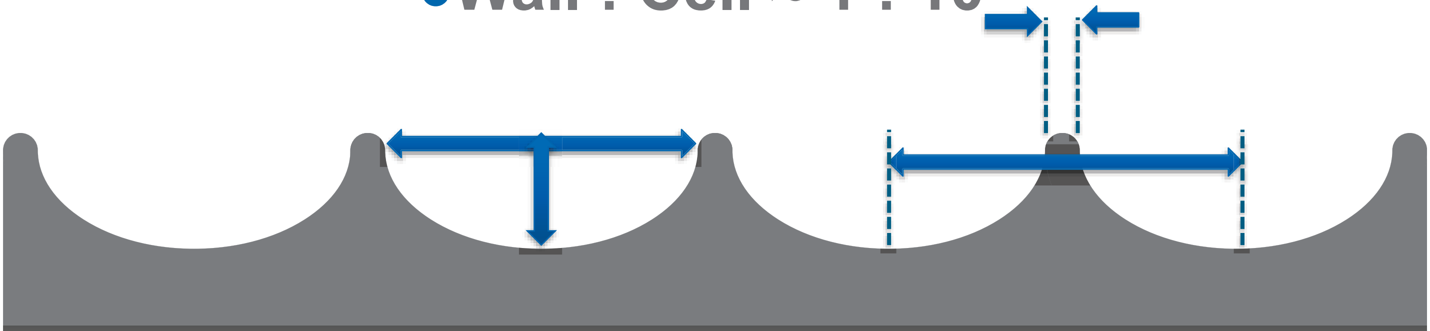

- But in electronics we often need thickness.......

# Too deep cell transfer less ink



## Ideal ratios

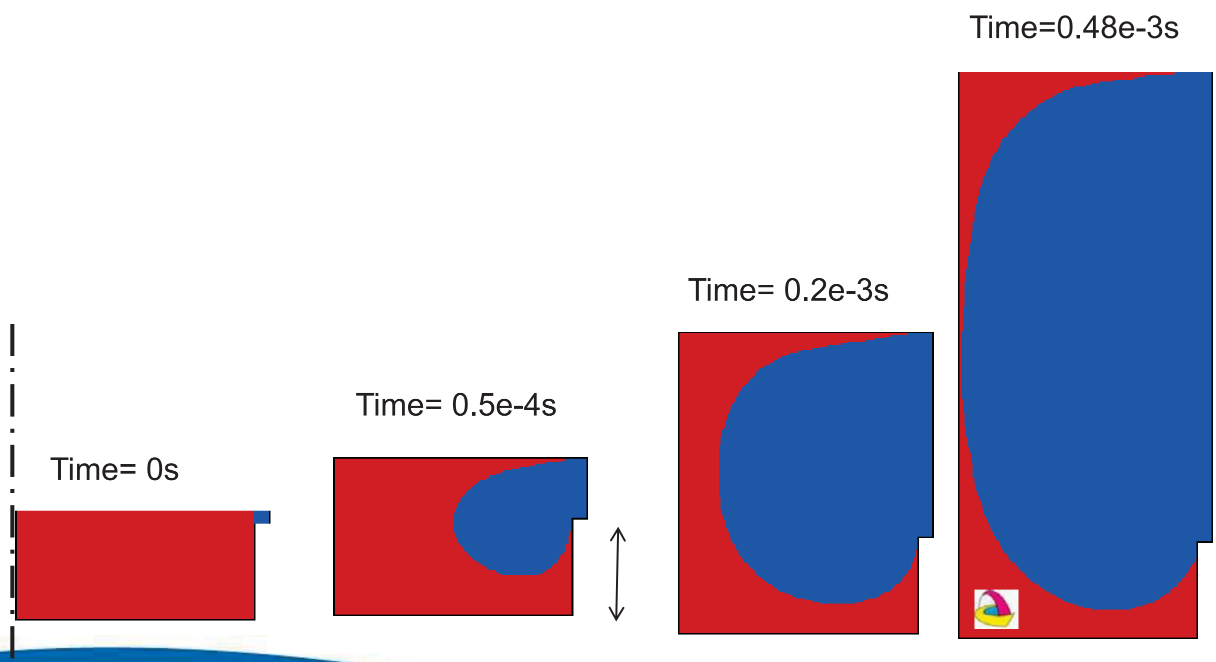
- Depth : Opening ≈ 1 : 3
- Wall : Cell ≈ 1 : 10



- *Note: parameters may change according to anilox manufacturer*

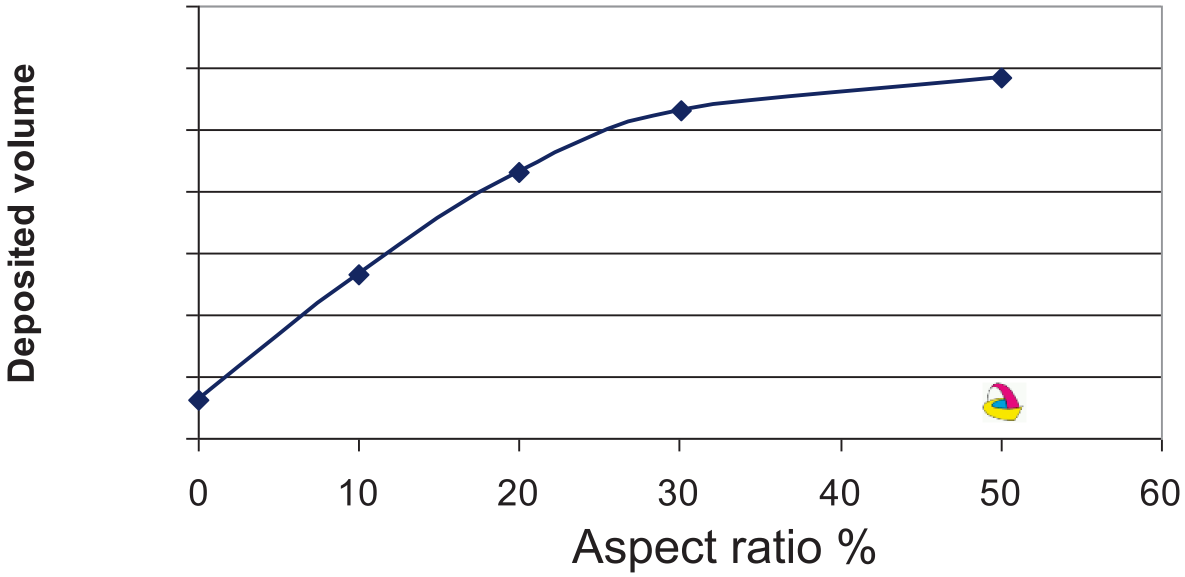
## Effect of depth to opening ratio

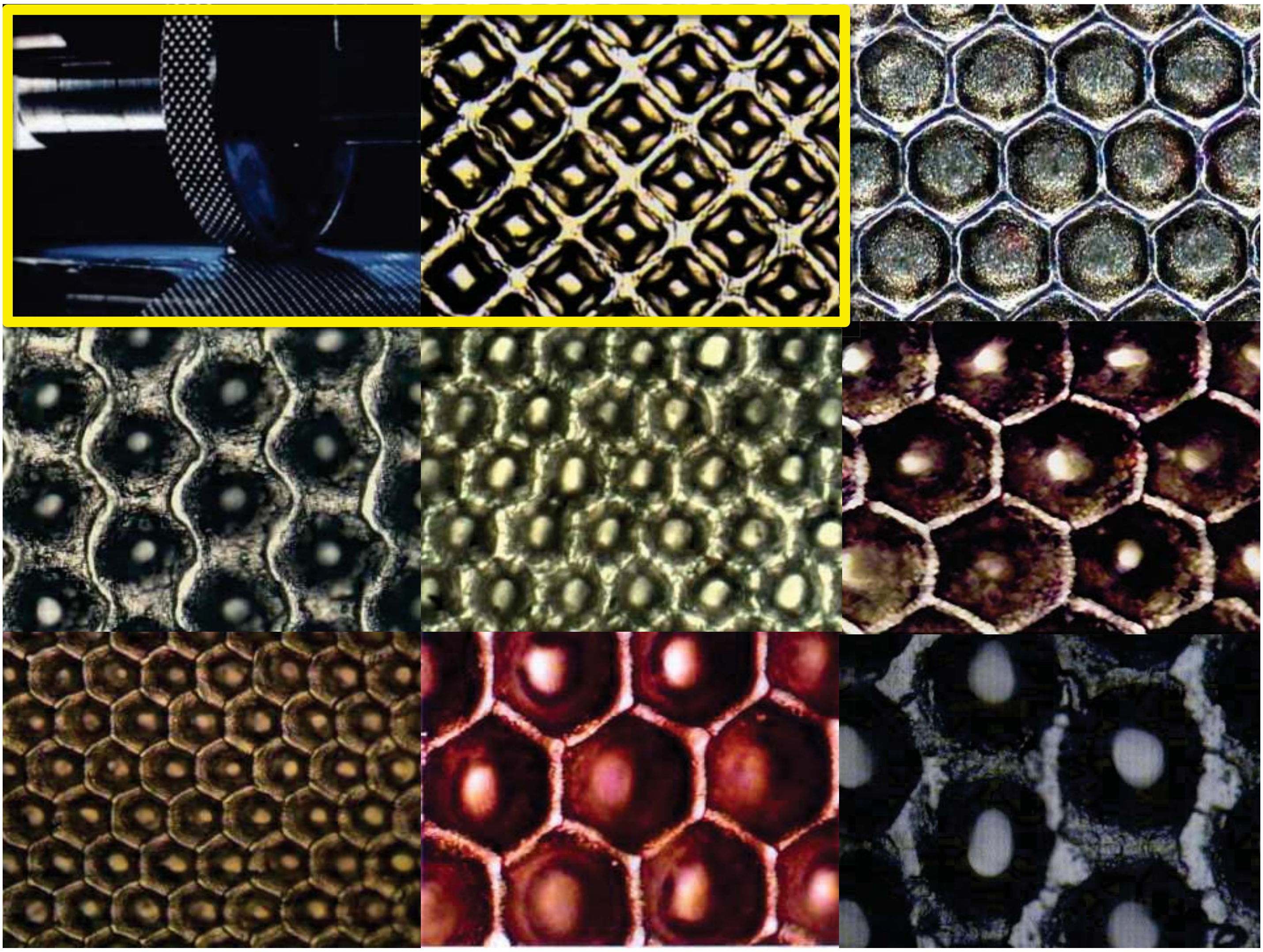
- CFD Modelling of Ink withdrawn from cavity
  - Early research model under development



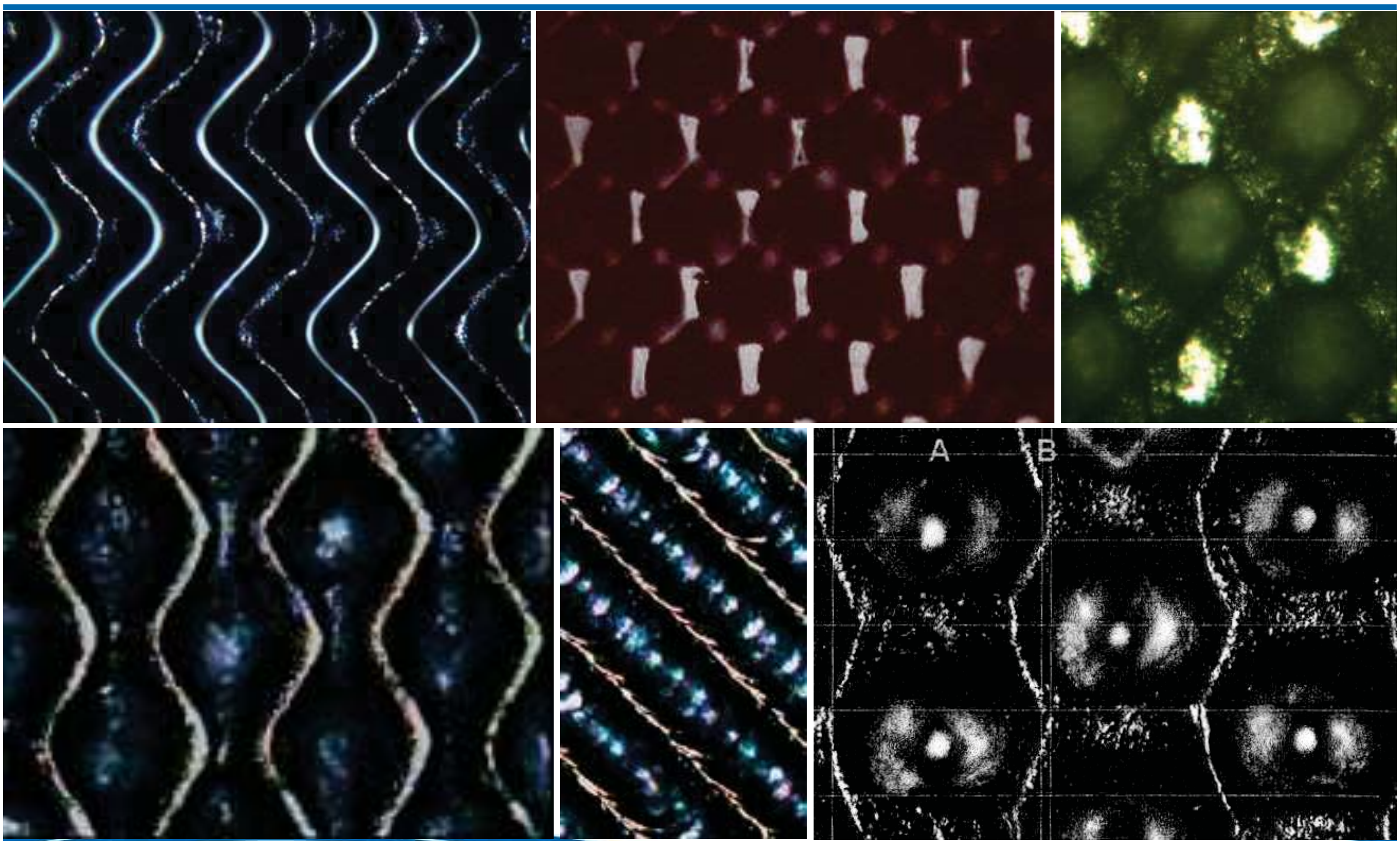
# Effect of depth to opening ratio

- Volume deposited on top plate
  - Volume deposited

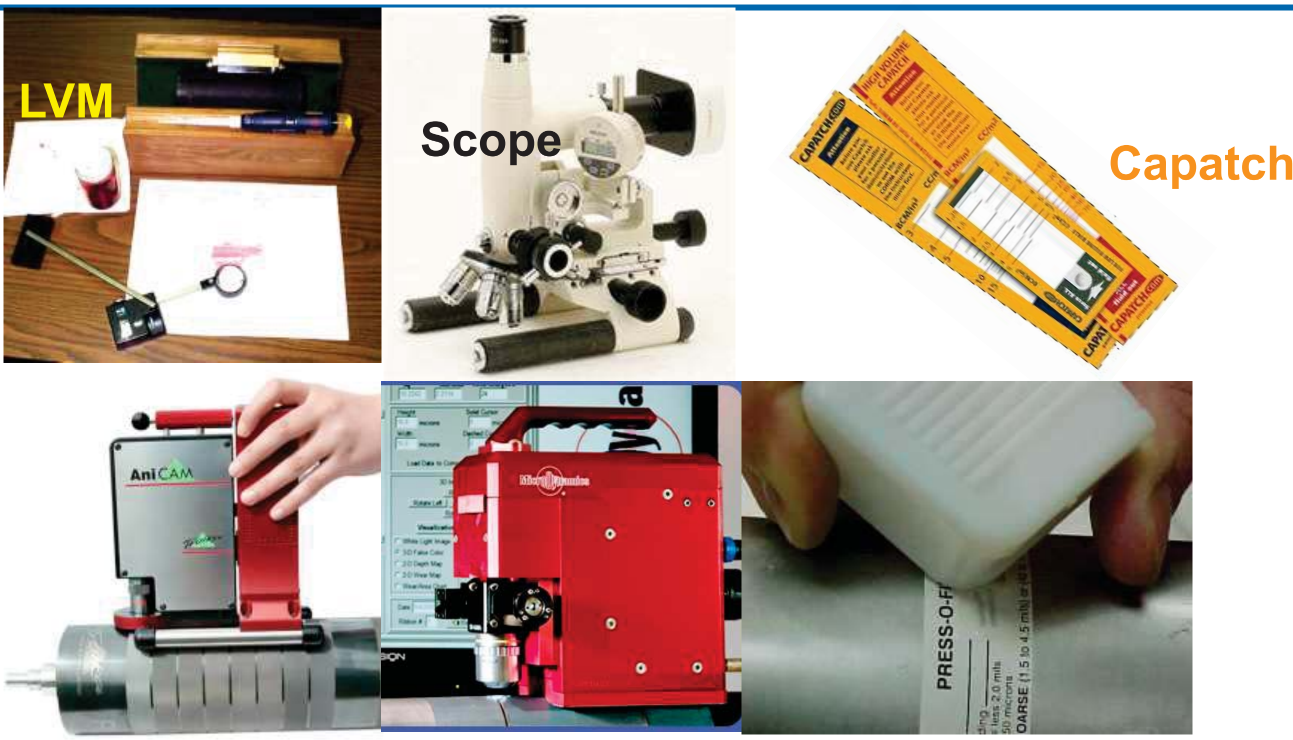


# Open cells

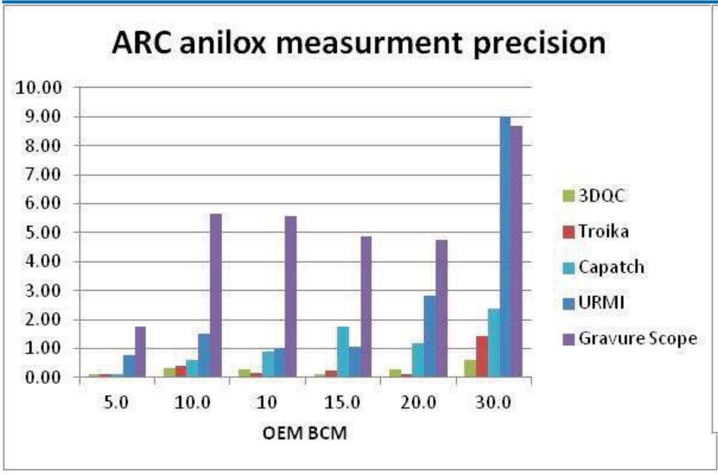


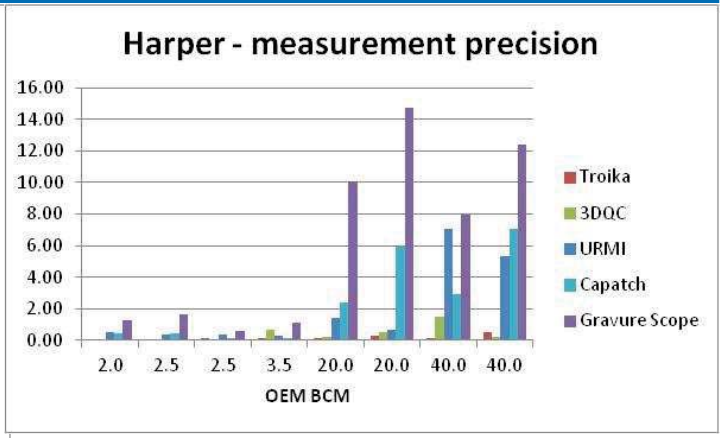

# Closed Cell study

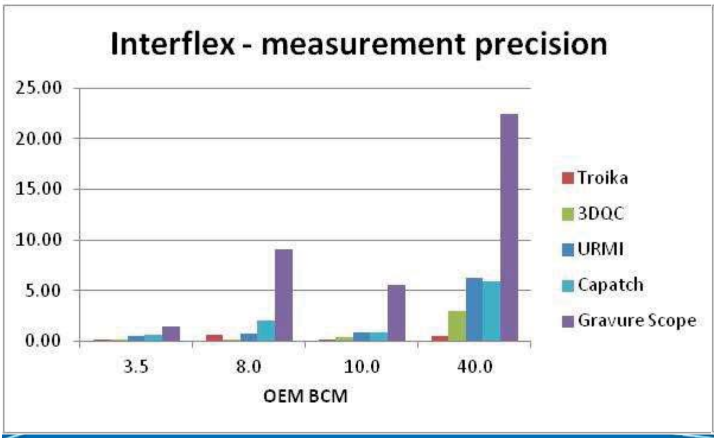


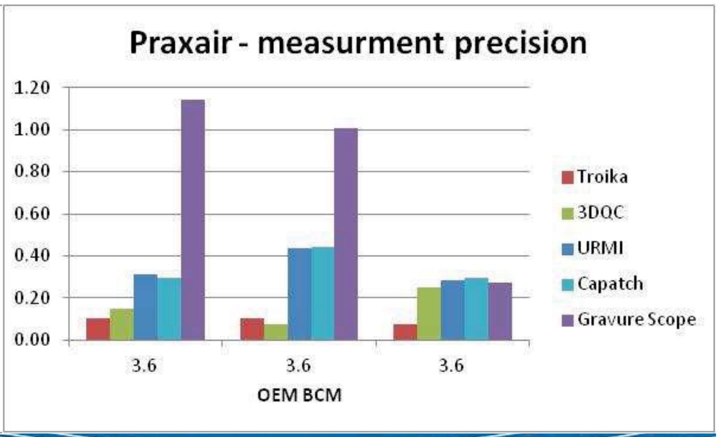

Troika Microdynamics Impression

# Measurement precision



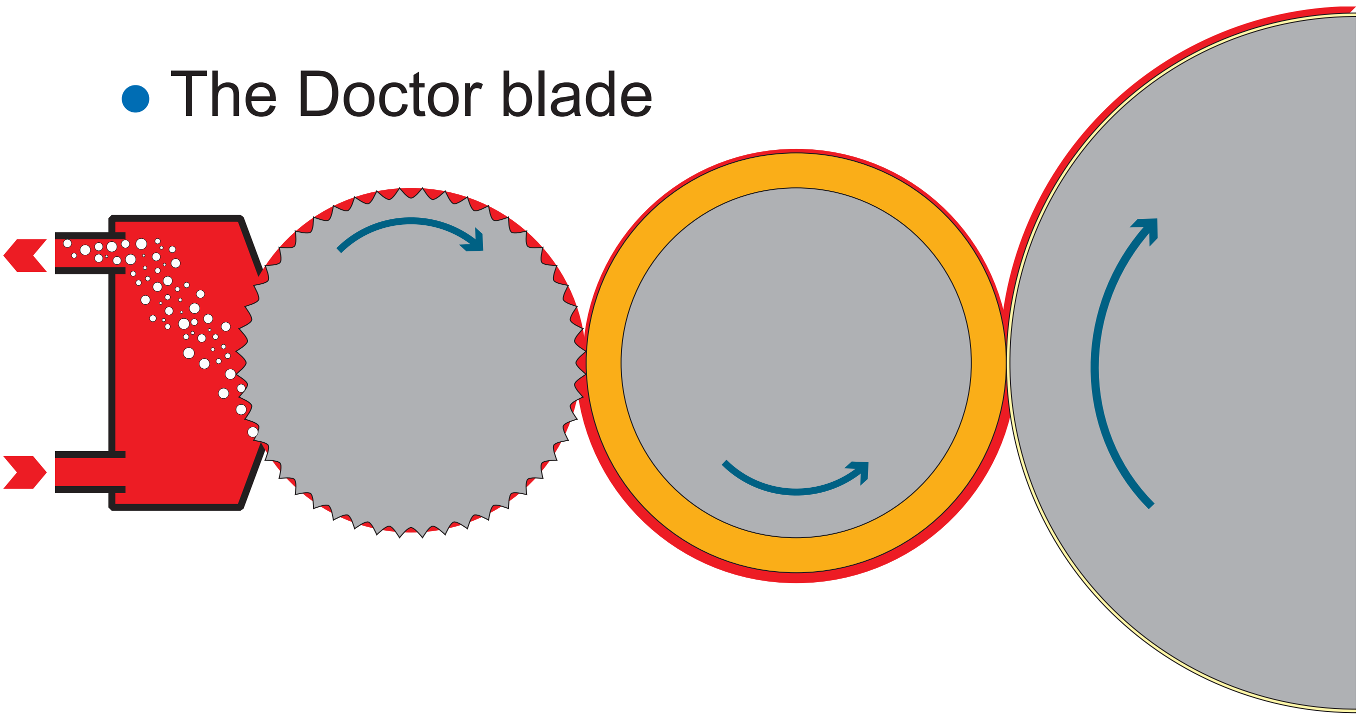



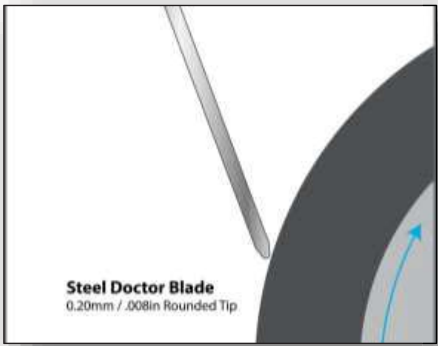

# Flexography: the components

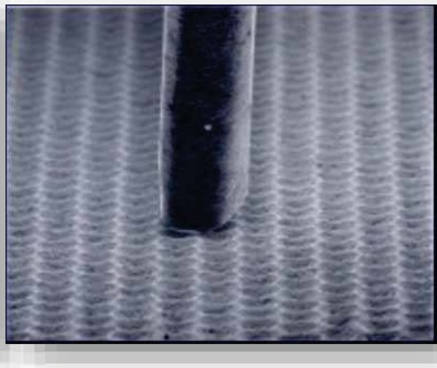
- The Doctor blade



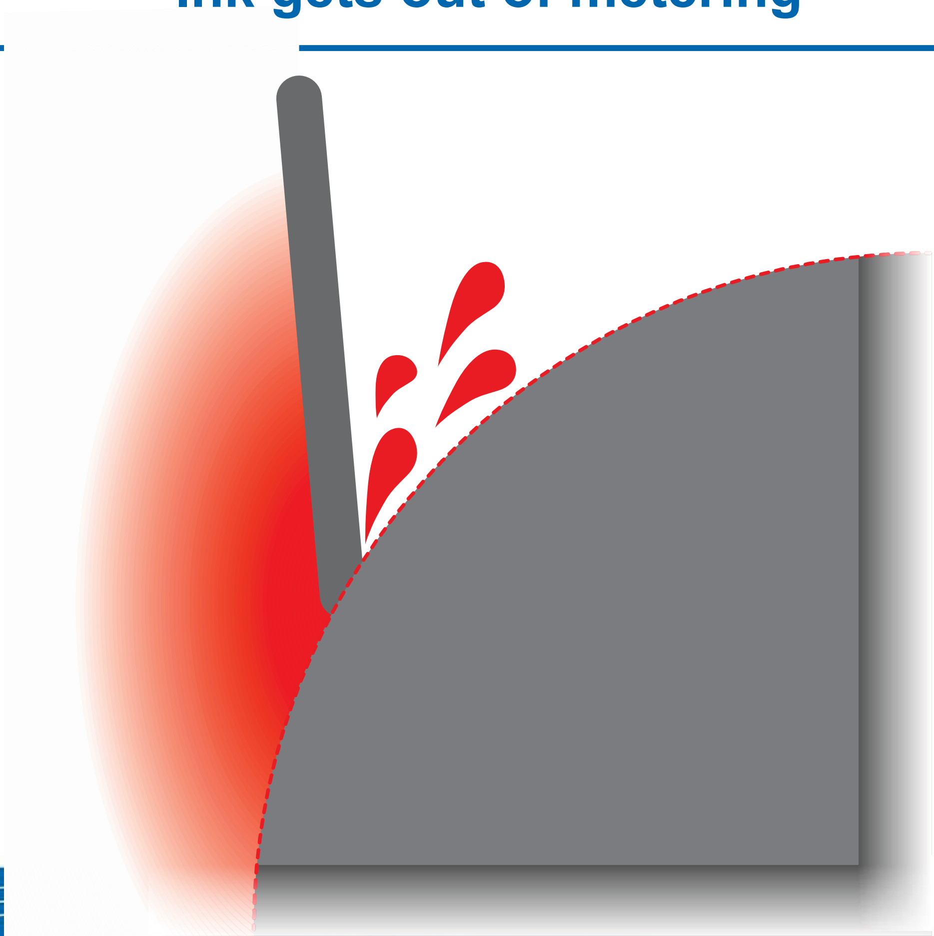
# The doctor blade

- Ensures the ink is transferred only by engraved areas
- Different design
- **It's the only system that ensures repeatable and predictable results**

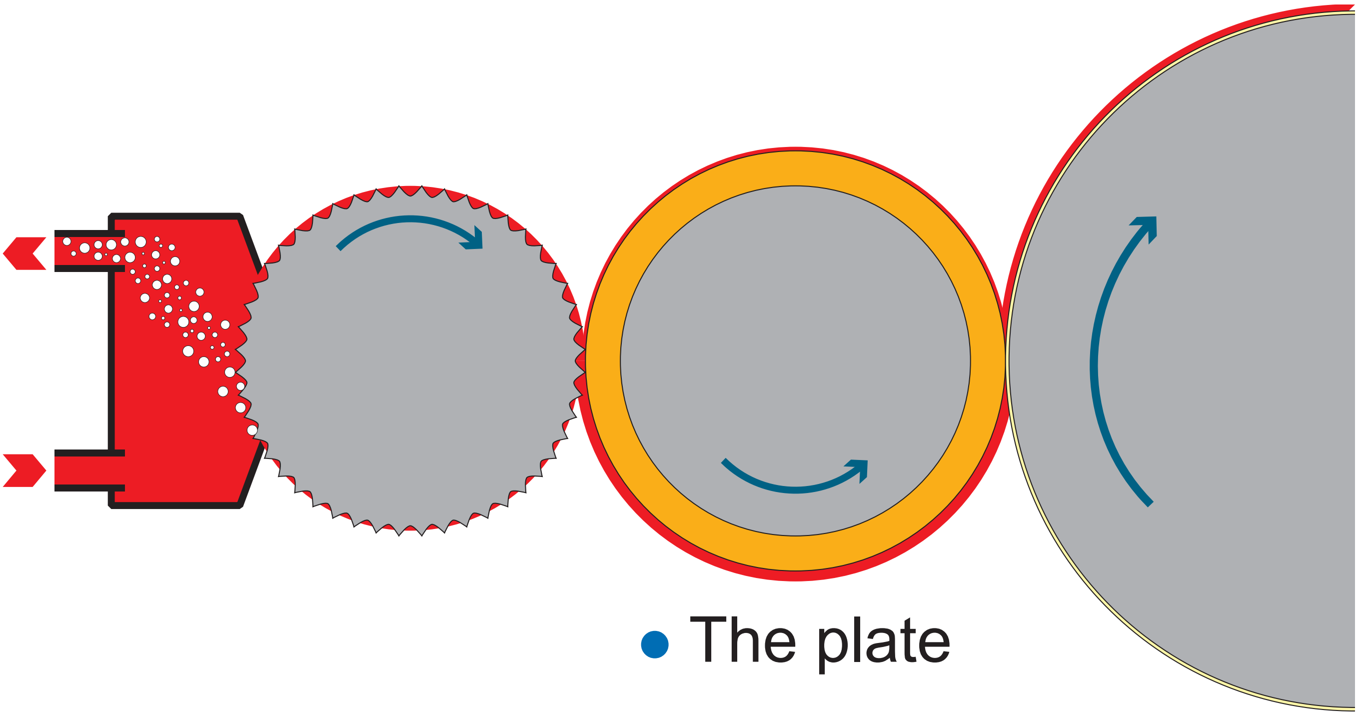


# Ink gets out of metering

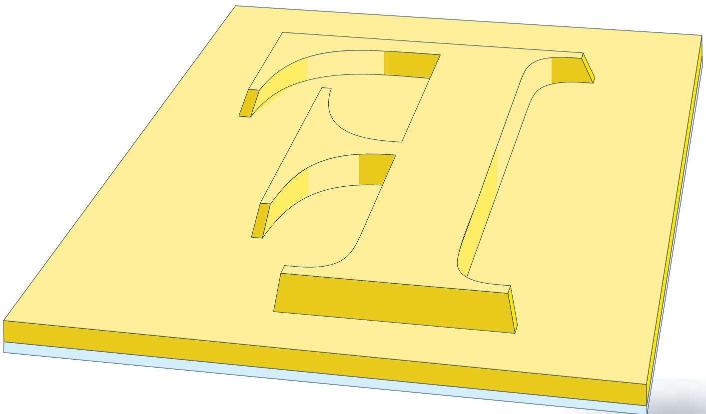


# Flexography: the components



- The plate

# The printing plate



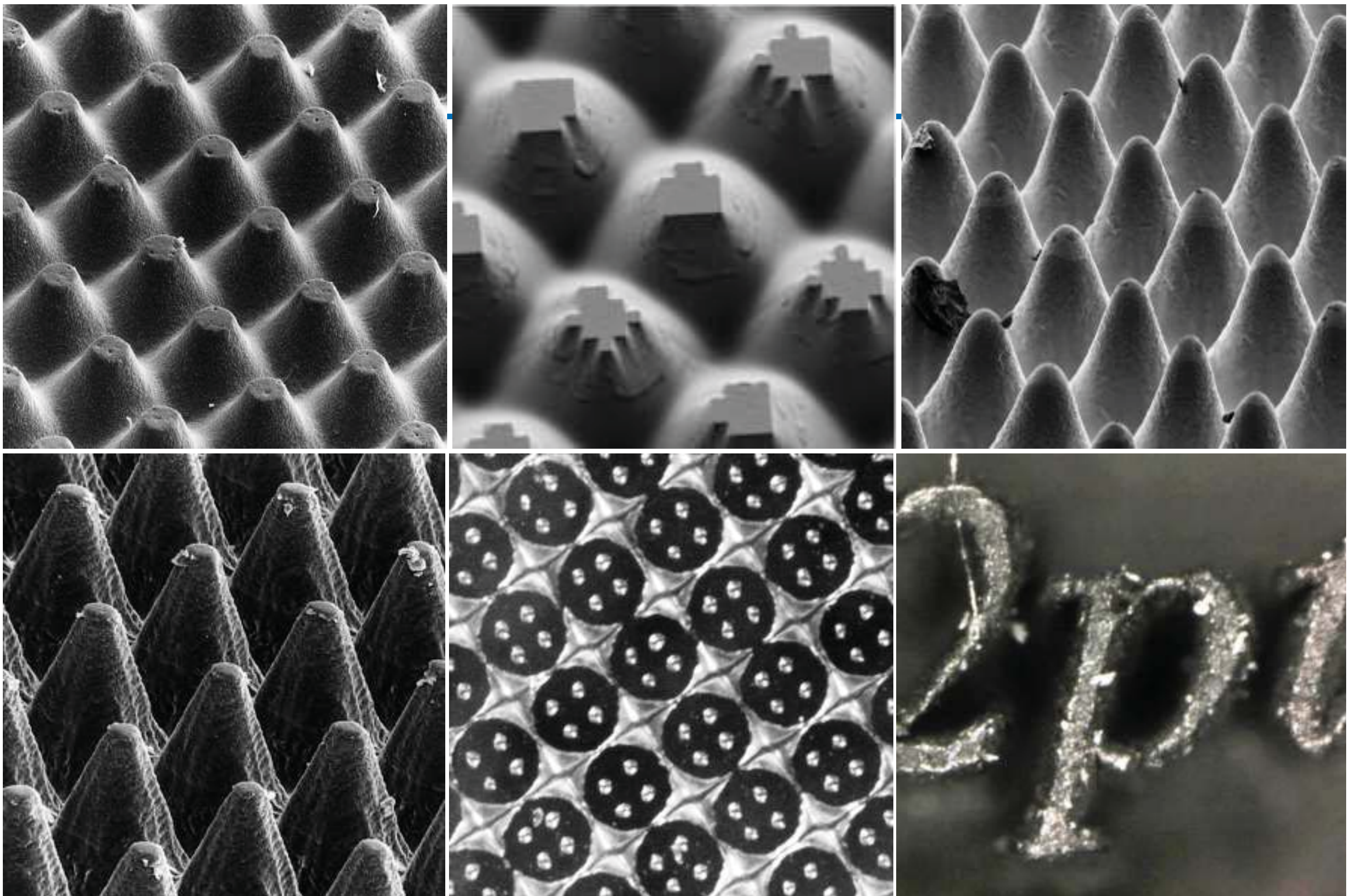

# Plates

## The plate:

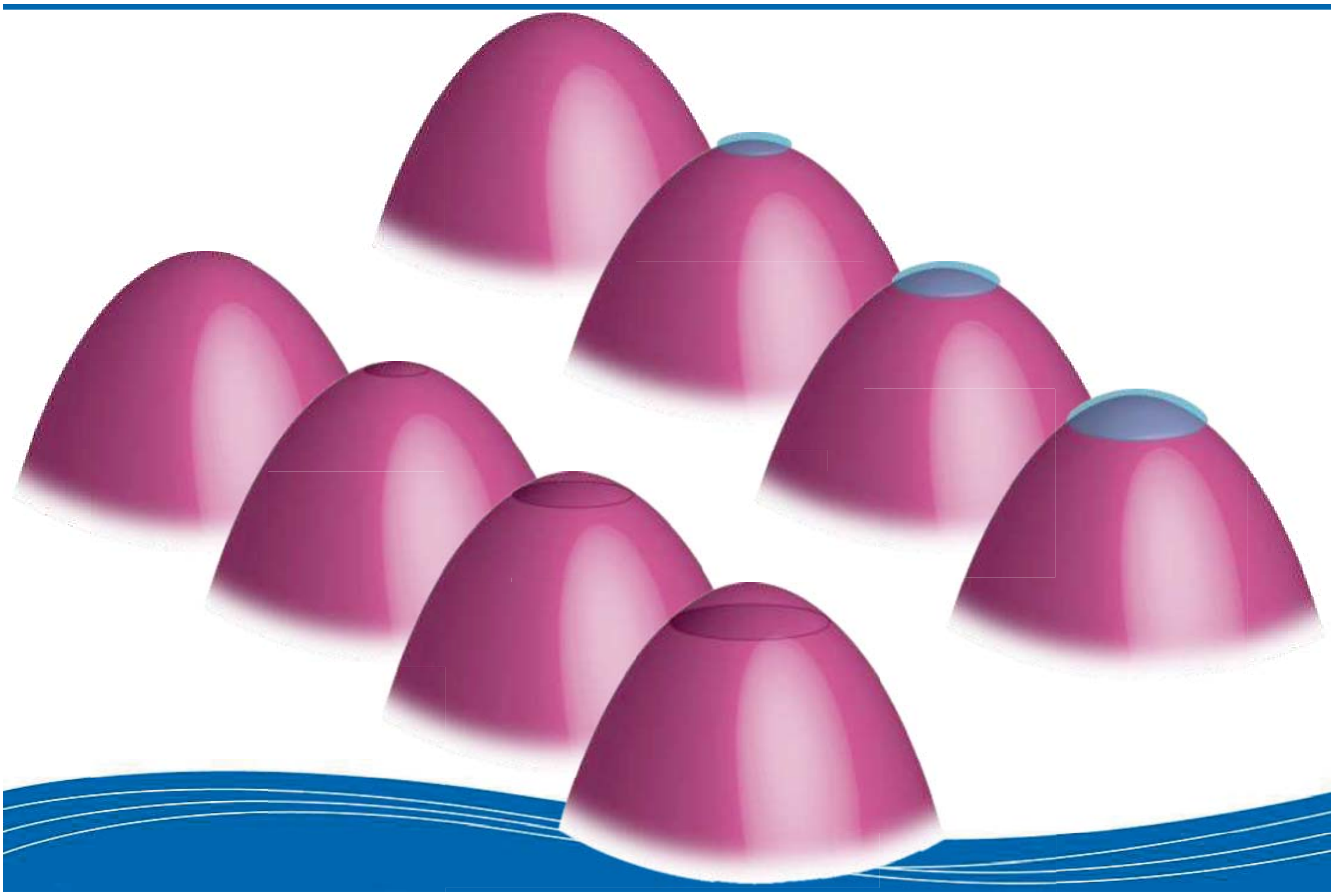
- Image carrier
- Soft Photopolymer
- UV exposure creates a raised surface from which to print
- Taped around cylinder/sleeve

Key Improvements:

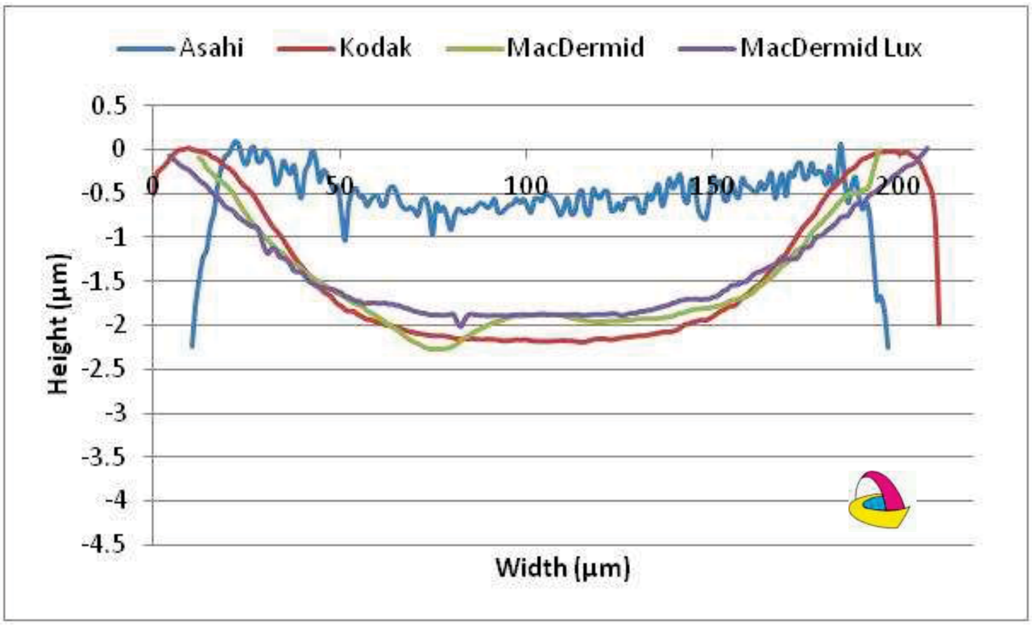
- Improvements in plate resolution
  - Various laser masking approaches
- Direct “in-the-round” exposure
- Direct Laser engraving of plate
- Improved materials
  - Elastometers, chemical resistant photopolymers



# Flat top vs round

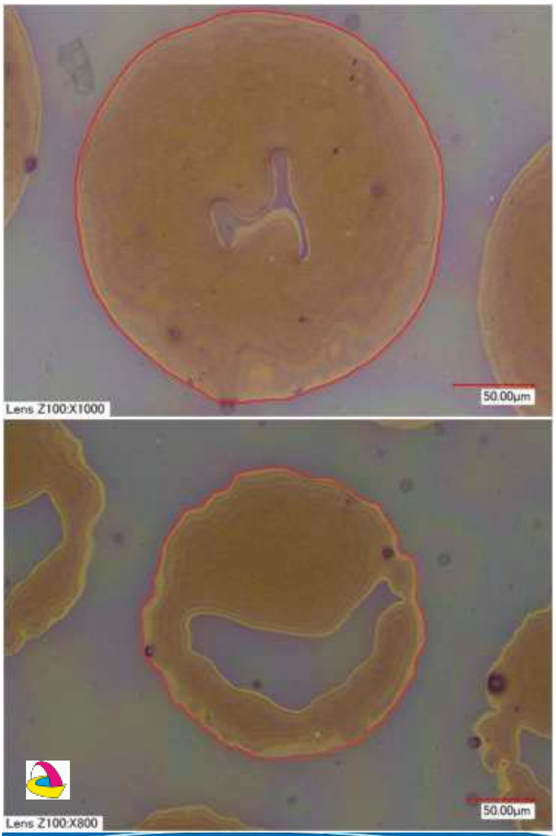


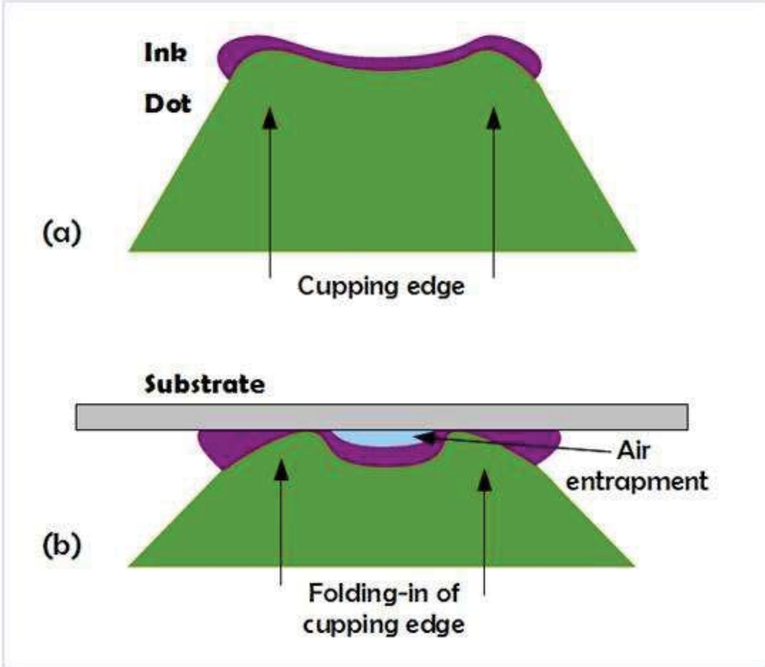
# How flat is the flat top dot?




Dot profiles at 50 % nominal area coverage and 100 lpi line ruling

# Contact Area for 70% Dot

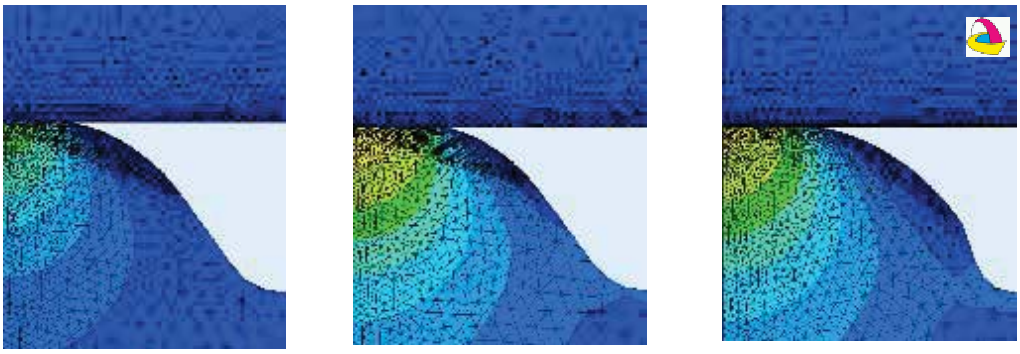



slides courtesy of Anja Hamblyn, currently writing her PhD

# Stressing the printing surface

•LAMS



•150 lpi

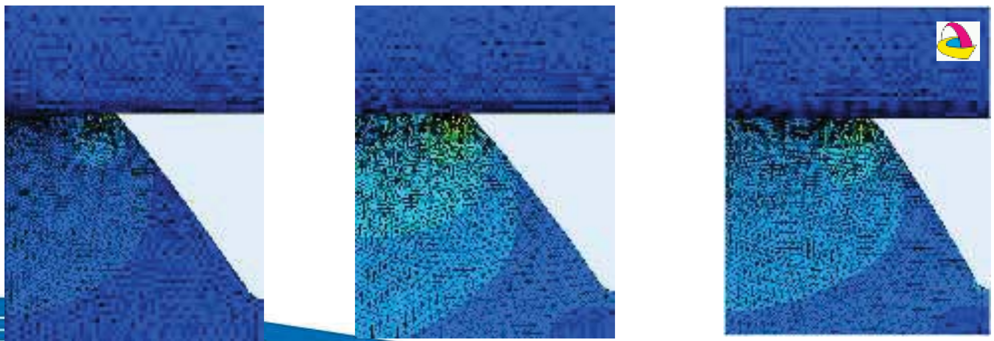
•60 l/cm

•30% with 75 µm compression

•30% with 125 µm compression

•50% with 125 µm compression

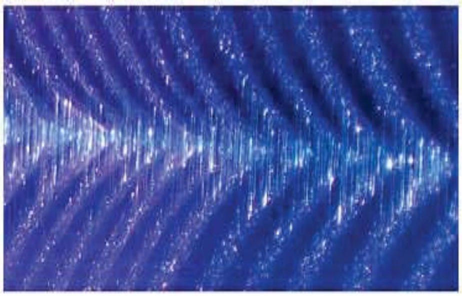
•Flat top

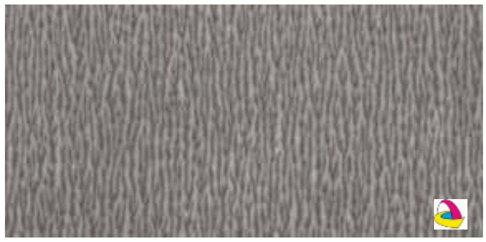


## Flexography: printing solids

An issue: viscous-extensional fingering

- Common to all R2R direct system
- Surface instabilities of front interface causes a fingering process
- Approximated  to Helle shaw cells



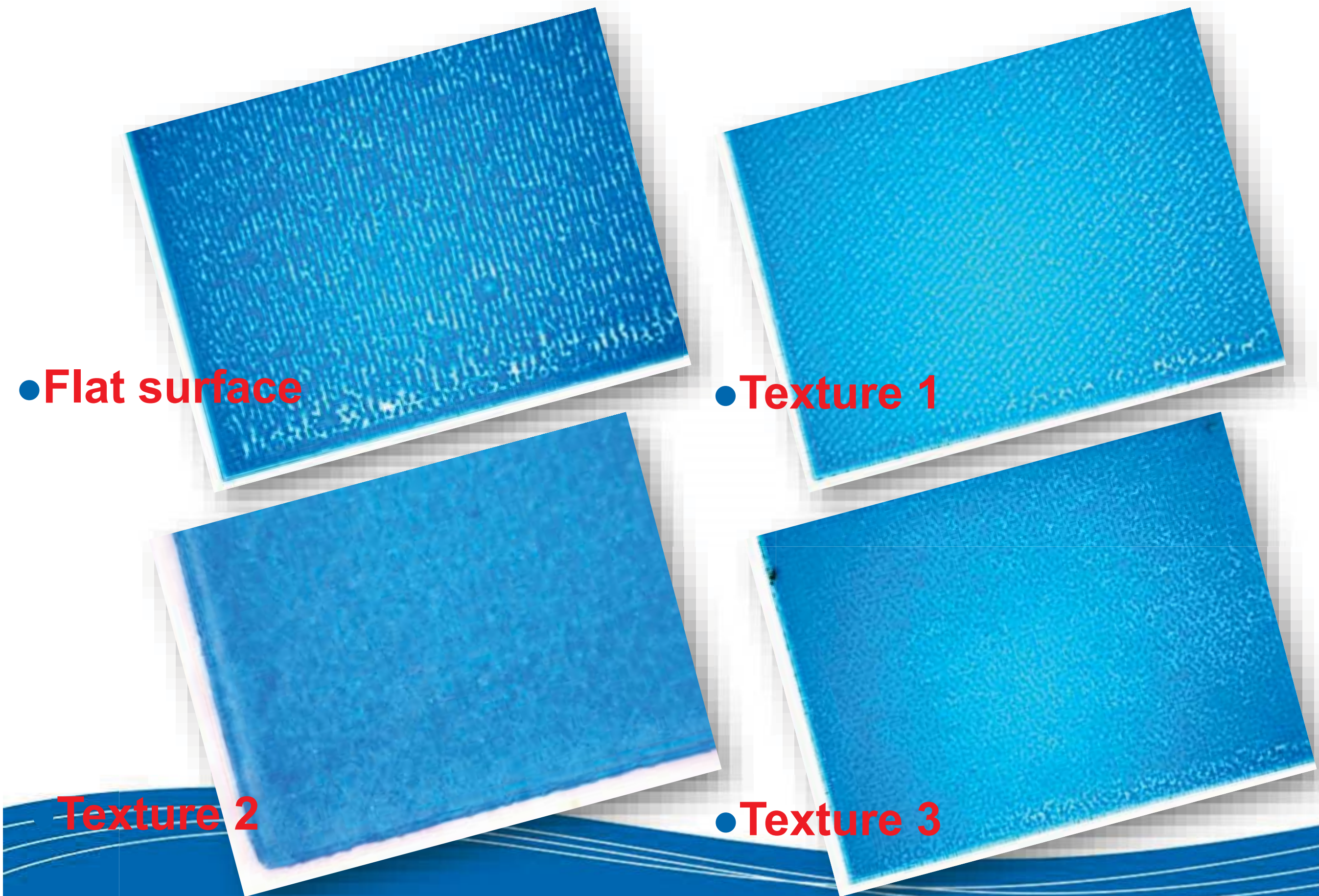


$$\lambda \propto DCa^n \longrightarrow \lambda_{ST} = \sqrt{\frac{\eta v_p h^3}{\sigma X}},$$

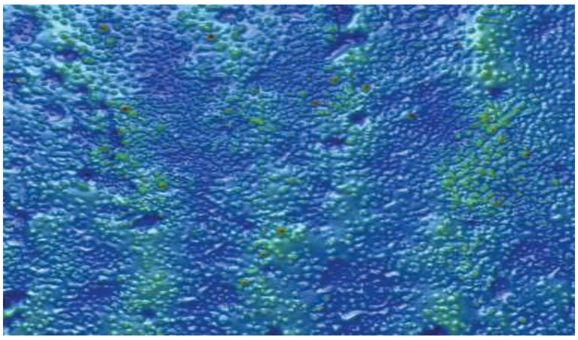
validity?

Journal of Imaging Science and Technology  55(4): 040201-1, 2011.

## Surface structure and ink transfer



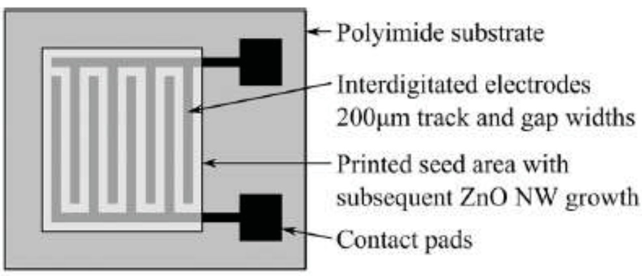
## Surface treatments

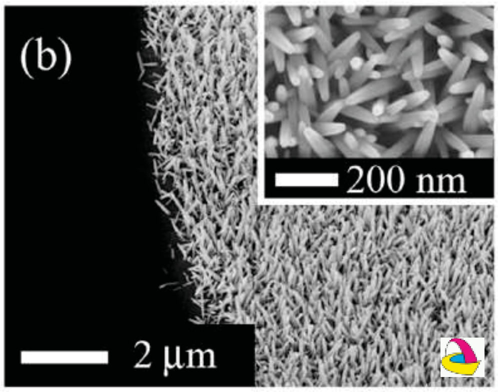


- Ozone Surface treatment for an elastometer plate: smoother final film deposit

## Flexography and solid areas: case study

- Development of Printed ZnO nanowire biosensors



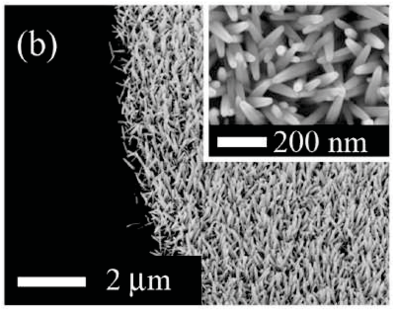




- ZnO seed layer deposited by flexography (p): high uniformity leading to excellent controlled nanowires growth
- Nanowires offer large surface areas for improved sensitivity
- Configurable sensors: oxygen, glucose,....

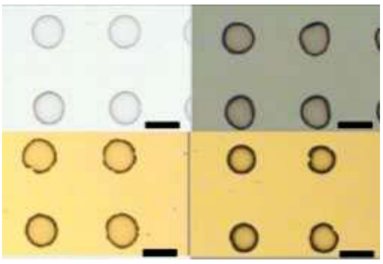
(P): patented

# Flexography and solid areas: case study

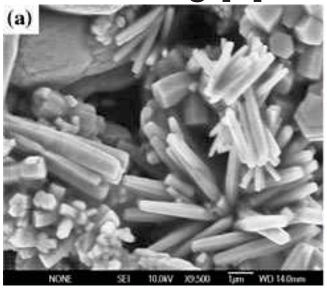
- Comparative growth tests adopting other printing methods showed lower uniform growth:




- Inkjet Printing [1]: Coffee ring effect



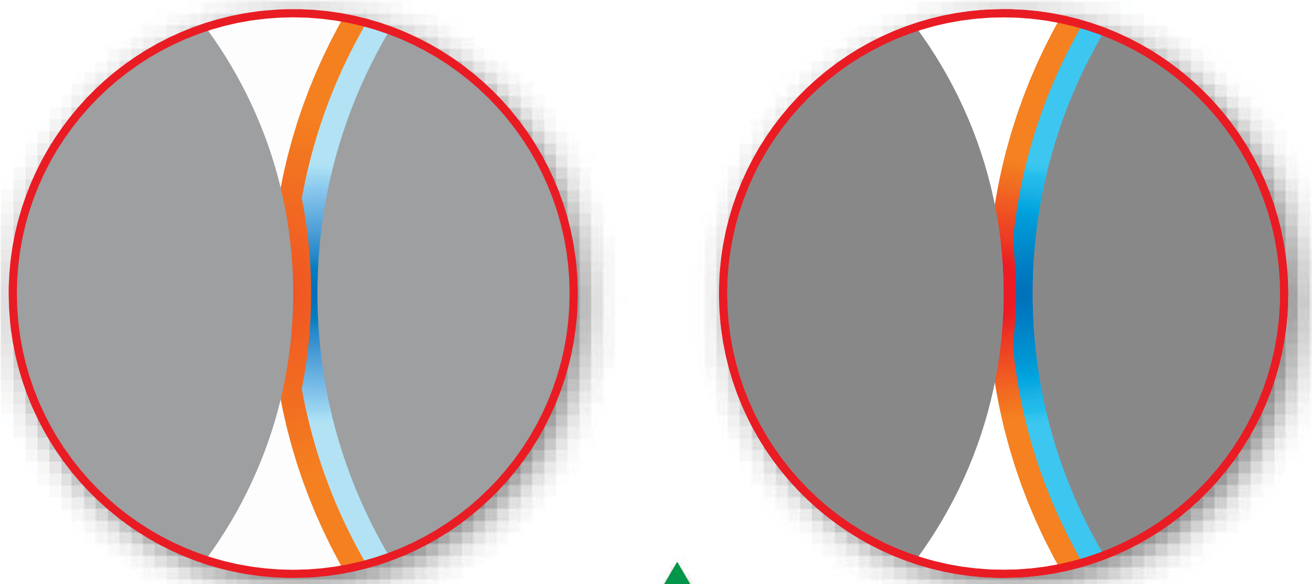
- Screen Printing [2]: clusters




1. Yen Nan Liang, boon Keng Lok, Xiao Hu
Spatially Selective Patterning of Zinc Oxide Precursor Solution by Inkjet Printing (2009)

2. G.Amin, M.O. Sandberg, A. Zainelabdin, S. Zaman, O. Nur, M. Willander
Scale-up synthesis of ZnO nanorods for printing inexpensive ZnO/polymer white light emitting diode (2012)

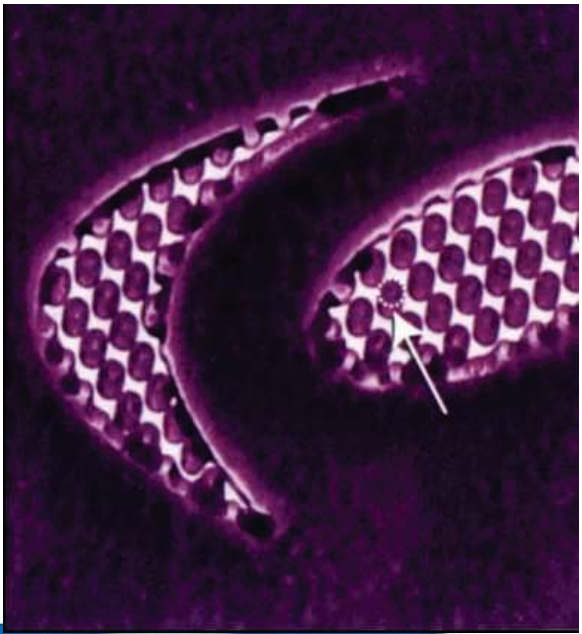
# Mounting tape and impression contact

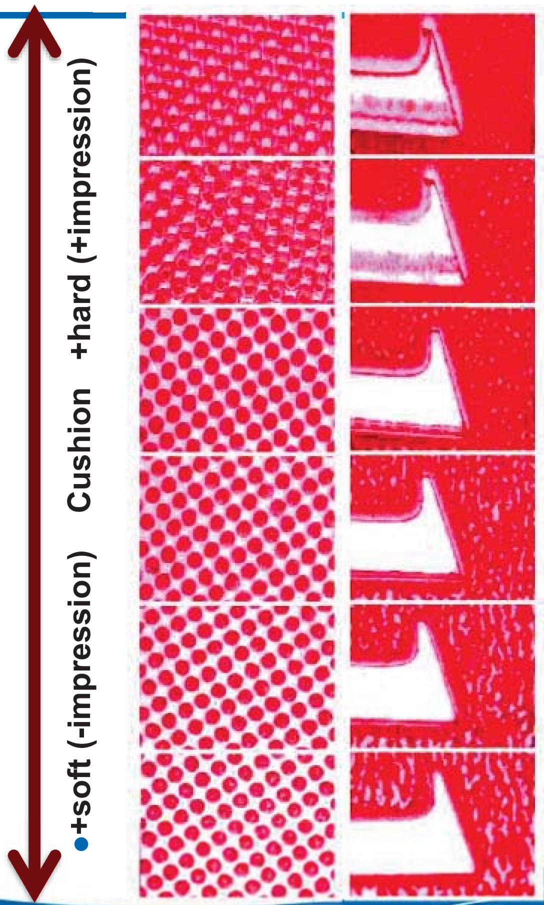


- Soft tape
- Hard tape
- Impression speed
- Plate speed

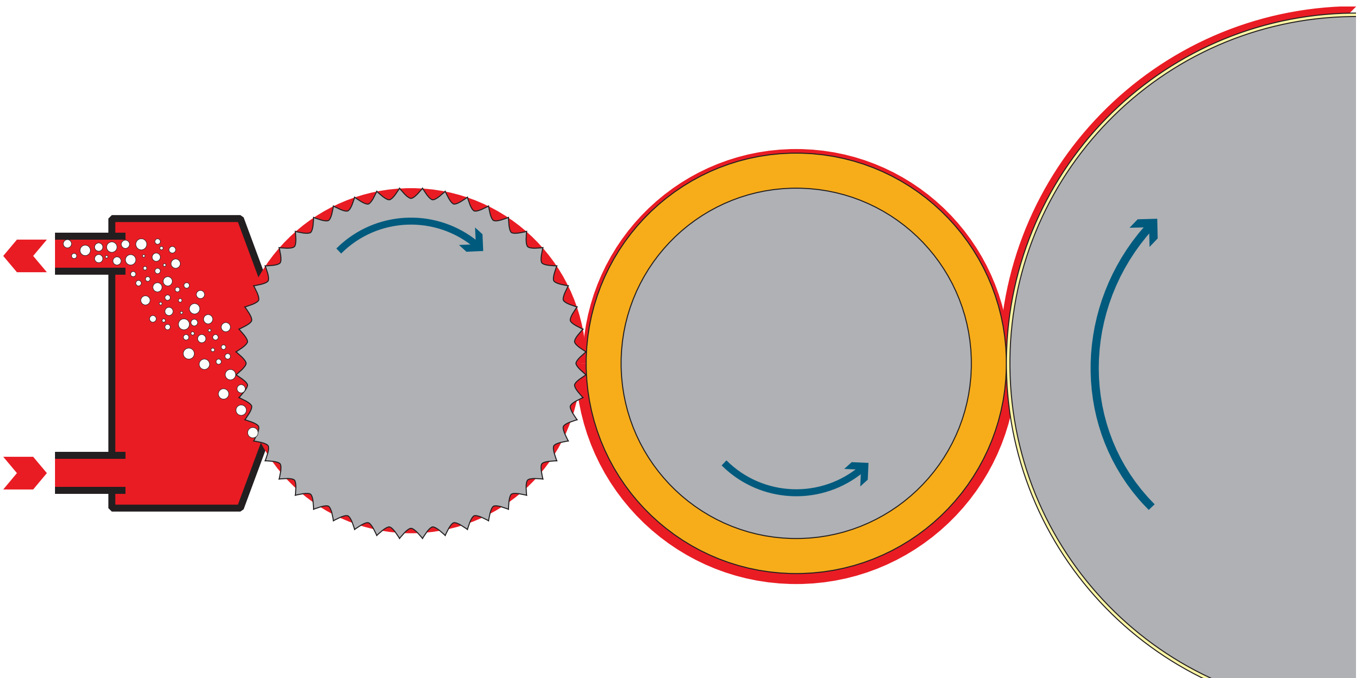
## Surface slurring

Influence on quality of transferred ink



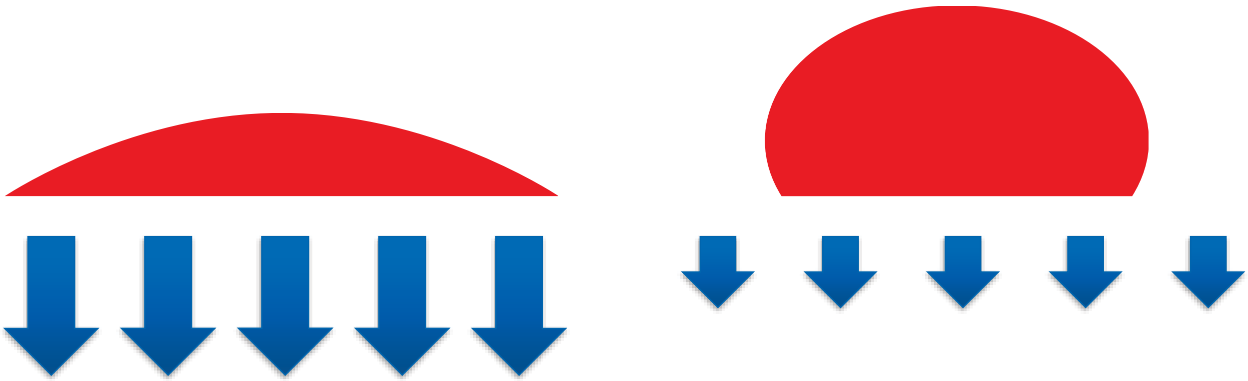



## Flexography: the components

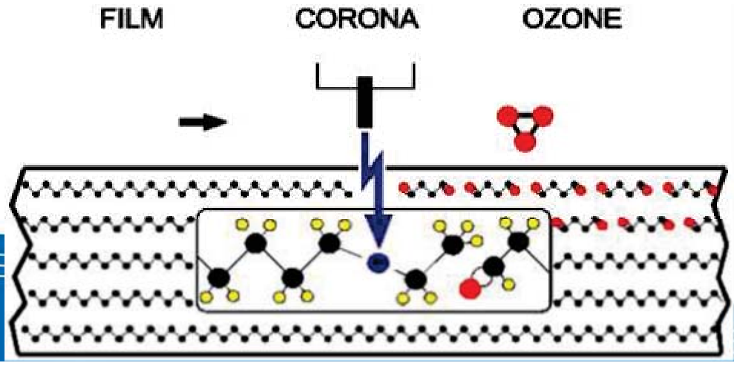


- The substrate

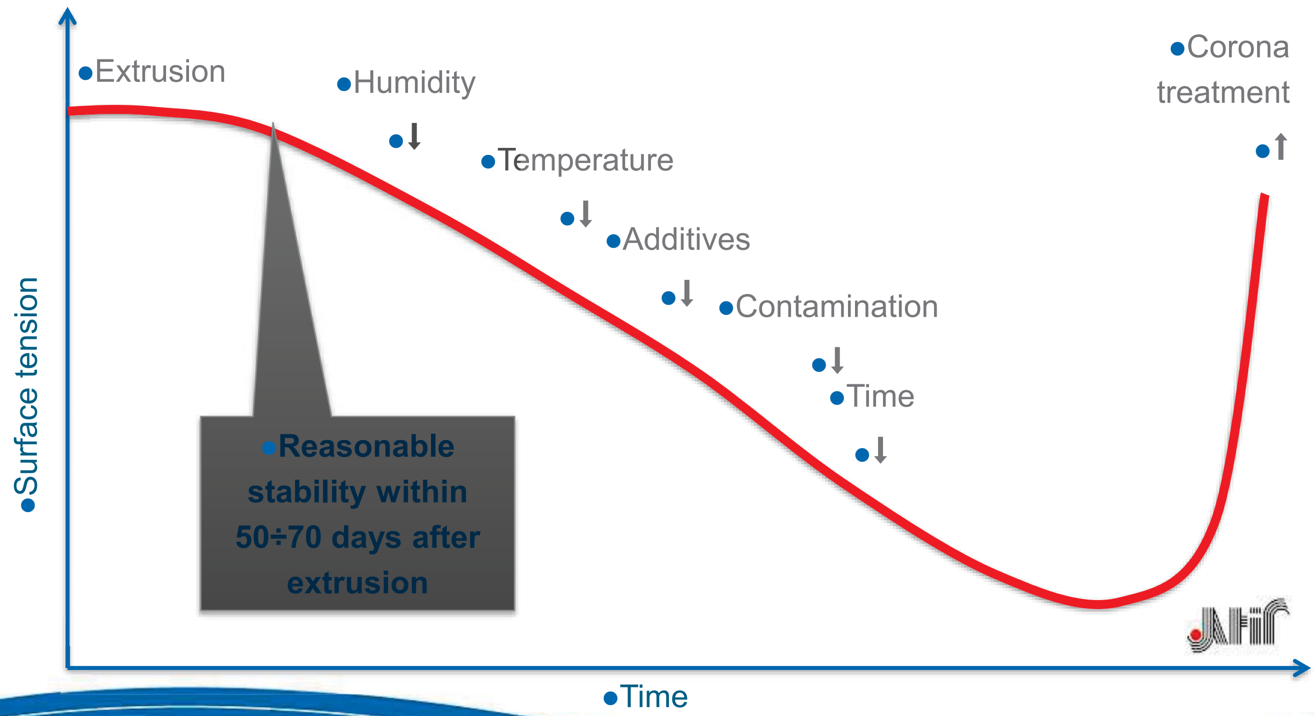

## All due to surface tension



# The corona treatment




## Effect of energy on substrate surface and factors that influence its decay



# Patterning by flexography

- Flexography:
- Ideal R2R patterning for functional materials
- High resolution
- Excellent accuracy
- Good deposition rate, smooth texture
- Fast & cheap process

- Any limitation for volume production?.. Next time

• D. Deganello et al. *Thin Solid Films*, 518: 6113–6116, 2010
• D. Deganello et al. *Thin Solid Films* , 520:2233-2237, 2012

# References


- J S Lloyd, C M Fung, D Deganello, R J Wang, T G G Maffeis, S P Lau and K S Teng, Flexographic printing-assisted fabrication of ZnO nanowire devices, Nanotechnology 24: 195602, 2013
- M. Cherrington, T.C. Claypole, D.T. Gethin, D.A. Worsley, D. Deganello, Non-contact assessment of electrical performance for rapidly sintered nanoparticle silver coatings through colorimetry, Thin Solid Films, 522:412-414, 2012
- D. Deganello, J.A. Cherry, D.T. Gethin, T.C. Claypole, Impact of metered ink volume on reel-to-reel flexographic printed conductive networks for enhanced thin film conductivity, Thin Solid Film , 520:2233-2237, 2012
- M. Cherrington, T.C. Claypole, D. Deganello, I.Mabbett, T.Watson, D.Worsley , Ultrafast near-infrared sintering of a slot-die coated nano-silver conducting ink , Journal of Materials Chemistry, 21:7562-7564, 2011
- D. Deganello, A.J. Williams, T.N. Croft, A.S. Lubansky, D.T. Gethin, T.C. Claypole, Numerical simulation of dynamic contact angle using a force based formulation, Journal of Non-Newtonian Fluid Mechanics, 166:900-907, 2011
- D. Deganello, A.J. Williams, T.N. Croft, A.S. Lubansky, D.T. Gethin, T.C. Claypole, Level set method for the modelling of liquid bridge formation and break-up, Computers & Fluids, 40:42-51, 2011
- D. Deganello, J.A. Cherry, D.T. Gethin, T.C. Claypole, Patterning of micro-scale conductive networks using reel-to-reel Flexographic Printing, Thin Solid Films, 518: 6113–6116, 2010
- Hamblyn, D. Deganello, T.C. Claypole, Surface patterning of flexo plates for improved ink transfer, IARIGAI 2012 proceedings: Advances in Printing and Media Technology, 39, pp. 153-158, 2012
- D. Deganello, J.A. Cherry, D.T. Gethin, T.C. Claypole, Roll-to-roll flexographic printing of highly accurate conductive micro-scale networks, Conference Proceedings Scientific Conference LOPE-C 2012, pp. 325-328, 2012
- Mogg, B., Claypole, T., Deganello, D. & Phillips, C. (2016). Flexographic printing of ultra-thin semiconductor polymer layers. Translational Materials Research 3(1), 015001


Welsh Centre for Printing and Coating
Thank You
Dr. Davide Deganello
d.deganello@swansea.ac.uk
SWANSEA UNIVERSITY
PRIFYSGOL ABERTAWE
School of Engineering

## 12. Screen printing

Gunter Hubner, HdM

### Biography

Since 1999 Prof. Huebner teaches at the University of Applied Science, Stuttgart Media University "Hochschule der Medien" (HdM) in Stuttgart, Germany.

From 2004 till 2014 he was the leader of the HdM study program "Print and Media Technology". Besides the entire printing technologies and printing processes his specialties in teaching are digital, screen and functional printing.

In 2006 the Institute for Applied Research (Institut für angewandte Forschung - IAF) was founded at the HdM. He took over the leadership of the IAF which is an umbrella organization over meanwhile about 30 research groups within the HdM. His own research group is called "Institute for Innovative Applications of the Printing Technologies" (IAD) and mainly deals with functional and fine line printing. Recent successful developments are printed antennae for automotive applications and screen printing of rechargeable batteries.

Before joining the HdM he worked for about 11 years with the companies AGFA Gevaert AG and DuPont de Nemours as a research and process engineer or system specialist, thus, combining mechanical and process expertise with a well-grounded knowledge in information technologies.

With his PhD-thesis about numerical simulation of ink-splitting processes in printing he 1991 obtained the Dr.-Ing.-title at the Technical University, Darmstadt, the place where he had passed his diploma in mechanical engineering, before.

### Abstract

n/a

# Screen Printing

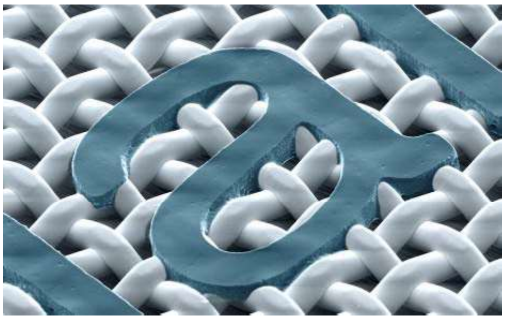


Image Source: http://ceepackaging.com/2013/04/22/gallus-becomes-a-strategic-supplier-to-schreiner-group-with-its-screen-printing-plates/

Prof. Dr.-Ing. Gunter Hübner
HOCHSCHULE DER MEDIEN

# Agenda Screen Printing

1) Introduction
2) Application
   – Graphic Arts
   – Industrial
   – Textile
3) Principles of Screen Printing Presses
4) Screen and Stencil Making
   – Screens
   – Frames
   – Stretching
   – Stencil
   – Exposure, CTS
   – Resolution
5) Printing Process

# Literature etc.

In German:
- Scheer, Hans Gerd "Siebdruck-Handbuch"1999 ISBN 3-925402-41-1
- Homann, H.J. "Lehrbuch Siebdruck Druckformherstellung" 1995
- Hahne, Peter "Innovative Drucktechnologien" 2001 ISBN 3-925402-94-2

In English:
- A.M. Peyskens, Screen/Stencil Making Technical Fundamentals Books
- John Stephens, Screen Process Printing

Dissertations
- Riemer, D.E., Ein Beitrag zur Untersuchung der physikalisch-technischen Grundlagen des Siebdruckverfahrens (Dissertation 1988) TU Berlin
- Hahne, Peter "Innovative Drucktechnologien" Dissertation 2001 als Buch erschienen ISBN 3-925402-94-2
- Anderson, John, T. "An Investigation In To The Physical Aspects Of The Screen Printing Process." Dissertation University of Wales, Swansea 1997
- Fox, Ian James "Ink Flow Within The Screen-Printing Process" Dissertation University of Wales, Swansea 2002

Organisations: ESMA, FESPA, SGIA

List of links see under www.hdm-stuttgart.de/~huebner

***magazines:***
- DER SIEBDRUCK Verlag der Siebdruck
- SIP (SIEBDRUCK INFOPOST) Verlagshaus Gruber
- Screen Printing Magazine Cincinatti, Ohio
- Specialist Printing (Magazin der ESMA) http://www.specialistprinting.com/

***Standards***
- DIN 16 609 (1981), DIN 16 610 (1984), DIN 16611 (1990)
- ISO 12637, part5 (2000), ISO 2846, part4 (2001), ISO12647 part5 (2000)

Wikipedia!! http://de.wikipedia.org/wiki/Siebdruck
(the German site is a very good compilation)





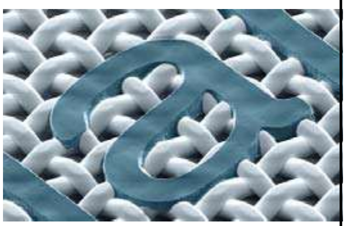
# Screen Printing is Unique

- Large variety of substrates
- High thickness (wet).
  Screen printing: 8µm to 500µm
  offset, gravure, flexo: 1µm to 3µm

Conclusions from that:
- elaborate drying
- rather opaque inks
- suitable for outdoor applications
- Great variety of inks substrates:
  - Textile, Glass, Ceramics, Plastics...
  - Adhesives, Flock, Foaming inks...
  - Electronics Thickfilm technology: conductive or resistive inks, masks

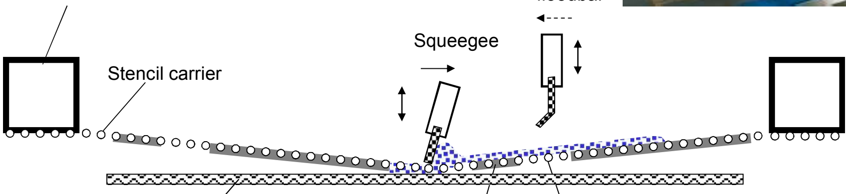
and a lot more.

S.P. on T-Shirt
several subsequent print runs with intermediate drying Source: own photograph at SGIA print workshop



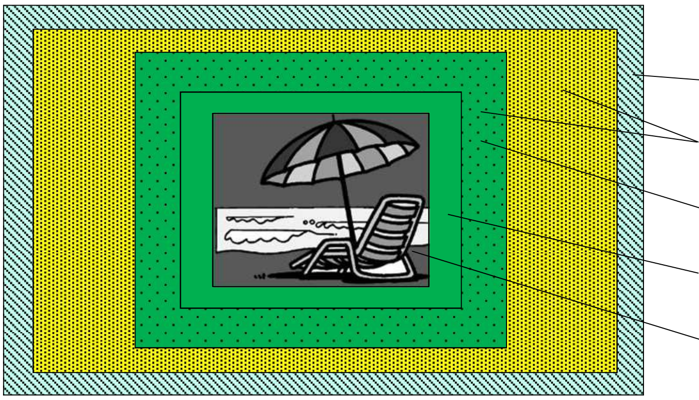
Screen Printing Form
Image Source: http://ceepackaging.com/2013/04/22/gallus-becomes-a-strategic-supplier-to-schreiner-group-with-its-screen-printing-plates/

# Basics

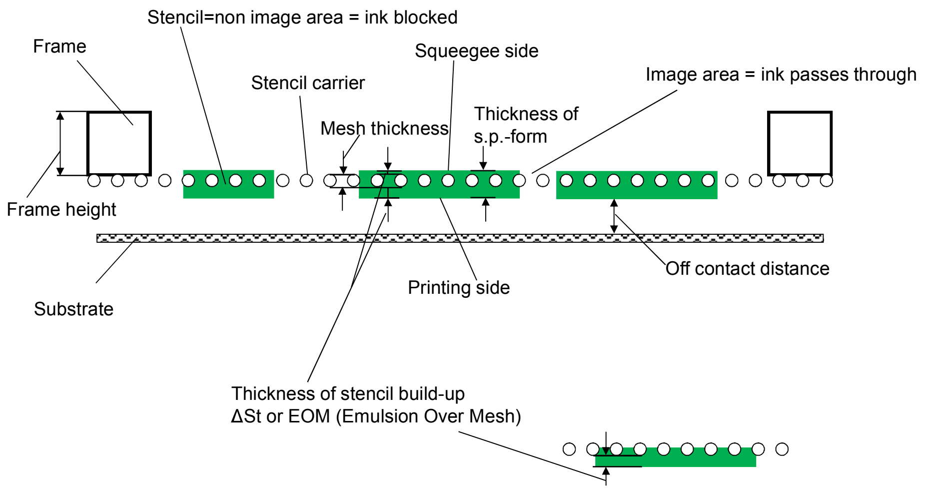





# Screen Printing Form



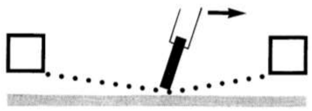
# More Screen Printing Terms



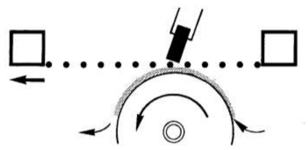




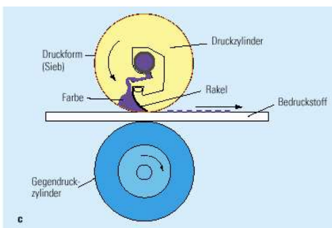

# 4 Types of Screen Printing



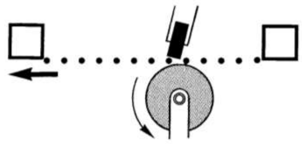
Flatbed



Flatbed-Cylinder S.P.




Rotational S.P.



In the round or 3-D objects

# Examples for 3-D


Source: www.kammann.de





# Screen printing presses

Classification regarding level of automation

- manual
- Semi automatic press
- 3/4-Automate
- Fully automated

Other printing processes like offset know fully automated presses, only.
Semi or ¾ automated presses can only found elsewhere in pad printing or digital large format printing
Lab presses mostly are semi-automatic

Screen Printing Presses

Prof. Dr.-Ing. Gunter Hübner

HOCHSCHULE DER MEDIEN

# Semi automatic press

- Substrate is manually fed and removed after print
- Squeegeeing: automatic (flooding and printing)

Thieme 1010 at Screen Printing Lab at HdM

EKRA E1 Lab Press at HdM

WCPC

Screen Printing Presses

Prof. Dr.-Ing. Gunter Hübner

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# Semi automatic Press

for flat glass 2500x5100mm


Quelle: www.fleischle.de

WCPC

# 3/4 Automatic press

- Substrate is fed manually but removed automatically (mainly fed into dryer) after print
- Squeegeeing: automatic (flooding and printing)

Thieme ¾ automatic press





# Fully automated press

- Substrate is fed automatically and removed after print
- Squeegeeing: automatic (flooding and printing)

- Examples: Multicolor lines (flatbed), “cylinders”, 3-D (in the round) printing presses

- Typically in photo voltaic “in-line”

Image: http://www.solarinternationalawards.net/shortlist2012

Screen Printing Presses

HOCHSCHULE DER MEDIEN

# Thieme 5000 Multicolor Line


Image: http://www.thieme.eu/de/thieme-5000-xl-siebdruckmaschine

WCPC

Screen Printing Presses

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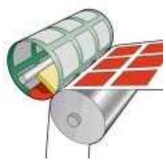
# Rotational S.P. (Labels)



Das Rotasiebdruckwerk Gallus Rotascreen als ideale Ergänzung im Kombinationsdruck für hohe Farbschichtstärken oder effektvolle Bildelemente.

TCS 250
**Hybrid Press:** Offset, Letterpress, Rotational S.P., (hot or cold) foil stamping, UV-varnish. Up to 11 units.

Source: http://www.gallus.ch

WCPC

# Rotational S.P. (Textile)

ROTASCREEN-G
Textile webs

Image source: http://www.zimmer-austria.com/



Screen Printing Presses
HOCHSCHULE DER MEDIEN

# Rotational S.P. (Textile) -2-

http://www.zimmer-austria.com/

Rotational S.P. on textile web with steam dryer

Imagesource: http://www.euro-fashion.com/firmen/diesing/produktion.htm

WCPC icmPrint cost

Screen Printing Presses

# 3-D Isimat

Körperdruckmaschine P1000

FB1008
500 kegs per h

Source: http://www.isimat.com/produkte.htm

FK 08-27 / 47
Fully automated multicolor press for beer cases 800 per h

FK 47
Two color for beer cases

Screen Printing Presses

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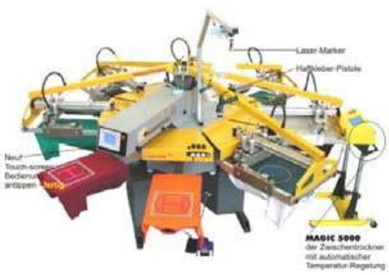
# T-Shirt machines (Carousel, “Spider”)




Fa. Hebbecker with intermediate dryer

Source: http://www.hebbecker.com/de

M&R "Terminator" up to 16 printing units, 6m diameter

Source: http://www.mrprint.com/

Printing Forme Making

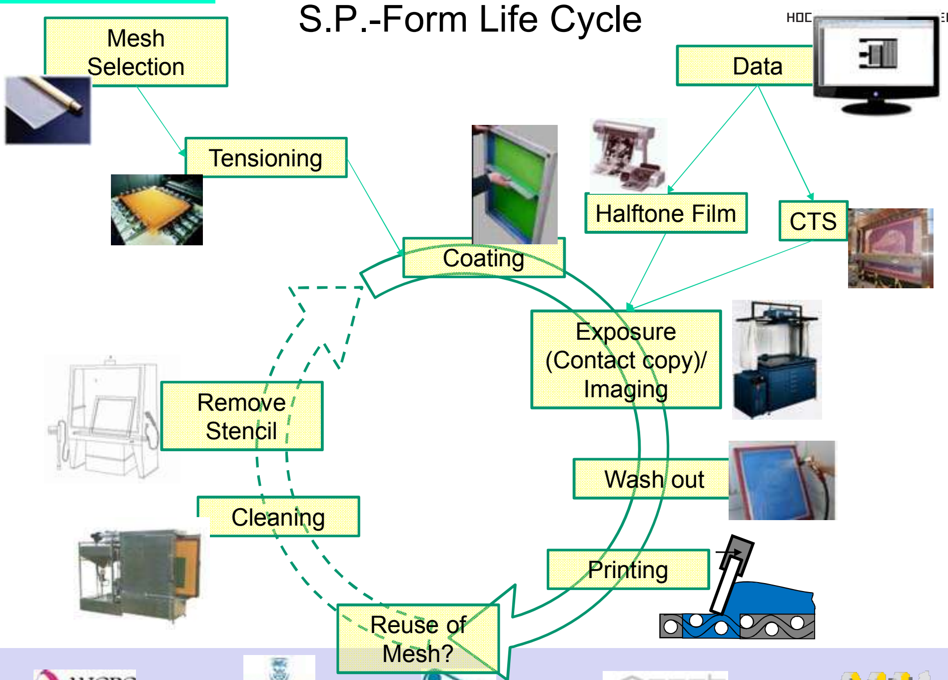
# Parts of the Printing Forme, Making of perfect printing forms:

We will look at (in the order of form-making)

- Stencil carrier (mesh)
- Frame
- Stretching of mesh and fastening to frame
- Stencil
- Quality Control, measuring techniques
- Print process

Printing Technologies Screen Printing

# S.P.-Form Life Cycle



# Mesh Materials

(fibers, fabric)

- Textil fibers
  - Natural fibers (protein based)
    - Silk (today of no importance)
  - Chemical fibers (Polymers)
    - Polyamid (Nylon)
    - Polyester
- Metallic fibers
  - Metals (nickel, nickel plated steel)
  - Stainless steel
- Specialties:
  - Core and shell (jacket) structure
    (core: high-strength, jacket: soft and well wettable)
  - Carbon fibers,
  - metalized Polyester





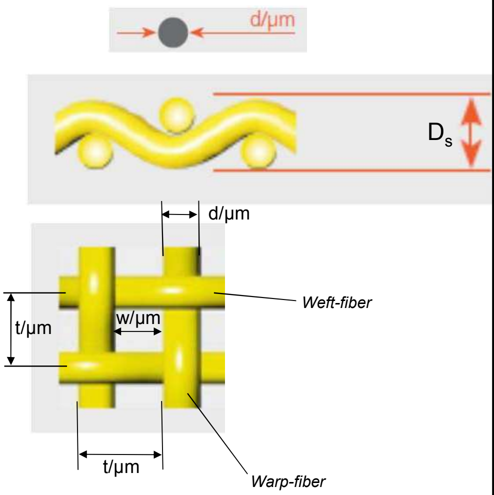
# Mesh geometry

$D_s$ = thickness of mesh in µm
d = fiber diameter in µm
t = mesh division=w+d in µm
w = width of mesh opening in µm

n = mesh count
number of fibers per cm (or inch)

Warp and weft (Kette und Schuss)
$\alpha_0$ = open mesh area percentage in %
$V_{th}$ = theoretical ink volume in cm³/cm²
Product of $\alpha_0$ times $D_s$

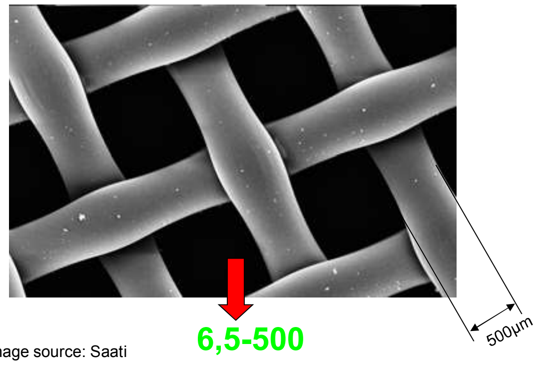
Nomenclature (mesh is named after)
n-d



# Geom. Properties of Screen Printing Meshes

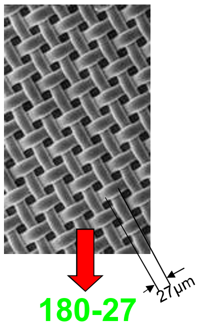
**Mesh geometry: threads per cm and thread diameter**

**coarse mesh**




**6,5-500**

**fine mesh**




**180-27**

Image source: Saati





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# Open Mesh Area Percentage

Geometry: same # of threads/fibers per cm but different thread diameter

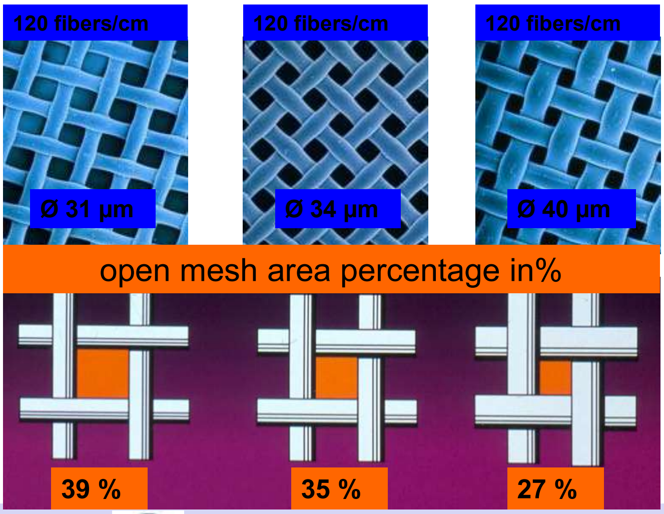


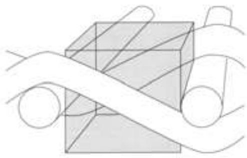

Image source: Saati

Printing Forme Making: Mesh

HOCHSCHULE DER MEDIEN

# theoretical ink volume $V_{th}$

- Very important parameter. Rules the printed layer thickness
- Is the amount of ink necessary to completely fill the mesh openings and ready to be transferred to the substrate
- Value typically provided by mesh manufacturer
- Unit: $cm^3/m^2$
- In first approximation is the number of $V_{th}$ in $cm^3/m^2$ directly corresponding to the layer thickness in µm



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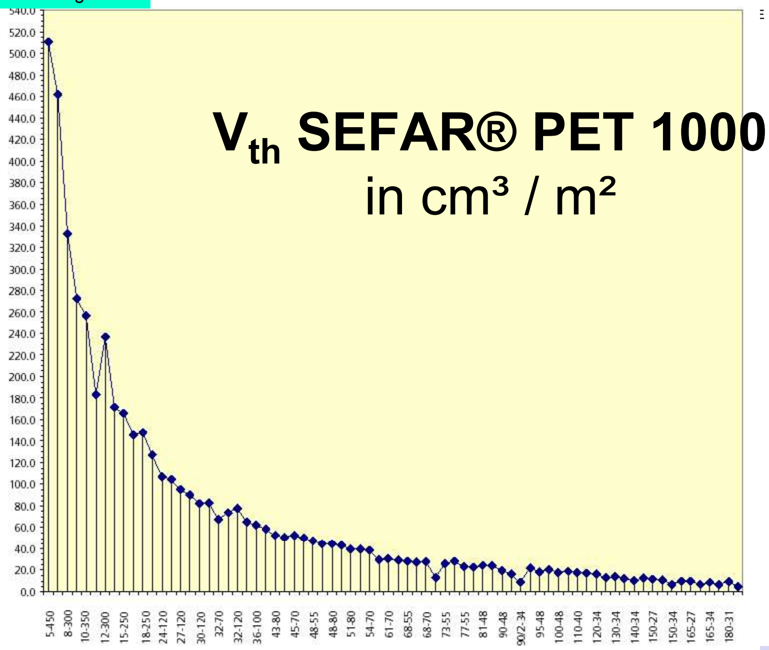
Printing Forme Making: Mesh

HOCHSCHULE DER MEDIEN




WCPC | Swansea University | icmPrint | cost | AcTinPak

# Frame Materials

| Material | Modulus of Elasticity | Density | remarks |
|---|---|---|---|
| Aluminium | 71000 N/mm² | 2.7g/cm³ | no corrosion |
| Steel | 210000 N/mm² | 7.8g/cm³ | corrosivie |
| V2A Stahl | 195000 N/mm² | 7.1g/cm³ | no corrosion |
| Wood | ca.15000 N/mm² | <0.8g/cm³ | no longer used |

Image source: www.hurtz.de



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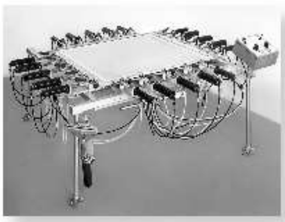
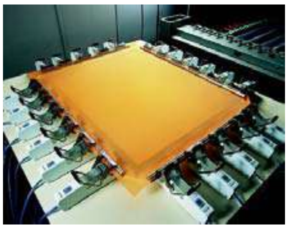
# Stretching devices are used for Tensioning

Harlacher AG
H24-D
mechanical
stretching dev.



Harlacher AG
H34
pneumatic
stretching dev.



Saati

pneumatic
stretching dev.

1. Mechanical stretching devices
2. Pneumatic stretching devices (more precise!)

After stretching mesh is attached to frame by
2-component adhesive or UV-hardening glue

Printing Forme Making: Stencil

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# Stencil Making

- manually
  - For arts (serigraphy)
- Photo mechanical
  - Using light sensitive material films (Capillarfilm, Direct film, Indirect film)
  - Coating with liquid photo sensitive emulsion,
    - with automatic coating machine or manually
  - Exposure with graphic films
    - Contact copying or projection
- Filmless imaging
  - Computer To Screen

pouring liquid emulsion in scoop coater

Moving upwards slightly tilted

Wet in wet coating

Image source: Andreas Rombold „siebdruck und serigraphie"

WCPC

Printing Forme Making: Stencil

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# Automatic Coating Machine at HdM

WCPC

# Films for Contact Copying

Optical Density >3

- Conventional Graphic Arts Silver Halide film
  - Needs chemical exposure
  - Resolution: Silver grain ca. 1µm
- Chrome Master
  - Chip processing, needs chemical etching
  - Resolution: ca. 0.05µm
- Film Inkjet „plotted“
  - Specialty substrate needed
  - Resolution 1400dpi (20µm)
- LADF (Laser Ablation Dry Film)
  - Material from Flint Group
  - Resolution >2400dpi (10µm)





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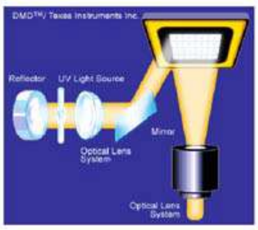
# CTS Computer to Screen

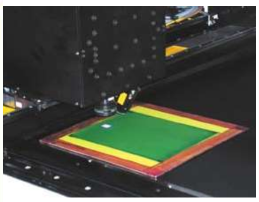
Systems for filmless form making:

1. Inkjet (masking)
2. UV-Direct exposure
   - DMD (Digital Micromirror Device) Texas Instruments
   - Laser (Kammann, Signtronic, Lüscher)

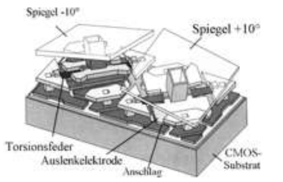
Lüscher Jet Sreen

Texas Instruments DMD Technique



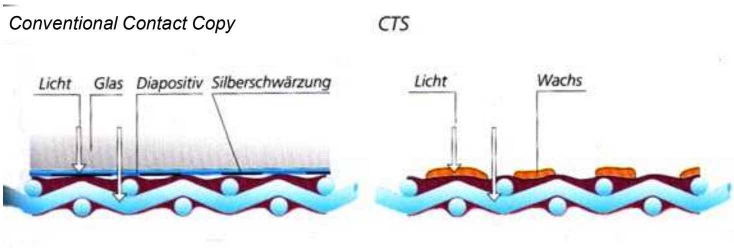
KIWO Screensetter unsing DMD




Micromirror two positions

Imagesource: http://www.science-vision.at/dataprojectors.html

# Comparison Conventional Contact Copy vs CTS Inkjet masking technique




*Glasscheibe und Film bei der traditionellen Kopie absorbieren bis zu 30% Licht. Lufteinschlüße zwischen Film und Schicht sind fast unvermeidlich, wohingegen bei CTS ein absoluter Kontakt zwischen Wachs und Schicht vorhanden ist.*

Image from serigraphis 2-3/98 p49



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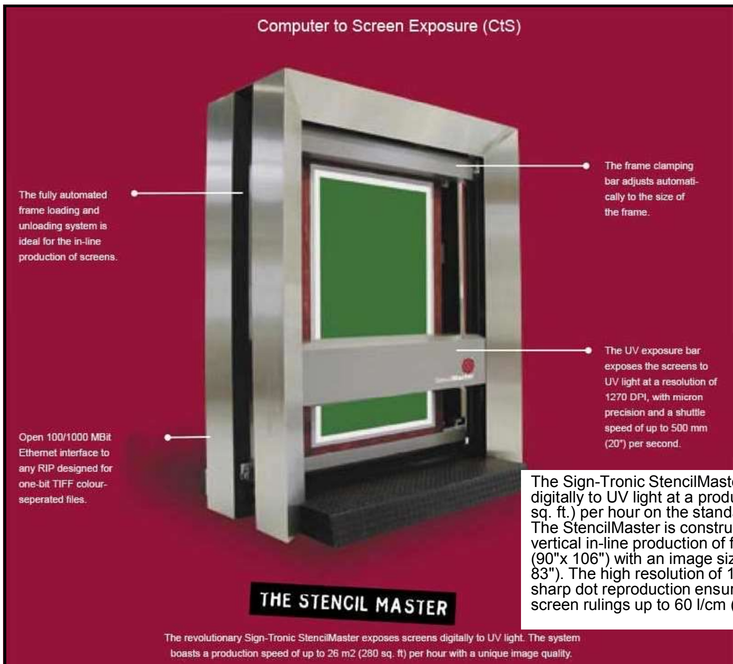



## Signtronic UV Direct-exposure using DLP from Texas Instruments

The Sign-Tronic StencilMaster 1621 exposes screens digitally to UV light at a production speed up to 26 m² (280 sq. ft.) per hour on the standard emulsions available today. The StencilMaster is constructed for the fully automated vertical in-line production of frames up to 2300 x 2700 mm. (90"x 106") with an image size of 1600 x 2100 mm. (63" x 83"). The high resolution of 1270 DPI, micron precision and sharp dot reproduction ensure a unique image quality with screen rulings up to 60 l/cm (150 lpi).

http://www.sign-tronic.ch/

# Signtronic Stencil Master

Own Photo
FESPA 2007



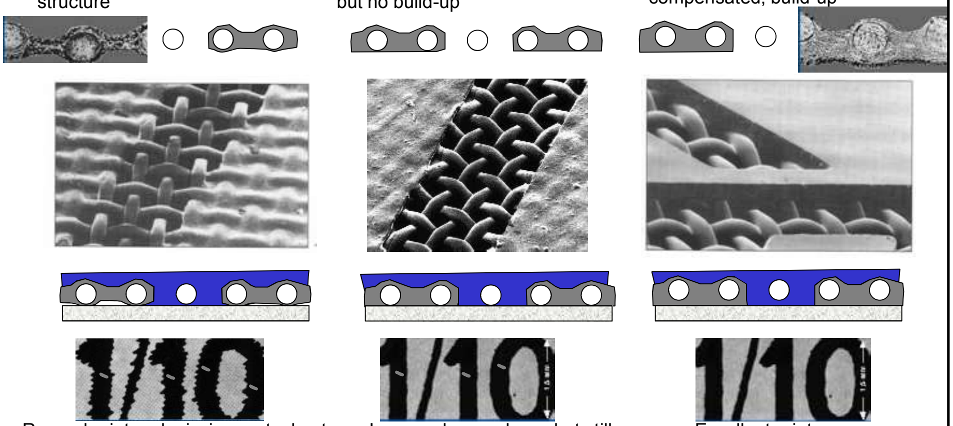


# World largest CTS-device

- Signtronic Stencilmaster at Keck in Ulm
- Max. frame format: 4'600 x 11'000 mm
- Max. Image format: 4’100 x 9'000 mm
- Average frame weight >300 kg. (!)
- Resolution :
  - Large frames1270 x 1270 dpi.
  - Smaller frmes up to 2400 x 2400 dpi possible
- CTS weight: 13 tons (!)
- Imaging Speed: 2.5 hrs for 40 m² (68 $cm^{-1}$ mesh, 2:2 coating, Diazo-Monomer-Emulsion, EOM 10µm).
- Sorce: Press release Signtronic 8/2009

# Stencil making
## important: thickness of stencil build-up

Poor compensation of mesh structure | Mesh structure compensated, but no build-up | Mesh structure compensated, build-up




Ragged print and missing parts due to blocking by threads | Improved raggedness but still missing parts because threads are in contact with substrate | Excellent print

Images schematic!!

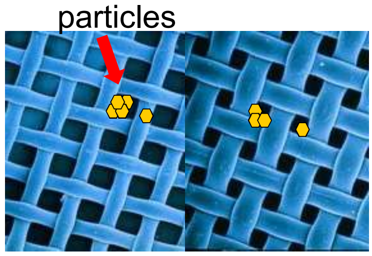
Source: http://www.silkscreenhistory.com/einfuer/einfuer.html and Hohmann "Lehrbuch Siebdruck Druckformherstellung"





# Some Major Screen and Mesh Parameters:

- Mesh count
- theoretical ink volume
- Pigment size content in ink
  - Mesh opening should be 3 - 4 x larger than biggest pigment contained in ink
- Resolution
  - Rule of thumb: smallest dot should have minimum diameter of two fibers plus mesh opening!



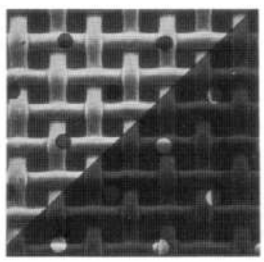
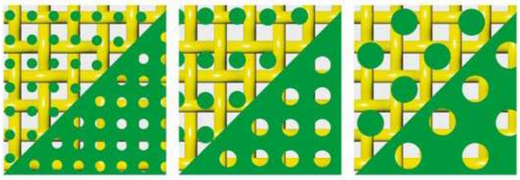



Image source: Saati and Rombold

# Screen Printing Resolution

- Due to the fact that the stencil used in screen printing must strongly adhere to the underlying mesh and according to the rule that the smallest element should be at least twice the thread diameter plus the mesh opening the smallest printable elements can be estimated easily. Similarly valid for fine lines.



*dots fairly too small* *dots still too small* *good minimal size*

- Polyester: finest mesh (ca 200 threads per cm and 27 microns thread diameter) the finest well printable structure roughly is around 80µm.
- Stainless: finest mesh (ca 300 threads per cm and 13 microns thread diameter) the finest well printable structure roughly is around 45µm.
- Goal: 30µm (20µm)

Image source: Sefar Handbook of screen-printing







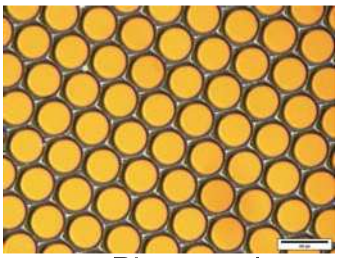
# Non Woven Stencil Carriers

Galvano-plastic fabrication

Company Stork Graphics (NL) funnel shaped opening towards printing side

- Rotamesh (for cylindrical sieve)
- Planomesh (flatbed)

Source: Google Images



Planomesh

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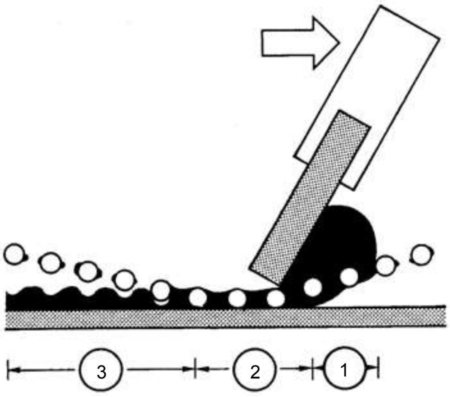
# Three Phases of Printing Process




1=Filling of mesh openings with ink

2=Contactphase

3=snap off

Some more important parameters:
- Snap off distance
- Squeegee angle
- Squeegee tip
- Squeegee pressure
- Squeegeeing speed

And many more…

Source: Scheer

WCPC · Swansea University · icmPrint · cost · AcTinPak



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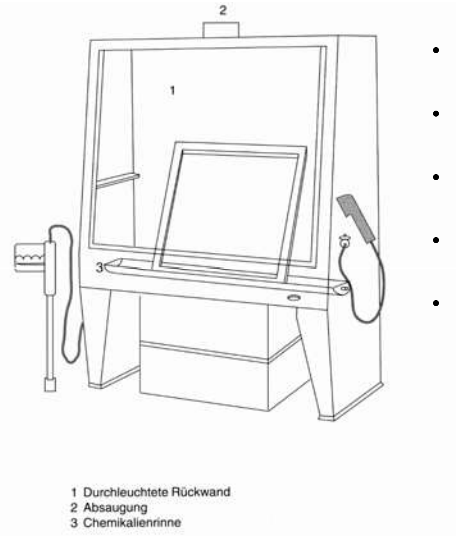
# After Print Job: stencil removal




- Manually or automated
- Wash out ink
- Pre rinse with water
- Apply stencil removal liquid
- Wash out
  - Water jet
  - High pressure brush

WCPC · Swansea University · icmPrint · cost · AcTinPak

# Screen Printing

In former times!

Thank you for your attention and enjoy the rest of the program!

## 13. Extrusion coated materials, surface treatment techniques, films and foils

### Barrier properties

Johanna Lahti, Tampere University of Technology

### Biography

Dr. Johanna Lahti has a doctoral degree in Paper Converting and Packaging Technology from Tampere University of Technology (2005). She is currently Senior Research Fellow and Project Manager in Paper Converting and Packaging Technology research group at Tampere University of Technology (TUT). She started her career (1999) by studying dispersion coatings and usage of pigment particles to improve barrier properties. In 2000 she started her doctoral thesis research about digital printing of extrusion coated packaging materials. In the research focus was on improving printability of polymeric surfaces by surface treatment. Since 2005 Dr. Lahti has participated in several national and international projects. Research areas include different topics relating to paper technology, paper converting and packaging technology. These include e.g. (co)extrusion coating, dispersion coating, surface treatments (e.g. plasma, corona, flame), nanoscale thin coatings (e.g. plasma deposition, ALD), substrates for packaging materials (plastic films, fiber-based substrates, coated materials, etc.), and printing technology. She has also coordinated one large-scale FP7 project (PlasmaNice, 2008-2012) with topic Atmospheric Plasmas for Nanoscale Industrial Surface Processing. Currently she is mainly working in FP7 project NanoMend (2012-2015). Nanomend aims to pioneer novel technologies for in-line detection, cleaning and repair of micro and nano scale defects for thin films coated on large area substrates. Examples include thin films used in the production of packaging materials, flexible solar panels, lighting and indoor and outdoor digital signage and displays. Since 2000 Dr. Lahti has supervised several thesis works and produced several conference papers, articles and presentations in the field of paper converting and packaging technology.

### Abstract

n/a


TAMPERE UNIVERSITY OF TECHNOLOGY

TAMPERE UNIVERSITY OF TECHNOLOGY

”Printing of Functional Applications – Summer School”

# *“Introduction to fibre-based and polymeric materials, their processing methods and products”*

Swansea University, Swansea, UK
July 12, 2016

**Dr. Johanna Lahti**
Senior Research Fellow
Tampere University of Technology (Finland)

Department of Materials Science
Paper Converting and Packaging Technology

# Content of the lectures

- **Introduction**
- **Part 1: Production technologies of fibre-based and polymeric materials**
  - Extrusion coating, coextrusion
  - Lamination techniques
  - Cast film and blown film technology
- **Part 2: Fibre-based and polymeric substrates** and some examples of applications
- **Part 3: Barrier properties**
- **Part 4: Surface treatments** and nanoscale R2R surface modification and novel thin film technologies



# Tampere (Finland)

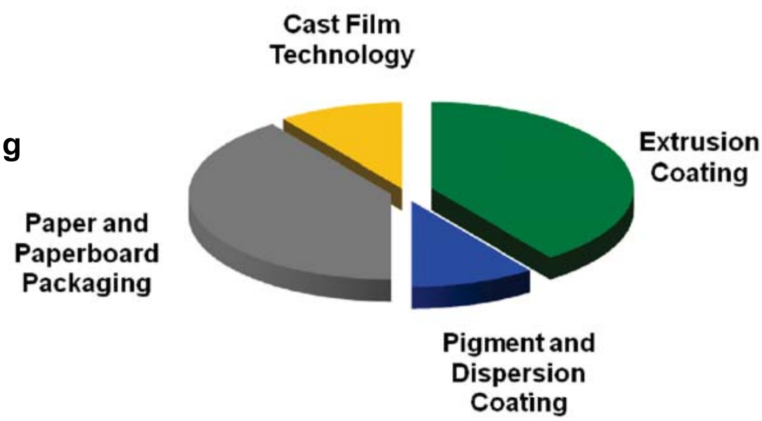
- The third largest city in Finland with over 200,000 inhabitants. One of Finland's fastest growing urban centres and, according to a survey, the most popular city to live and study in.
- Two universities: **Tampere University of Technology** and the **University of Tampere** with ~30,000 students in total.

# Tampere University of Technology (TUT)

- Established in 1965
- Started operating in the form of a foundation in 2010
- The second largest university of technology in Finland
- ~9200 students (2014)
- Personnel ~1713 (2015)
- Collaborates with 250 universities around the world



# Paper Converting and Packaging Technology research group

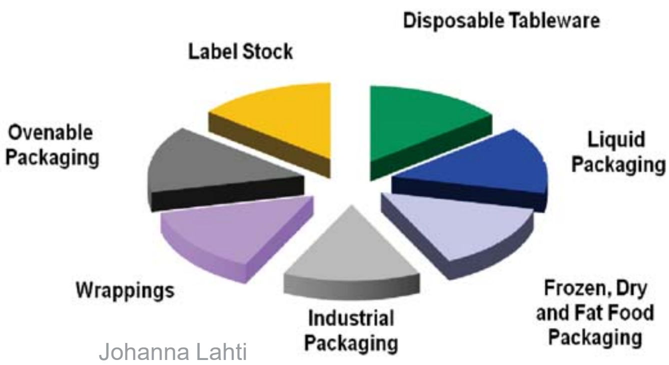



## R&D Focuses on

- Paper and paperboard converting technology and materials
- Packaging technology and materials
- End products

## R&D Customers

- Paper industry
- Paper and paperboard converting industry
- Packaging industry
- Polymer manufacturers



## PAPER CONVERTING AND PACKAGING TECHNOLOGY

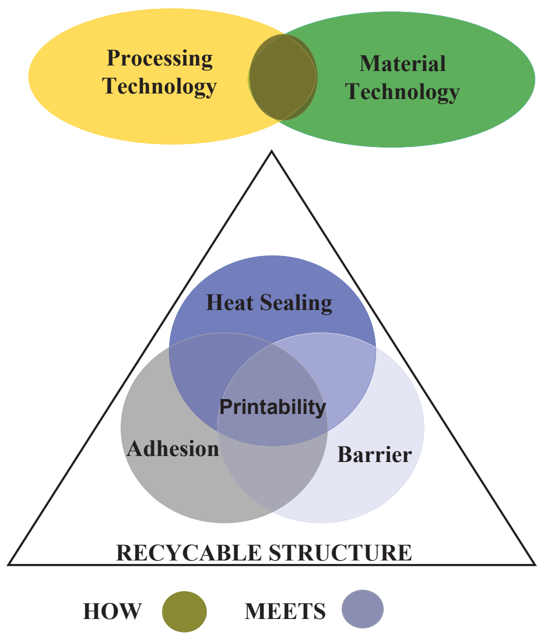
### CO-OPERATION WITH

- Paper Converting Industry
- Packaging Industry
- Paper and Plastics Chemical Industry
- Research Institutes / Research Centres
- Pulp and Paper Industry
- Paper Machine Industry
- Engineering Offices
- Chemical industry

TAMPERE UNIVERSITY OF TECHNOLOGY

## R&D Objectives

- Improve processing and handling
- Enhance barrier properties
- Improve end-use properties
- Discover environmentally friendly processing methods and materials




## Current R&D projects are dealing with

- High barrier coextruded coatings and films
- High barrier paper and paperboard packages
- Biodegradable polymer coatings & biobased materials
- Pre- and post-surface treatments of fiber-based materials and their coatings (flame, corona, plasma)
- Nanoscale thin films and coatings (ALD, LFS, plasma deposition)

TAMPERE UNIVERSITY OF TECHNOLOGY

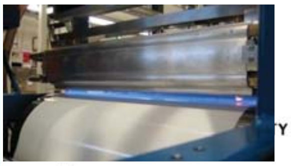
## Our facilities

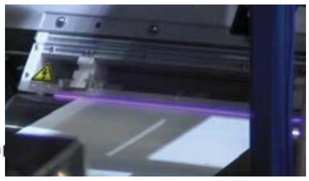
YouTube: “NanoMEND pilot line”

### Versatile Roll-to-Roll pilot lines

- Production of packaging materials via
  - (co)extrusion coating and lamination
  - dispersion coating
  - cast film (co)extrusion
  - Max. speed ~400 m/min, max. width 550 mm

Coatings, treatments and functionalisation of surfaces, e.g. plasma, IR, UV, LFS




### Well-equipped laboratory for packaging materials and packages

- Barrier properties (WVTR, OTR, CO2, grease)
- Sealability & hot tack
- Surface energy
- Adhesion etc. etc.

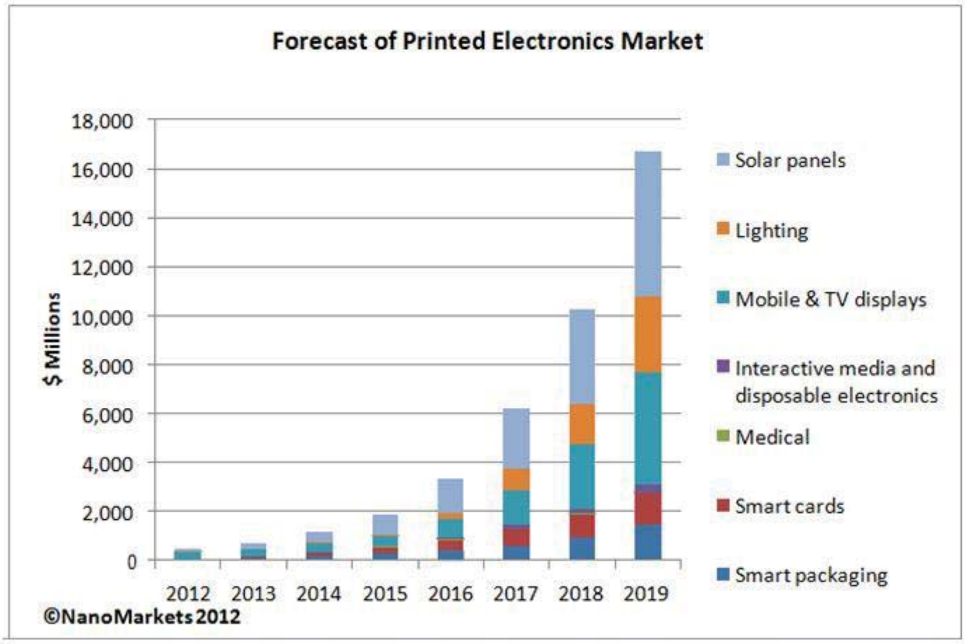




# Part 1: Production technologies of fibre-based and polymeric materials

- Extrusion coating, coextrusion
- Lamination techniques
- Cast film and blown film technology

# Flexible, printed electronics



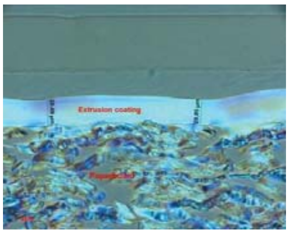

Printed Electronics Market Forecast from NanoMarkets

Sensors, power, communications, lighting, photovoltaics, “stretchable electronics, logic and memory, thin film sensors, wearable biomedical sensors and imagers, displays, consumer packaging, toxic and structural sensors. smart packaging and embedded electronics, RFID,….

http://www.semi.org/en/node/48211



# Introduction 1(2)



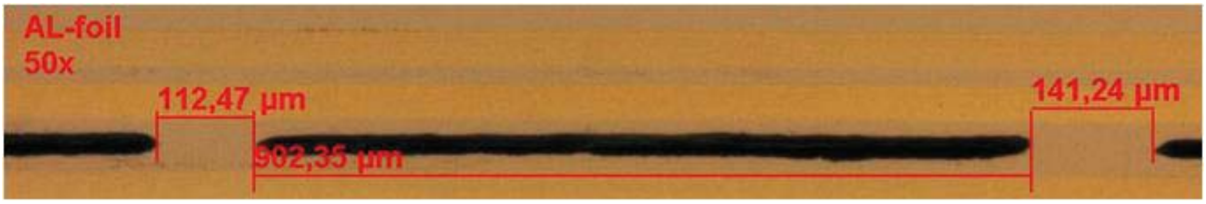
- Extrusion coated materials, plastic films and polymers are used in various applications – **packages** and **packaging materials** and **printable electronics etc**. These include **flexible packages** (such as wrappings, pouches and bags), **liquid packages** (folding cartons, bottles etc.), **rigid packages** (cups, trays, etc.) and **other products like labels.**
- In packages, the most important function of a packaging material is to shield the product inside the package, i.e. barrier.
- Depending on the polymer type, extrusion coating or plastic film generally give a barrier against water, water vapor, aroma, grease, oxygen, etc.
- However, some materials and applications require improved barrier properties. Furthermore, new functionalities are targeted with materials.

→ One way to improve barrier or create new functionalities is surface modification or nanoscale thin layer coatings

- ✓ Prevent harmful gas/vapor transmission through material
- ✓ Towards thinner and thinner coatings
- ✓ New functionalities & improved properties

# Introduction 2(2)

- Integrity of the material is very important – especially in packages
- Pinholes are microholes, and like other discontinuity or non-homogeniety, they strongly reduce barrier properties
- Pinholes in material or coating layer can restrict or even prevent the usage of the material in certain applications ⇨ Barrier properties become weaker






# Multistructure (multilayer) products

- **Extrusion coating**
  - Extrusion coating
  - Co-extrusion coating
- **Film manufacturing** (Co-extrusion)
  - Cast film
  - Blown film
- **Lamination**
  - Extrusion
  - Dry
  - Wet
  - Solventless
  - Hot melt/wax
- **Dispersion coating**
  - Barrier coatings
  - Functional coatings

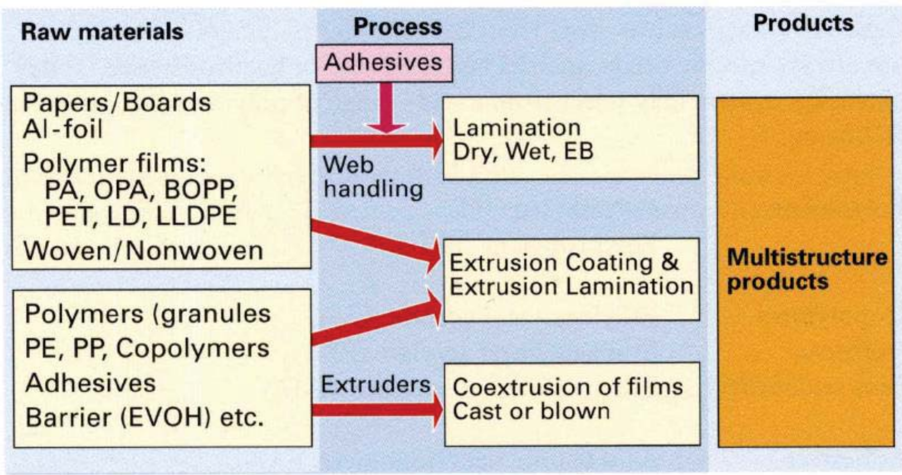
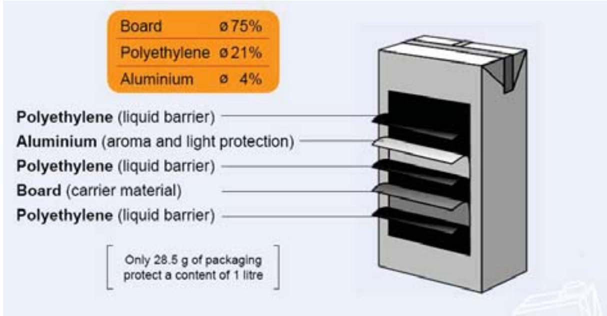



Figure 3. Multistructure product flow

## Typical construction of extrusion coated multilayer packaging




outside

| layers | g/m2 |
|---|---|
| PE-LD | 15 |
| Board | 300 |
| PE-LD | 20 |
| Adhesive (tie layer) | 6 |
| Barrier (EVOH) | 6 |
| Adhesive (tie layer) | 6 |
| PE-LD | 20 |

inside

# Extrusion coating

- **Extruding a high molecular weight, high melt temperature polymer in film form onto a rapidly moving web**
- Web (substrate) can be, e.g. paper, paperboard, Al-foil, plastic film
- Co-extrusion technology provides a multilayer extrusion coated product for more demanding applications, particularly food packaging applications, e.g. liquid packaging board (milk, juice, soup) and flexible packages
- In co-extrusion there are usually 2-4 extruders, and the polymer melts coming from different extruders are combined to the desired order before the die

# Extrusion coating & plastics

Advantages of extrusion coating and using polymers:

- tightness (barrier properties)
  - → water vapour, water, grease, aroma, gas, light
- heat sealability (i.e. closing of package)
- suitable friction properties for converting operations
- toughness, resistance to abrasion
- etc.

Main demands of extrusion coating:

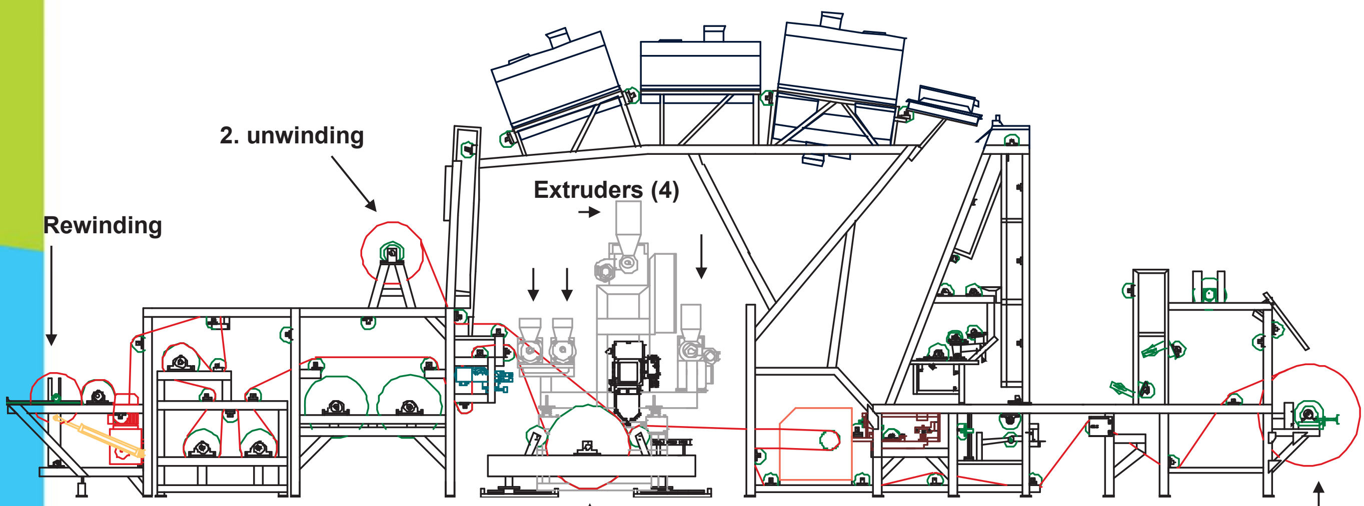
- very high processing temperatures (around 300°C)
- suitable viscosity of a polymer (rhelogical properties of the polymer are very important)



# Extrusion coating pilot line at TUT


Video available in YouTube: ”Nanomend pilot line”

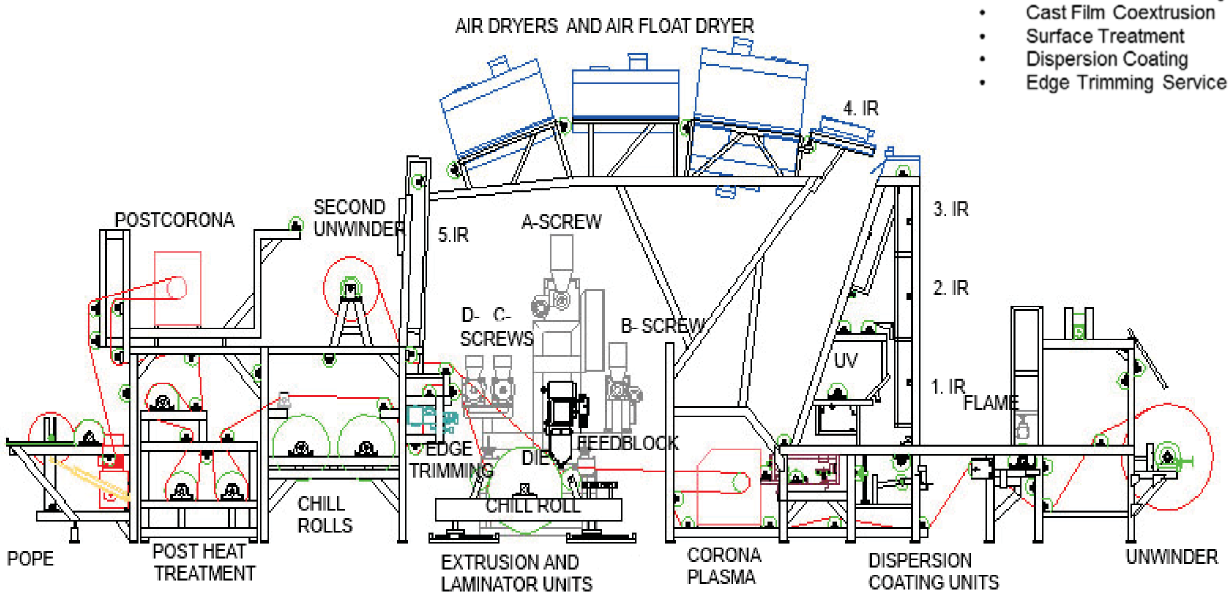
# Extrusion coating and lamination pilot line (TUT)






## Coating and Laminating Pilot Line

- Coextrusion Coating
- Coextrusion Laminating
- Cast Film Coextrusion
- Surface Treatment
- Dispersion Coating
- Edge Trimming Service




**Winders**
Main unwind
Second unwind
Rewind

### Extrusion coating:

**Extruders**
**Extruder A**
D 60, L/D 30
**Extruder B**
D 40, L/D 24
**Extruder C**
D 30, L/D 25
**Extruder D**
D 30, L/D 25
**Die:** EBR (Cloeren)
+Encapsulation
**Feedblock:**
5-layer possibility

**Laminator**
Working width:
max 550 mm
Max.speed: 400 m/min
Press roll
Chill roll (matte/glossy)
Release roll
**Surface treatments**
Corona (Vetaphone)
Flame (Hill GmbH)

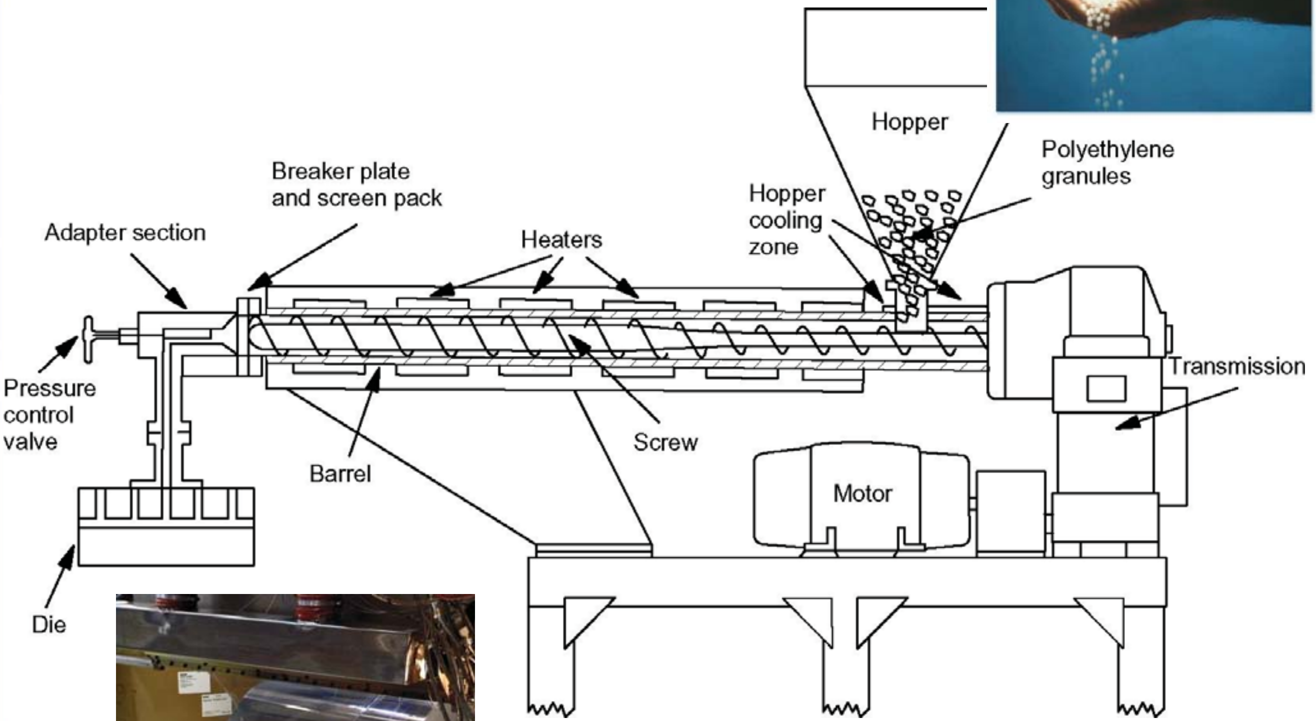
**Other units**
Relaxation

### Dispersion coating:

**Coating units**
Dispersion coating unit
-Blade or Rod

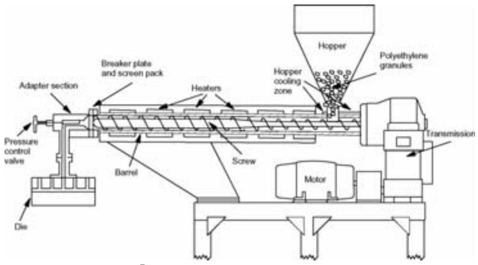
**Other units**
Chill rolls
**Dryers**
IR-dryers
Air dryers

## Main parts of an extruder






## Process technology includes



- ✓ **infeed (hoppers);** granulates to the extruders
- ✓ **barrel and screw;** polymer is melted and homogenised
- ✓ **screen pack** filters the impurities and **breaker plate** creates smooth laminar flow
- ✓ **adapter;** adjusts the back pressure in the extruder
- ✓ **feedblock;** forms the film structure
- ✓ **die;** widens the film to the desired width
- ✓ **laminator** (pressure, release and chill rolls); polymer film is pressed to the web

- **Processing temperatures vary depending on the polymer concerned**
- Usually temperature increases from the beginning to the end
For example PE-LD:

screw: 220-250-280-300 °C
adapter: 280-290
die: 300-310

# Feedblock: Selector plug

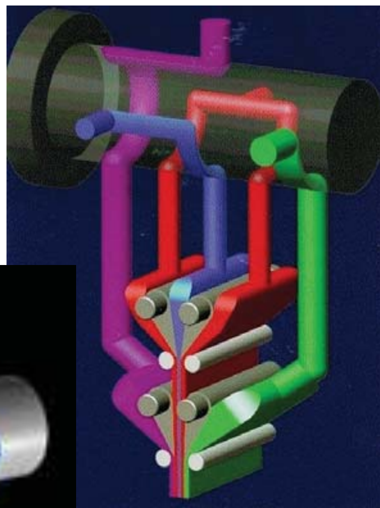
- **Co-extrusion combines two or more polymer layers into one film or layer structure.**
- The adhesion between the polymers must be sufficient
- Selector plug organises the polymer melts coming from the extruders to the desired order before the die
- A converter usually has several selector plugs to put together structures of various layers
- For example:
  - 3 extruder (A, B, and C) line has a possibility to use three polymer materials
  - By changing the selector plug, the following coating structures are possible:
    - web / A / B / C / C / C  (3 layers)
    - web / A / A / C / B / B  (3 layers)
    - web / A / B / C / B / A  (5 layers)



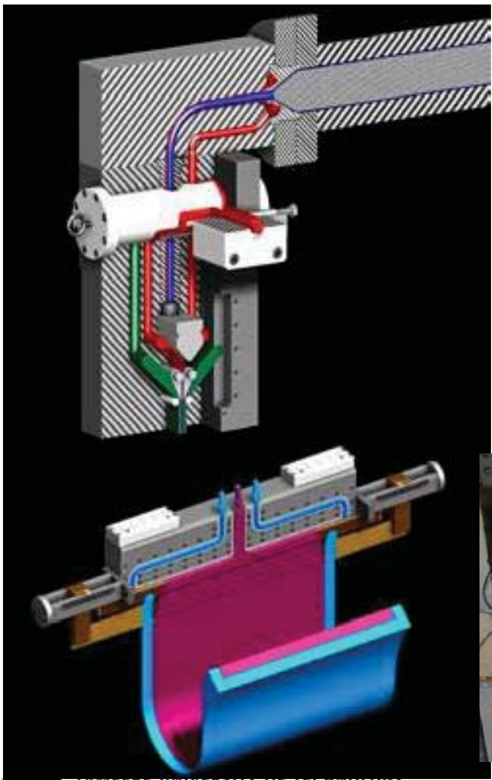
# Feedblock & Selector plug

- **<u>Common to all feedblocks:</u>**
  - **Polymer melts are combined into a one film before the actual die**
  - **The flow viscosities of the different polymers must be in the same range to prevent mixing of polymers, instabilities in flow and product surfaces, and non-uniform layer thickness profiles**
  - **Extruder screw speed adjusts the thickness of each layer**






# Cloeren-feedblock with encapsulation

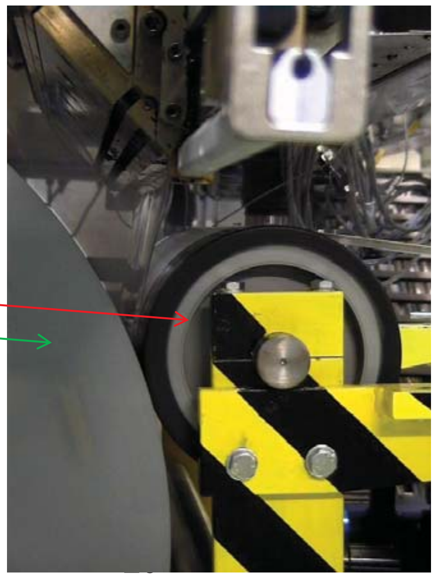


Encapsulation (polymer) is used to control the edges of the polymer film and to prevent neck-in




# Laminator

- The purpose of the laminating operation is to create adhesion between the resin and the moving web and to solidify the resin
- The surface properties of the chill roll affect the surface properties of the final coating
- Laminating system consists of:
  - **pressure and stripping (release) rolls**
  - **chill roll**
- The pressure or nip roll has a rubber covering and is water cooled. Pressure rolls strongly influence adhesion, coating integrity, appearance, and caliper.
- Double-walled, spiral chill rolls can provide adequate cooling. The temperature range of the cooling water is often 15-25°C.



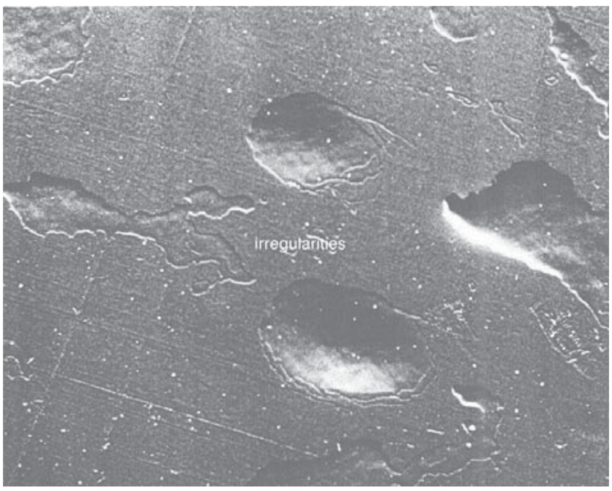
# Chill roll

- The surface finish of the chill roll is critical. It determines the release characteristics, the optical properties, and the coefficient of friction (COF) of the coating.
  - A glossy or polished finish: high optical properties of excellent gloss, good transparency, and low haze. Polished finishes also provide high COF.
  - Matte rolls: the poorest optical properties of low gloss, poor transparency, and high haze. Good release properties. Produce coatings with low COF.
  - Tacky resins such as ionomers and methyl acrylate modifications of polyethylene normally use matte rolls because of their good release properties.
  - Other chill roll finish types are satin or semi-glossy and mirror pockets.

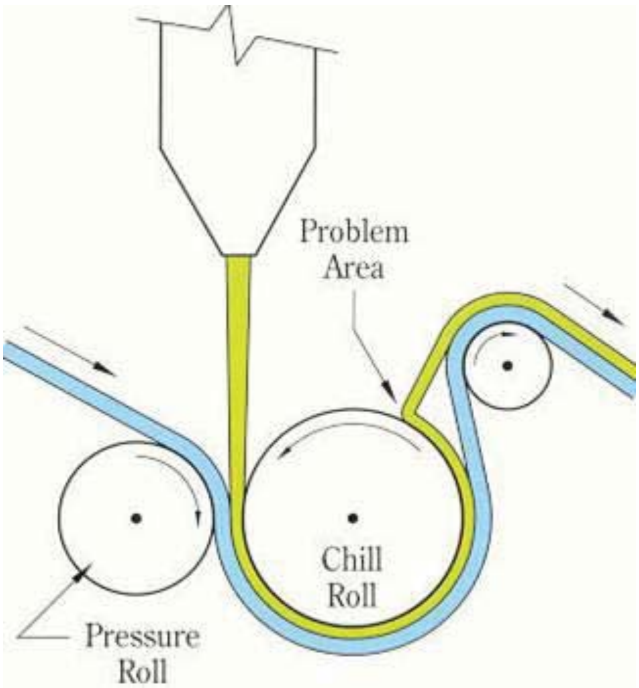



# Effect of chill roll surface properties

- Surface of the chill roll affects the friction and release properties and surface texture of the coating

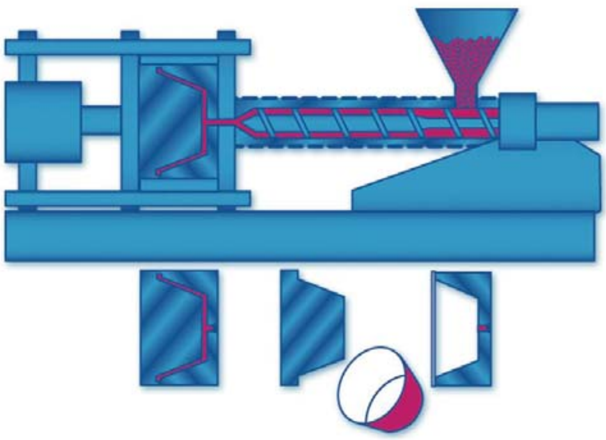



'air pockets' on a PE surface



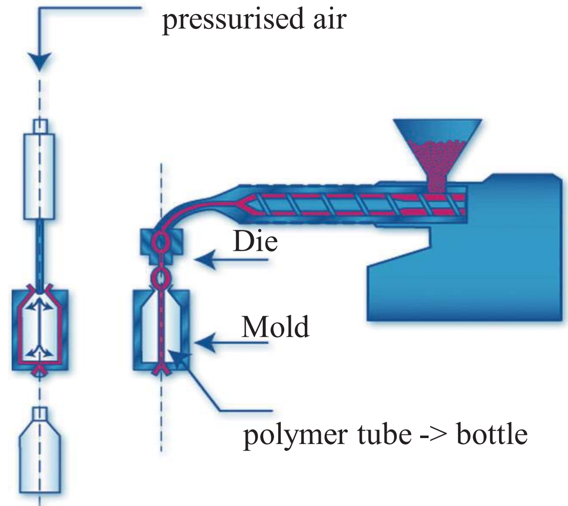
# Other extrusion processes (examples)

## Injection molding



Very precise products
by using a mold

## Blow molding




Manufacturing
of hollow products

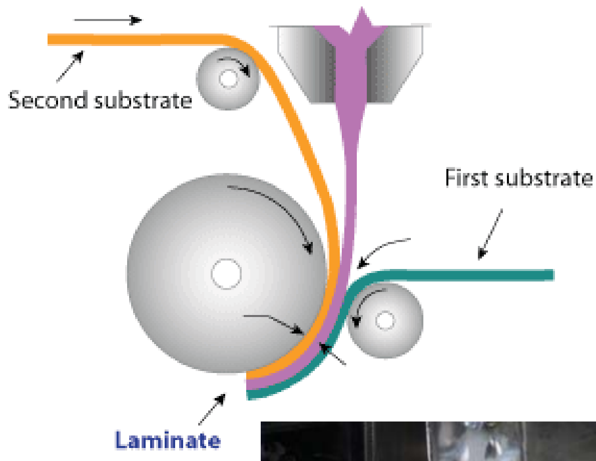


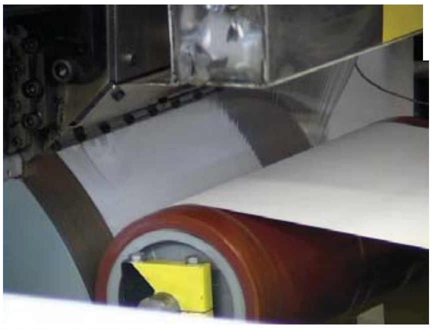
# LAMINATION

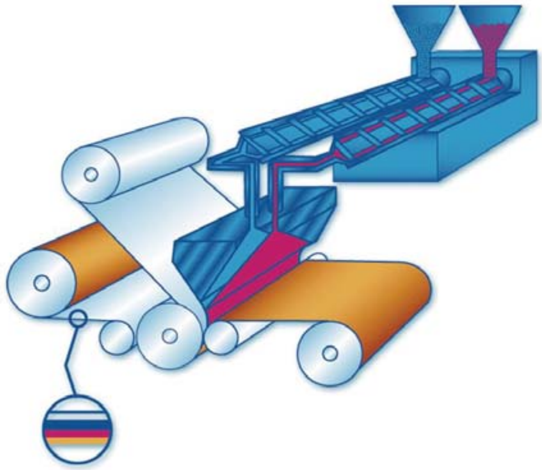
- **Lamination is used to achieve properties that cannot be achieved by a single material**
- **Lamination method depends on e.g. materials to be combined**

- In lamination process two or more webs will be glued and pressed together to get a board grade with a higher grammage level.
- The lamination can be:
  - wax lamination (molten wax is applied to board surface)
  - glue lamination (two or more webs are glued together)
    - wet lamination
    - dry lamination
    - solventless lamination
  - extrusion lamination
  - hot melt
- Wax or resin modified wax are used as a hot melt adhesive in wax lamination. The wax will be heated, applicated to the surface and cooled.

# (CO)EXTRUSION LAMINATION

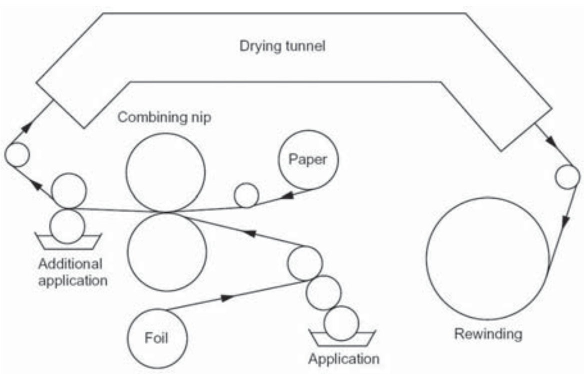


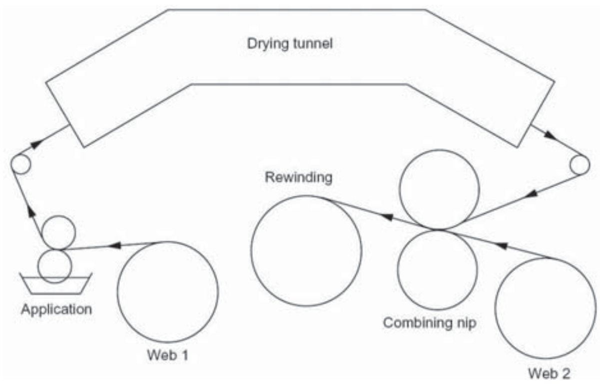




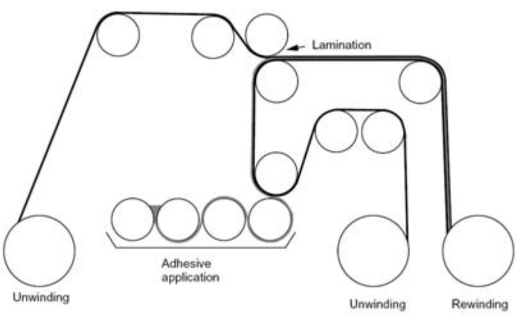
## WET LAMINATION



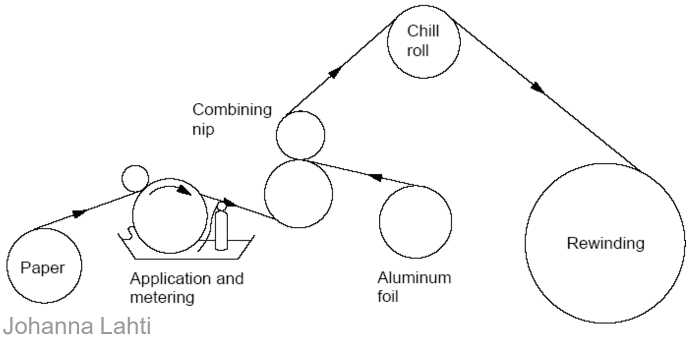

## DRY LAMINATION




## SOLVENTLESS LAMINATION

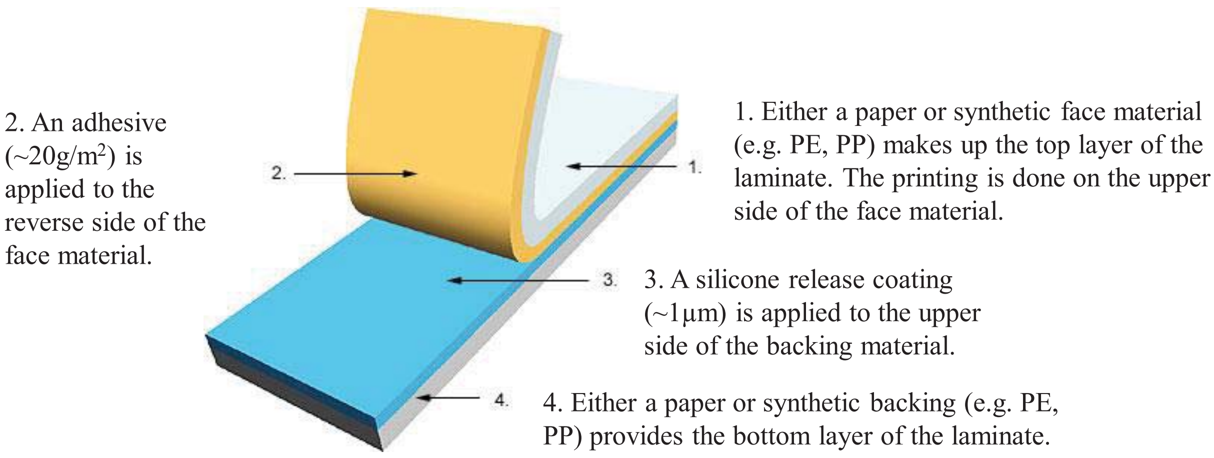



## WAX & HOT MELT LAMINATION



# Example: Production of **pressure sensitive adhesive (PSA) laminates**

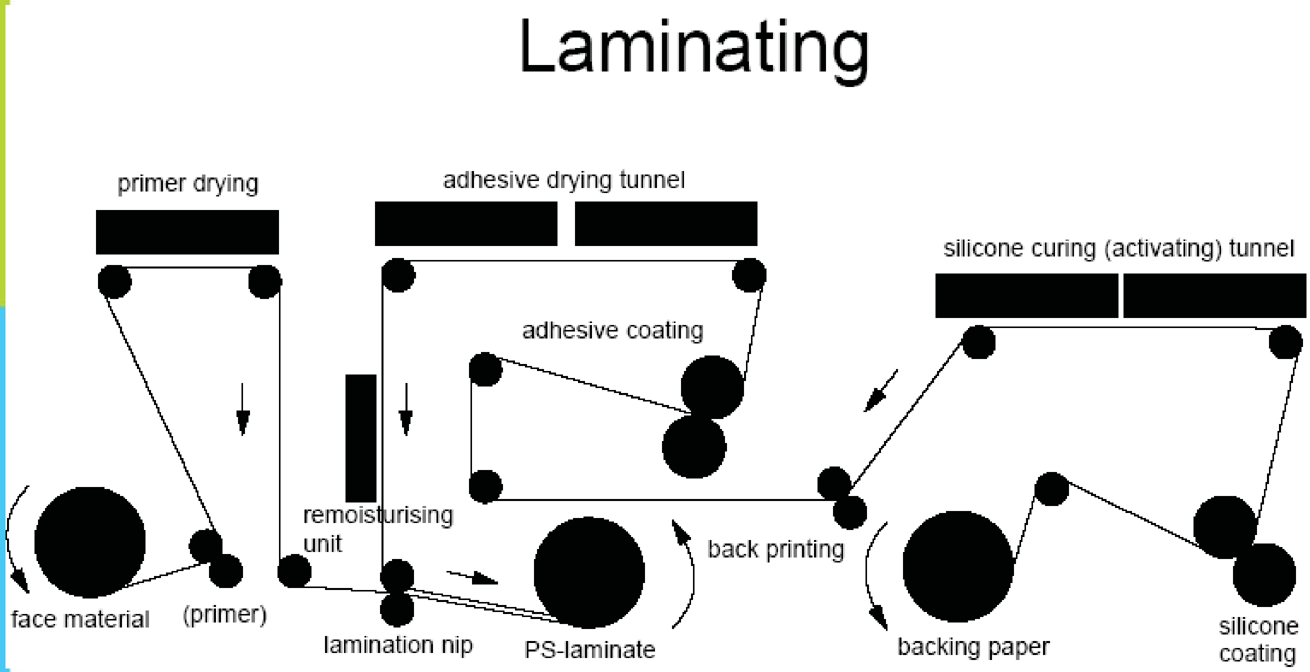
- The backing is siliconized so that the label is easy to remove
- Silicone is very expensive, hence the backing paper is the most expensive part of a label




Picture: www.raflatac.com



# Production of pressure sensitive adhesive laminates (labels)



# Manufacturing of plastic films/foils: Cast and blown film technologies

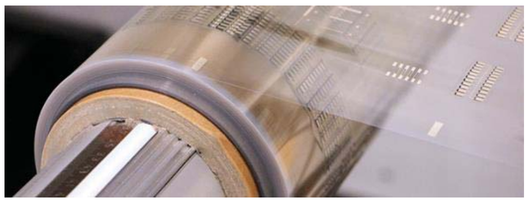
## Plastic films

- 'rough' definition: less than 250 µm thick; sealable to itself hermetically
- uses/advantages: especially in food packaging; protection (barrier); printable; clarity/transparency; easy handling and package forming
- Flexible and rigid plastic products
- other uses: wraps in building and construction, agricultural, waste/shopping bags, labels, etc.
- packaging: overwrap, blister packaging, shrink packaging, stretch packaging, etc.



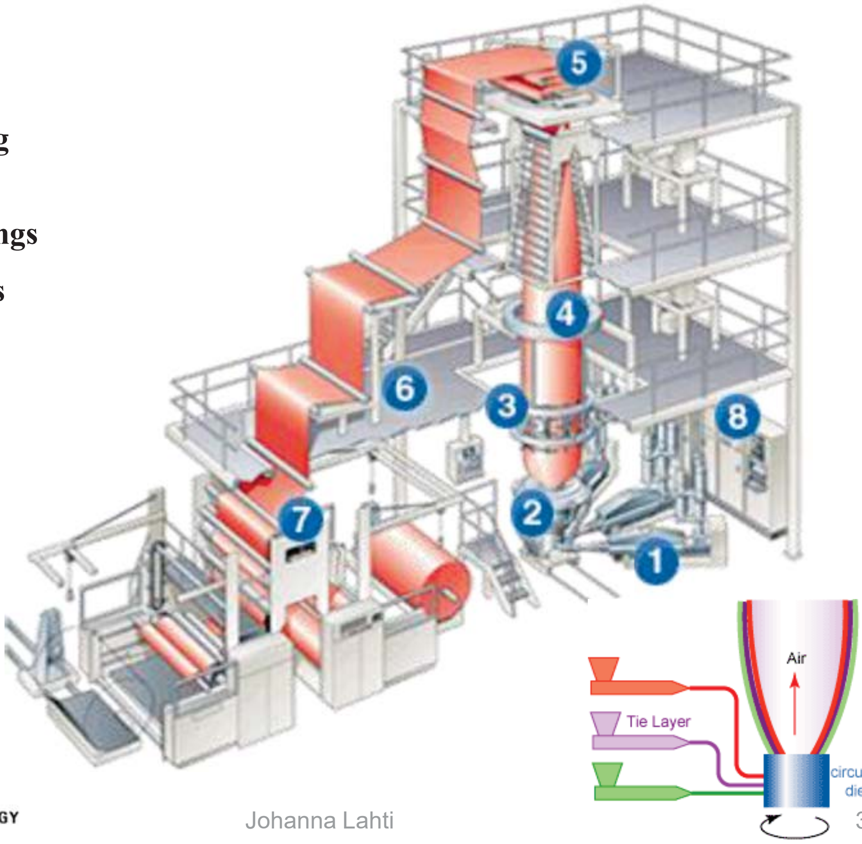
- *Two production technologies*:

  Blown films vs. cast film
  - Blown film technology saves space due to vertical configuration
  - With cast film technology, higher speeds can be used and the clarity of the films is slightly higher




# Blown film technology

1. Extruders
2. Film forming and cooling (solidification)
3. Possible additional coatings
4. Layer and total thickness measurement
5. Returning unit
6. Control of film edges
7. Rewinding
8. Automation systems

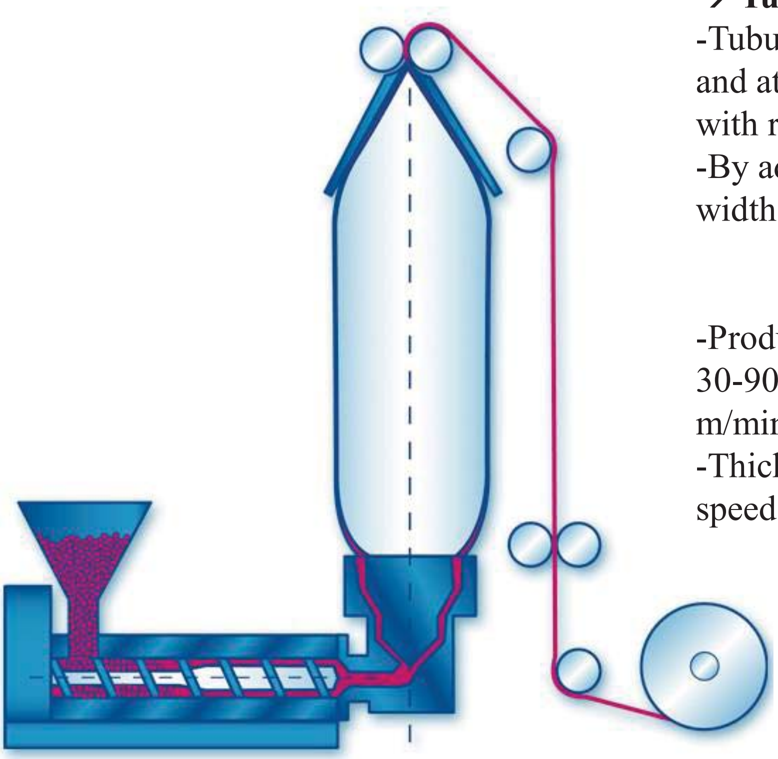




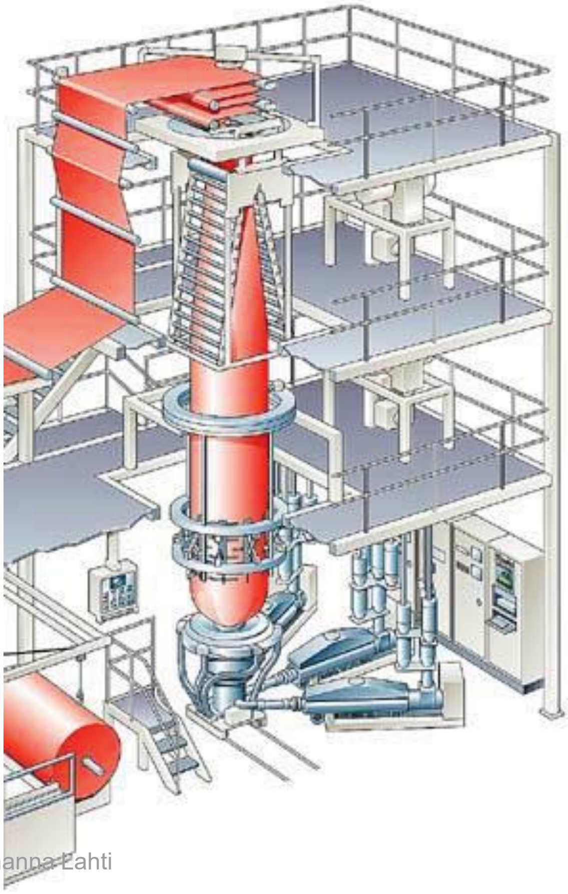

# Blown film technology

Polymer granulates are fed into the extruder → heating, melting and mixing
→ **Tubular die**
-Tubular polymer melt is cooled with air and at the end the cooled film is pressed with rolls into web
-By adjusting the amount of air, the web width can be adjusted

-Production speeds with thin films 30-90 m/min, and rarely even 300 m/min.
-Thicker films are produced with lower speeds.

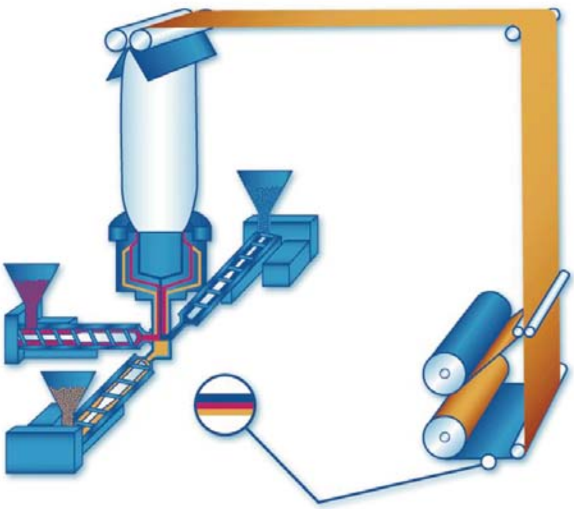


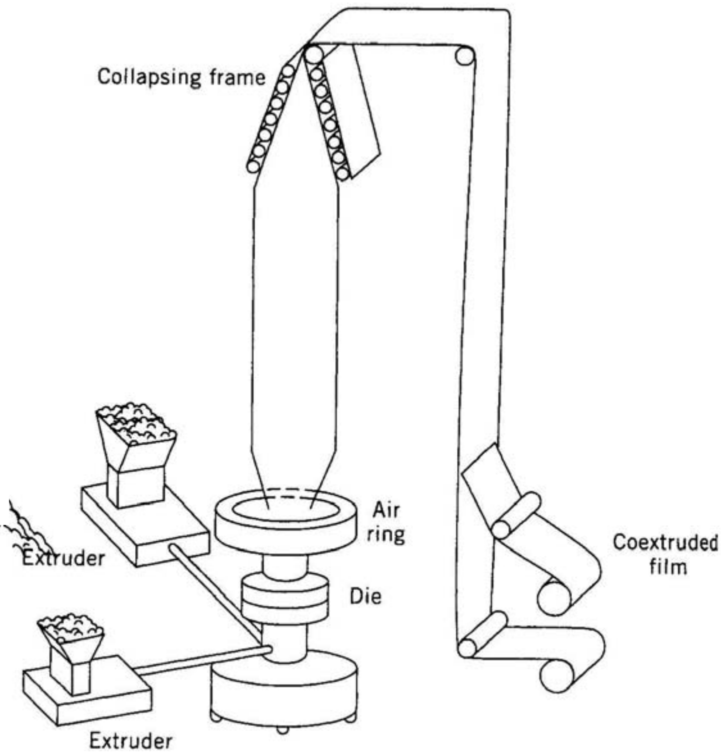
# Blown film technology



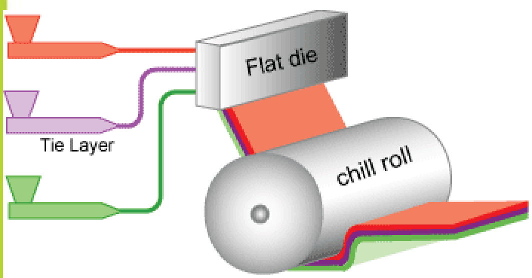


# Blown film technology, coextrusion

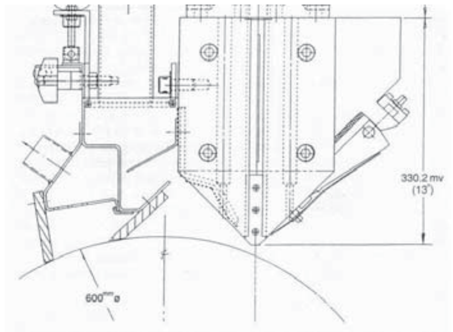


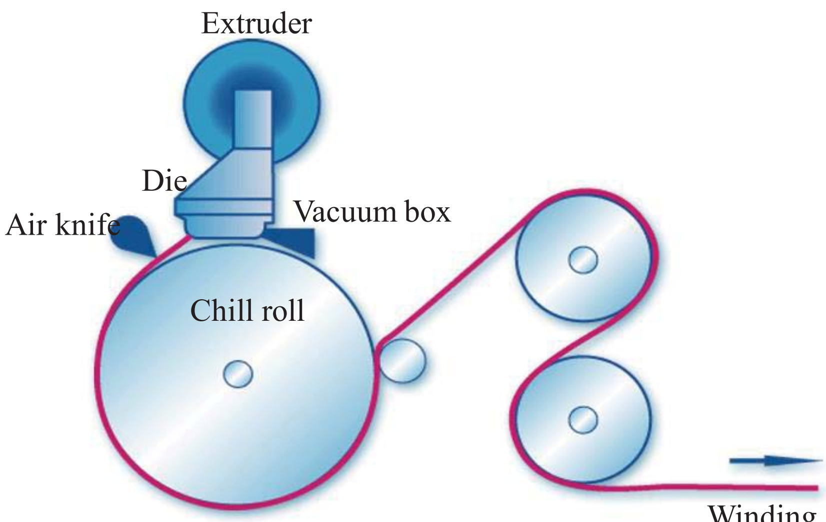


# Cast film




- **Target is a short air gap → fast cooling**
- Web widths usually 1-3m, production speeds 100-300 m/min
- Can be combined to deep drawing
- Film thickness 0,2 -2,5 mm
- Can be single or multilayer structure





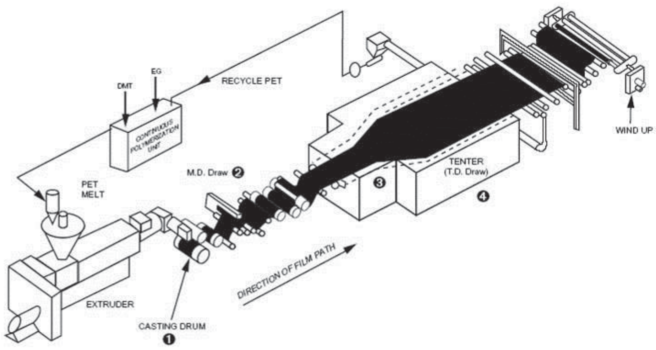



# Film orientation

= **Orientation of the plastic film (at temperature below polymer's melting temperature)** in

a) cross direction,
b) machine direction, or
c) in both directions (=biaxial)

- For example: OPP=oriented polypropylene, BOPP=biaxially oriented PP
- Polymer chains are oriented in the direction of the draw → strength is improved
- <u>Orientation improves barrier and mechanical properties</u>



# PART 2: Fibre-based and polymeric substrates and some examples of applications

Paper
Paperboard
Corrugated board
Other substrates
Polymers

## Examples of packaging papers

- **Kraftpaper**
  - Based on virgin brown sulphate pulp or bleached chem. pulp (➔ strength)
  - Grammage 60 – 120 g/m$^2$
  - Wrappings, bags, pouches, laminates, sacks, etc.
- **MG-paper (machine glazed)**
  - One side is glossy
  - Grammage 20 – 120 g/m$^2$
  - Wrappings, labels, flexible packages (laminates), etc.


- **C1S, coated one side**
  - Bleached chem. pulp
  - High quality
  - Grammage 45 – 120 g/m$^2$
  - Cosmetic packages, lid laminates, pet food packages, soup and spice packages, etc.

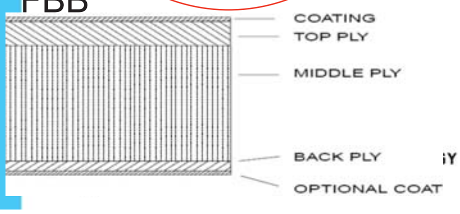
➔ *Papers*: good printability, good adhesion, solvents are absorbed quickly by the paper, fast drying but porosity of paper can have a negative effect on conductivity.

# Paperboard & Cartonboard grades in general

**Paperboard Grades**

- Cartonboards
  - Folding Boxboard
  - White Lined Chipboard
  - Solid Bleached Board
  - Solid Unbleached Board
  - Liquid Packaging Board
    - Bleached
    - Unbleached
- Containerboards
  - Linerboard
    - Brown
      - Kraftliner
      - Recycled
    - Mottled
    - White Top
    - Coated White Top
  - Corrugating Medium
    - Semichemical
    - Recycled
- Special Boards
  - Core Board
  - Wallpaper Base
  - Plaster Board
  - Book Binding Board
  - Woodpulp Board
  - Others

FBB




Corrugated board

Ref.: Paper and paperboard grades (FAPET)



# Other packaging materials (examples)

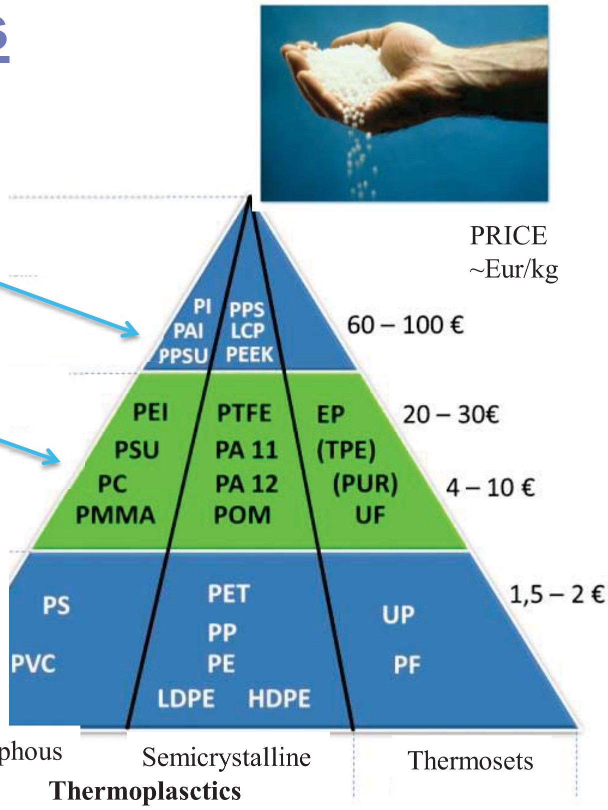
- **Al-foil**
  - Easily deformable
  - Thickness usually 6-20µm; max. web width ca. 2m
  - Very good barrier, especially light barrier
  - Dead fold property
  - Usually used together with some other flexible packaging material like plastic film
- **Metallized films**
  - Mainly to replace Al-foil
  - Good barrier properties
- SiOx coated materials (like plastic films)
  - Very expensive; Good gas barrier
- Cellophane
  - Clear and stiff; good dead fold-property
  - Usually coated with e.g. PVCD or vinylchloride/vinylacetate copolymer

# Categories of polymers

**3) Specialty polymers:**
- 'Extreme' applications
- LCP, PEEK, PI, etc.

**2) Engineering plastics**
- More demanding applications
- Usually have some specific technical properties
- PTFE, PEI, PUR, PA11, etc.

**1) Commodity plastics**
- PS, PVC
- PE, LDPE, HDPE, PP, PET, etc.



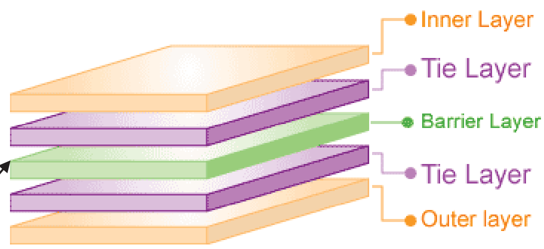

*Plastics*: good printability, longer drying and curing time, adhesion can be a problem. No interference from substrate (no porosity). If curing and sintering are good→ optimal conductivity

TAMPERE UN

# Polymers for extrusion coating and plastic films

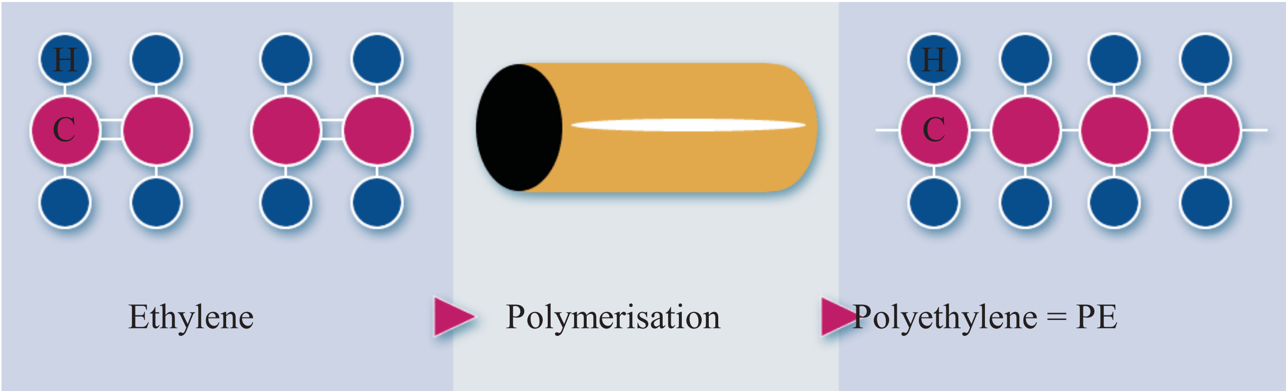
- **Polyolefins**
  - PE (polyethylene)
    - PE-LD, PE-MD, PE-HD
  - PP (polypropylene)
- **Copolymers**
  - E/VAC (ethylene vinyl acetate)
  - E/BA (ethylene butyl acrylate)
  - E/MA (ethylene methyl acrylate)
  - E/EA (ethylene ethyl acrylate)
- **Adhesives (TIE-layers)**
  - Acid copolymers (Ionomers, E/AA)
  - Grafted polyolefins (MAH grafted)
  - Modified polyolefins (e.g. Bynel, Admer)
- **Barrier polymers**
  - EVOH (ethylene vinyl alcohol)
  - Polyamide
    - PA 6, PA 66, PA 11, PA 12
    - MXD-6 (amorphous polyamide)
  - COC (Cyclo-olefin copolymer)
- **Other polymers**
  - Polyester (PET); Polymethylpentane (PMP), polyethylene naphtalate (PEN)
- **Biopolymers**

**Example of multilayer structure**



# Polyolefins: PE & PP

- PE and PP are the most common polyolefins
- Thermoplastic resins polymerized from ethylene and propylene (polymerisation process)
- Hydrocarbons made up of many long chain molecules of carbon and hydrogen atoms
- May contain additives (antioxidants, antistats, slip additives, colorants)

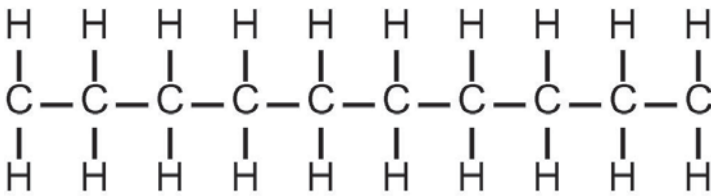





# Polyolefins: PE

•Ethylene monomer: $C_2H_4$

-> chemical linking of monomers -> polyethylene chain (hydrocarbon)



•Polyethylenes:

- **Different densitites, different molecular structures (i.e. polymer chains)**
- **PE-LD (low-density polyethylene)**
- **PE-MD (medium density polyethylene)**
- **PE-HD (high density polyethylene)**
- **PE-LLD (linear low-density polyethylene)**

•Molecular formula depends primarily on the polymerizing process of ethylene:

- high pressure polymerization (PE-LD): autoclave or tubular
- low pressure polymerization (PE-HD, PE-LLD): solution, slurry or gas phase

# PE-LD

<u>PE-LD</u> **(low density polyethylene)**

**Pros:**

- **easy to process**
- **moisture barrier**
- **heat sealability**
- **suitable appearance (matt, glossy)**
- **no odour, no taste**
- **transparent**
- **approved for food packaging**
- **economic**
- **easy to burn (recycling)**
- **basic polymer to various compounds**
- **process temperature usually 310-330°C**


Cons: poor gas and grease barier,
low mechanical strength,
low heat resistance

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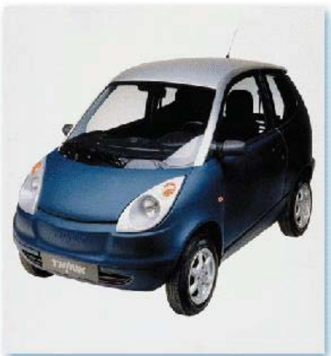
# Products from polyethylene



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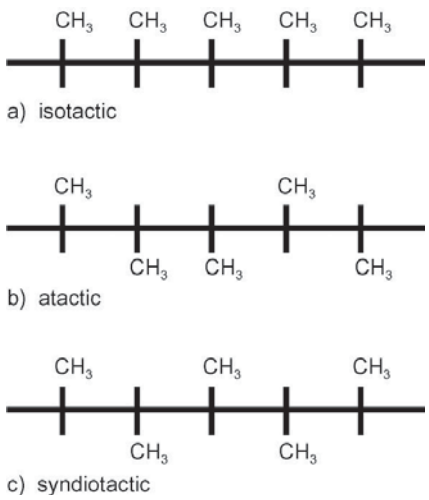
# PP (isotactic)

- melting point of 165°
- high tensile and modulus
- **excellent chemical resistance**
- **good grease resistance**
- **good abrasion resistance**
- **high temperature resistance** (micro-ovenable)
- **good stress crack and curl resistance**
- **stiffness**
- poor heat sealability
- adhesion to most substrates is poorer than with PE

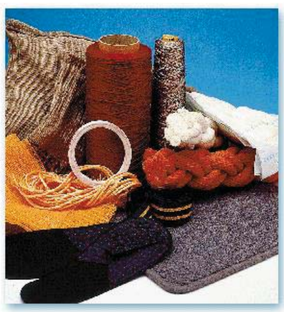
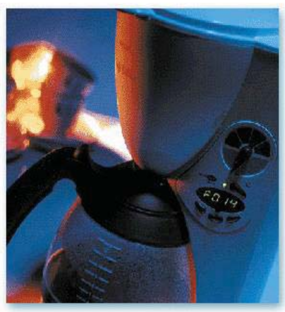


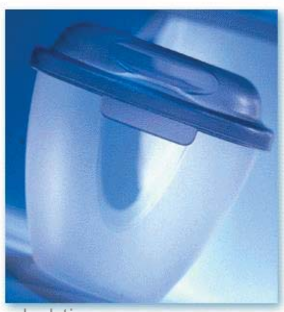
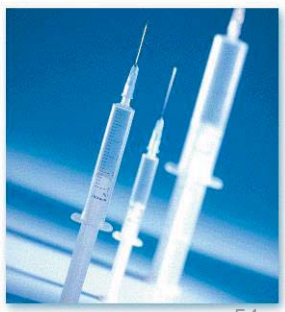



# Products from polypropylene

<u>Besides extrusion coating, PP is used for :</u>

-Biaxially oriented films
-Yoghurt cups
-Trays (deep drawn)
-Blow molded bottles
-Injection molded boxes
-Plastic bags
etc.

# Example: BOPP (biaxially oriented polypropylene)

**Interactive printed electronics labels light up beer bottles**

Innovia Films Ltd, a leading global manufacturer of speciality films, and PragmatIC Printing Ltd, the pioneer in imprinted logic circuits, has announced the successful integration of printed electronic functionality onto Innovia Films' Biaxially Oriented Polypropylene (BOPP) label substrates.

http://www.packagingeurope.com/Packaging-Europe-News/44375/Interactive-printed-electronics-labels-light-up-beer-bottles.html



# Barrier polymers

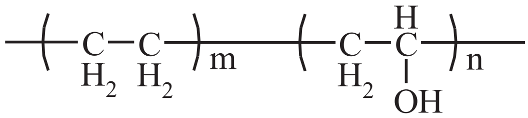
- **To improve especially <u>oxygen barrier</u>**
- Most used barrier polymers:
  - **Ethylene vinyl alcohol (EVOH)**
  - **Polyamide (PA)**

- Barrier polymers are moisture sensitive and when exposed to moisture, they loose their barrier property ➔ used in coex-structures with polyolefins
- Need usually an adhesive layer in polyolefin coex-structures
- Usually expensive and more difficult to process ➔ restricted use

| **Plastic** | **$O_2$TR ($cm^3/m^2/d$)** |
| --- | --- |
| E/VA | 5000 |
| PE-LD | 3500 |
| PP | 1800 |
| Oriented | 500 |
| PE-HD | 1300 |
| PET | 80 |
| Oriented | 40 |
| PA-6 | 25 |
| Moist | 120 |
| EVOH | 0.2 – 2 |
| moist | 30 - 50 |

Ref: Paper and paperboard converting (1998)

# Barrier polymers: EVOH and PA



**EVOH (ethylene vinyl alcohol copolymer)**

- **Excellent gas and aroma barrier properties are due to high crystallinity and high level of hydrogen bonding**; poor resistance to water vapour
- Very high resistance to hydrocarbons and organic solvents
- Easy to process
- Suitable for high-temperature laminates (retortable applications)
- EVOH properties and processability depend on the ethylene content in the molecule.
- The most common application in coextrusion coating today is for liquid packaging where oxygen barrier and aroma or flavor barrier are necessary

  Example: Juice packaging: LDPE/board/LDPE/adhesive/EVOH/adhesive/LDPE

- **PA (polyamide) (Nylon)**
- PA6, PA11, PA12, etc.
- Good tensile strength and rub resistance
- High impact strength and good puncture resistance
- Especially good gas & grease barrier

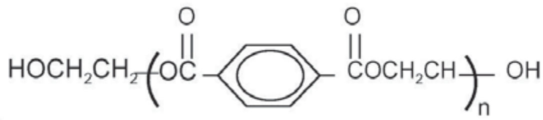
Polyamide 6 $H\text{-}(NH\text{-}C_5H_{10}\text{-}CO)_n\text{-}OH$



# PET (Polyethylene terephthalate)

- **Good barrier properties**

  (e.g. grease and aroma barrier)
- High gloss and clarity
- Low odour and taste
- **Good heat resistance** (60 – 235 °C) → ovenable packages, boil-in-bag packages, retortable packages
- Used in multilayer structures where LDPE is the sealing layer
- Somewhat difficult processing
- Generally coat weight of about 40 g/m$^2$ is needed for good adhesion to paperboard

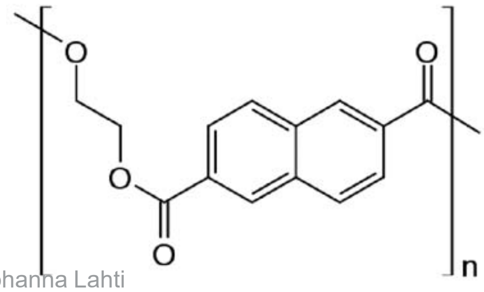


n = 100-200

POLYETHYLENE TEREPHTHALATE

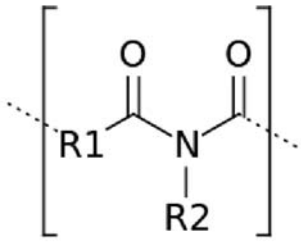
# Polyethylene naphthalate (PEN)

- **Polyethylene naphthalate** (**PEN**) (**Poly(ethylene 2,6-naphthalate**) is a polyester with good barrier properties (even better than PET).
- Because it provides a very good **oxygen barrier**, it is particularly well-suited for bottling beverages that are susceptible to oxidation, such as beer
- The two condensed aromatic rings of PEN confer on it improvements in strength and modulus, chemical and hydrolytic resistance, gaseous barrier, thermal and thermo-oxidative resistance and ultraviolet (UV) light barrier resistance compared to PET.



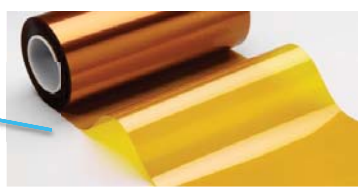



# Polyimide (PI)

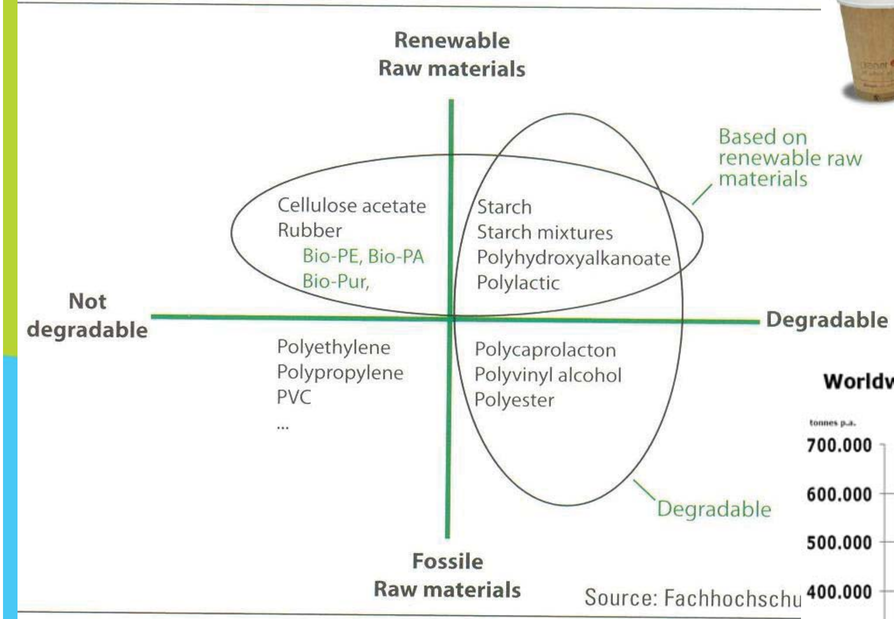


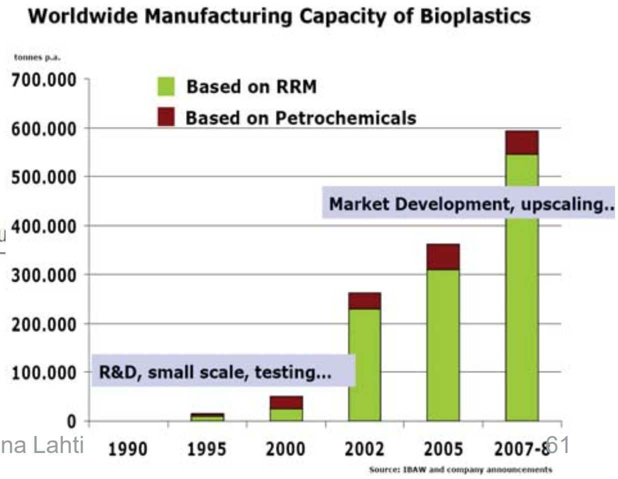

- According to the type of interactions between the main chains, polyimides can be:
  - **Thermoplastic:** very often called pseudothermoplastic
  - **Thermosetting**: commercially available as uncured resins, polyimide solutions, stock shapes, thin sheets, laminates and machined parts.

- Polyimide materials are lightweight, flexible, resistant to heat and chemicals.
- Thermosetting polyimides are known for thermal stability, good chemical resistance, excellent mechanical properties, and characteristic orange/yellow color.
- Example: DuPont Kapton®



## Biopolymers based on renewable and non-renewable raw materials






## Extrusion → Products

**Liquid packaging:** milk and juice gable top cartons, aseptic rectangular shaped drink boxes

**Flexible packaging:** snack foods, condiment packs, food, dry goods, medical packages, toothpaste type collapsible tubes, liquids, "bag-in-box"

**Paperboard packaging:** bakery boxes, microwaveable trays, frozen food boxes, detergent boxes, animal food boxes

**Industrial wraps:** drum liners, ream wrappers, composite cans, soap wrappers

# Examples of package applications and multilayer products

**Gable Top Carton**
Printing
LDPE
Paperboard
LDPE

**Drink Box**
LDPE
Printing
Paperboard
LDPE
Foil
Coextrusion

**Snack Food Bags**
Polypropylene Film
Printing
LDPE
Metalized Film
LDPE

**Toothpaste Tubes**
Film
Printing
Coextrusion
Foil
Coextrusion
Film

**Detergent Boxes**
Film
Printing
LDPE
Paperboard
LDPE

**Ream Wrapper**
Paper
LDPE
Paper

**Photo Paper**
LDPE
Paper
Printing
LDPE

**Insulation Backing**
Foil
LDPE
SCRIM
Kraft Paper

**Tarpaulins**
LDPE
Woven Tape Fabric
LDPE

**Paper Snacks**
Paper
LDPE
SCRIM
Paper

SCRIM



## Vacuum packaging

- Air is removed from the package
- Vacuum packaging is used e.g. for meat, sausages, and fish products.


## MAP, Modified Atmosphere Packaging

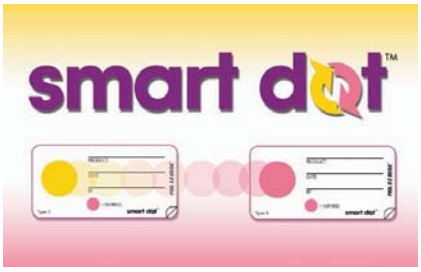
- The atmosphere inside the package is modified so that it differs from the normal gaseous composition of air.
- Usually oxygen is removed as well as possible and carbon dioxide is added to slow down the growth of microbes/micro-organisms
- E.g. meat, cheese, bakery products, snacks
- Examples of MAP gases: $CO_2$, $N_2$ and $O_2$

# Active packages

- Active packaging changes the condition of the packed food to extend shelf life or to improve safety or sensory properties, while maintaining the quality of the packed food
- **Intelligent packaging** systems monitor the condition of packed food to give information about the quality of the food during transport and storage,.
- **Active package** is designed to regulate conditions within the package and thereby inhibit deteriorate processes in packed food.
- Categorised as:
  – Absorbers (scavenger systems): Function is based on removing undesirable compounds from the inside environment of the package and thereby inhibit deteriorative processes in the packed food. For example oxygen scavengers.
  – Releasing systems: Add or emit compounds to packed food or into the head space of the package. For example carbon dioxide or ethanol emitters.
  – Other systems: antimicrobial and antioxidant packaging films (i.e. preservative releasers). Film contains material that prevents/slows down microbial/bacterial growth.

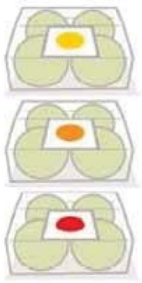


# Intelligent packages

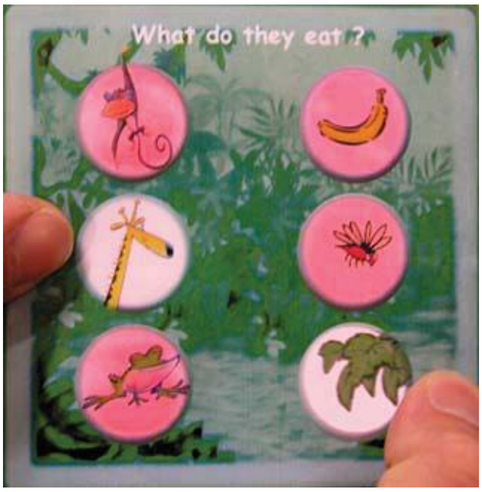



- Package contains an **external/internal indicator** that monitors the quality of packed food.
- External indicators monitor conditions during product distribution and internal indicators are used to indicate possible changes in the quality of packed food or leakages in packages
- Time-temperature indicator, leakage indicator and freshness indicator
- Currently available indicators are usually based on visually detectable colour change (on the label) caused by incorrect storage conditions, quality changes in food or package leaks
- Indicator labels are manufactured by e.g. UPM Raflatac

## Freshness indicator

## Play for kids




Ref. VTT



## COST Action FP1405 "Active and intelligent fibre-based packaging - innovation and market introduction" (ActInPak)

Oxygen Absorber OxyFree ©Bumaga

Humidity Indicators Clariant ©Bumaga

Time Temperature Indicators Timestrip ©Bumaga


Freshness indicator Student work KCPK ©Bumaga

It's Fresh! concept ©Bumaga

Temperature indicator SmartFlowerPack KCPK ©Bumaga

Active flower packaging SmartFlowerPack KCPK ©Bumaga

FreshPaper by Fenugreen ©Fenugreen

# Printed/coated functionalities

## Active components/structures

- Battery (primary, secondary)
- Battery Charger
- Photovoltaic – PV – (OPV, DSSC)
- Display, Light source – OLED, EL, electrochromic, thermochromic, electroforetic
- Sensor – chemical, bio, climatic, pressure, etc.
- Memory
- RFID
- diodes
- Transistors – OFET, OECT
- ISS – Smart Objects, Smart Sensor, Smart Textiles

## Passive components

- Electronic circuits
- Antennas – RFID
- Capacitors, resistors, induction coil, transformers

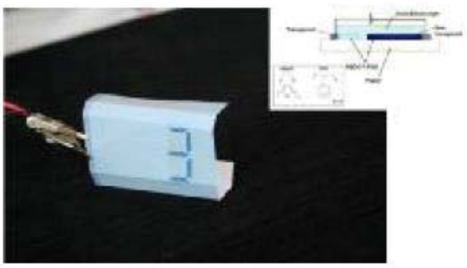
## Functional layers

- Healtcare aplication
- Drugs
- Termochromic, photochromic
- Catalytic layer
- Textile finishing layers
- Explosives

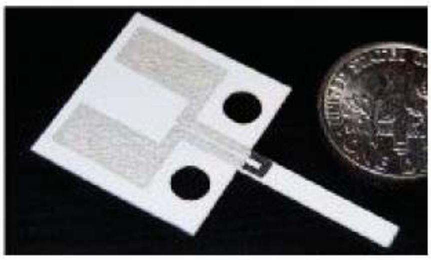
Ref. Tomas Syrovy, 2014 (COST FP1104, Swansea)



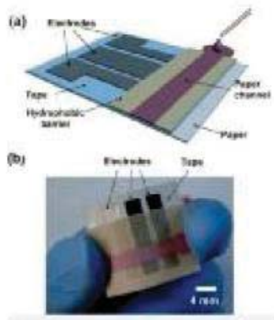
# Paper Electronics = Disposable Printed Electronics on/in Paper with Commercial Potential



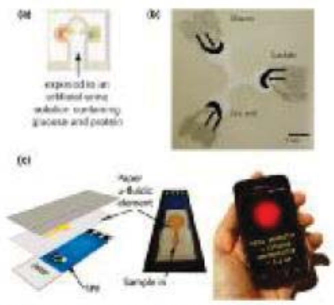
Electrochemical Paper Display, Acreo, SE



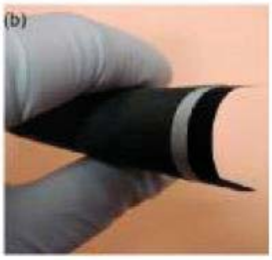
"Paper Accelerometer Could Mean Disposable Devices," X. Liu, et al.



"Zero-Cost Diagnostics," G.M. Whitesides

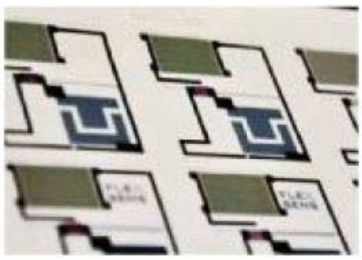


μPADs & paper-based microfluidic devices, X. Li et. al., Biomicrofluidics 6, 011301 (2012)



Li-ion paper-batteries, Jabbour et al.

Pharma DDSi, StoraEnso



Gas sensor on paper, Peltonen et al., FunMat/FlexSens

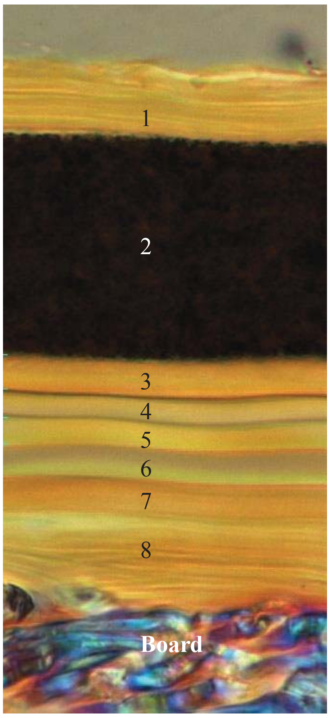
Martti Toivakka 2014

Ref. Martti Toivakka, 2014 (COST FP1104 Swansea)

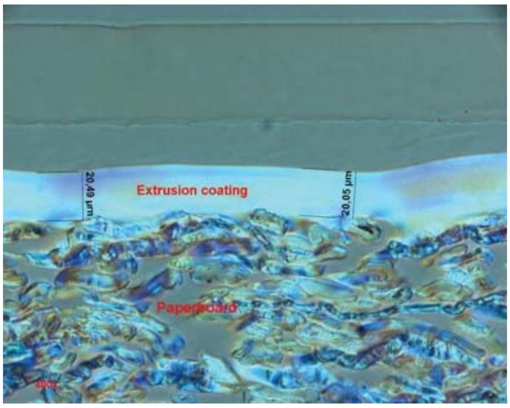
# PART 3: Barrier properties & measurements

## Selection of polymer(s)

- Material selection is a compromize between
  - Adhesion
  - Friction properties
  - Uniform coating profile (both in the whole coating and single layers)
  - Barrier properties
    - Water vapour
    - Oxygen
    - Light
    - Grease
    - Aroma
  - Heat sealability
  - Printability etc.
- Co-extrusion allows thin layers and minimizes the amount of expensive special polymers
- There are less pinholes in co-extrusion coated material because of multilayer structure (vs. one layer coating)



# Coat weights in extrusion and co-extrusion

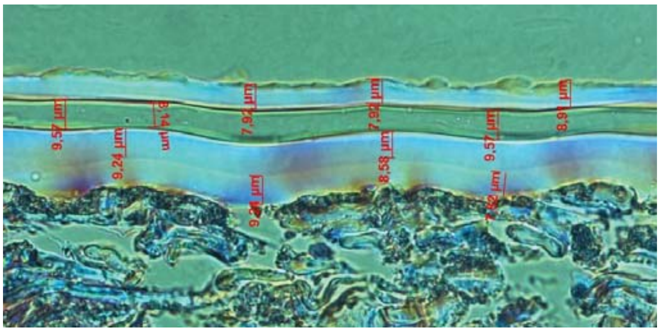



•Coat weight depends on various matters: polymer and its properties (draw down etc.), substrate, adhesion, application etc.

•In extrusion coating usually about 10-60 g/m²

•In co-extrusion can be achieved very thin layers, because there are more layers supporting each other

•With plastic films, thicknesses can also vary depending on if it's a monolayer or a multilayer structure



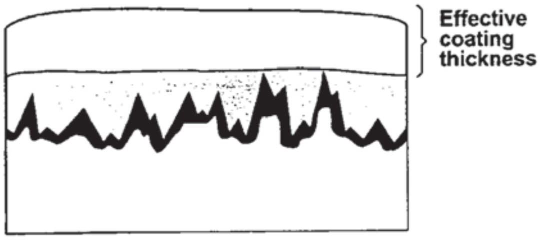



# Advantages of co-extrusion

- **Adhesion enhancement** can occur by selection of the proper polymer bonded to the substrate or by using higher temperatures
- **Thin layers:** minimization of expensive polymer use with thinner layers of cheaper polymers as support layers around the main polymer
- **Less pinholes** in the coating enhances the barrier properties: running only one polymer with co-extrusion into a two-layer structure improves the pinhole resistance compared to a one-layer coating
- **Better heat sealability**: extruding the surface layer at a lower temperature reduces the oxidation of the polymer. Selection of the heat-sealable skin polymer can provide good heat sealing properties by using, for example, an ionomer
- **Layers containing additives and pigments**: only the surface layer needs to contain any additives to reduce cost and protect the die metal. Two dissimilar colors are also possible.
- **Less manufacturing processes**: machine time savings
- Polymers that are difficult to process can be run supported by other polymers
- Increase in capacity
- Combine polymers having special barrier properties as thin layers as are necessary
- Non-slip surfaces or ultra low heat seal temperatures by the selection of the skin-polymer.

## Pinholes

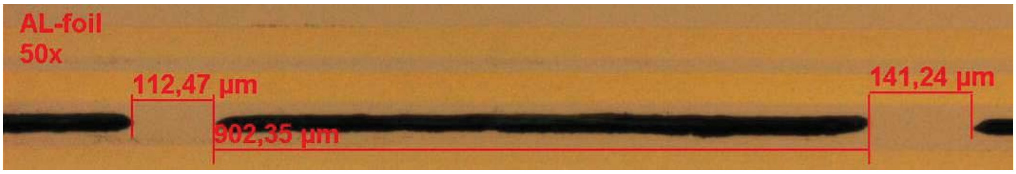
- **Pinholes are microholes and like other discontinuity or non-homogeniety they strongly reduce barrier properties**
- **Pinholes in material or coating layer can restrict or even prevent the usage of the material in certain applications ⇨ barrier properties become weaker**
- Formation of pinholes:
  - -Before coating (thin films)
  - -When the film and substrate meet
  - -In the nip
  - -During release from chill roll
  - -During converting, (e.g. during sealing)

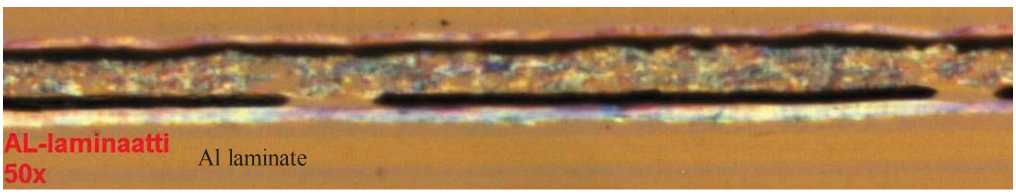



- Pinholes can be caused by:
  - -Air/gas bubbles in the polymer melt
  - -Impurities in the polymer melt, e.g. gels
  - -Uneven or rough substrate (Fibers sticking from the substrate can puncture the thin film)
  - -Impurities on the surface of the chill roll or other rolls
- Can be random or accumulate
- In real, leak is rarely an idealised "hole", it can be f.ex. a tear, slit, crack or combination of these

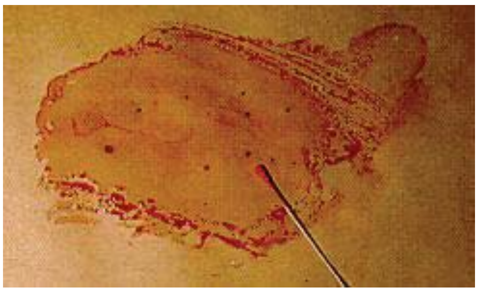


## Pinholes




Al laminate



*Visual testing of pinholes with coloured test liquid*

# Barrier properties

•Polymers are usually classified as semi-permeable materials because they allow the passage of small molecular species such as carbon dioxide, oxygen, nitrogen or water, while restricting the flow of structurally larger organic molecules

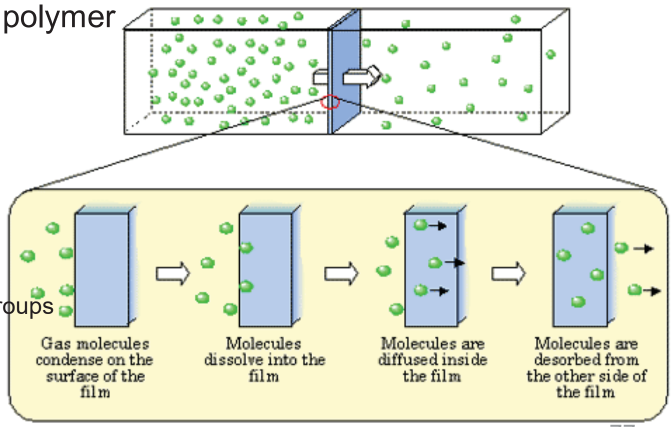
•Barrier against: Water (vapour), oxygen, CO2, aroma, grease, light, etc.

•Small molecules ($H_2O$, $O_2$) penetrate through polymer

- *Absorption* on the surface of polymer
- *Dissolution* in the polymer matrix
- *Diffusion* through the polymer
- *Desorption* from the other side of the polymer

•Factors affecting permeability

- Temperature, humidity
- Permeating species
- Thickness of the polymer layer
- Glass transition temperature, molecular weight, density
- Moisture content of the polymer
- Crosslinking, crystallinity, orientation, functional groups

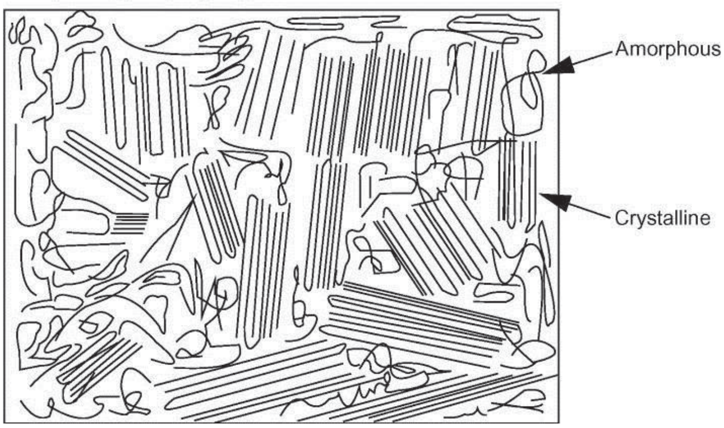





# Barrier

- Morphology: crystalline parts prevent penetration of water; water molecules penetrate through amourphous regions
- PE, PP, PTFE (teflon) hydrophobic polymers => good water vapour barrier, poor oxygen barrier
- PA, EVOH hydrophilic polymers (contain hydrogen bonds) => good oxygen barrier, poor water vapour barrier
  - O2-barrier of PA and EVOH decreases when moisture increases

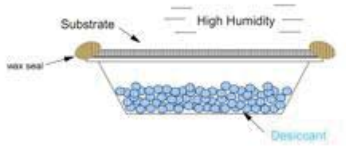
Morphology of polyethylene



- **Water vapor transmission rate, WVTR**, is the steady water vapour flow in unit time through unit area of a body, under specific conditions of temperature and humidity at each surface
- Standards for WVTR testing:
  - TAPPI 448 and T 464, ASTM E96/E96M -10, DIN 53122-1, ISO 2528, SCAN – P22:68

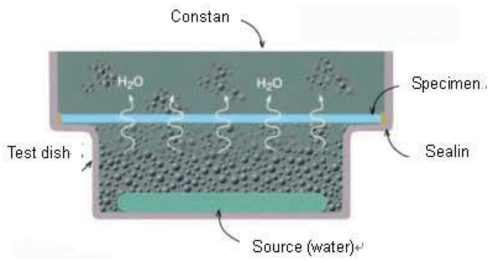
Testing conditions in barrier measurements can be varied, f.ex.

- Standard paper testing environment at 23˚C and 50%RH
- Tropical conditions at 38˚C and 90%RH




- Methods (Cup test):

1. The Desiccant Method
(e.g. anhydrous calcium chloride or silica gel)
2. The Water Method
(distilled water)

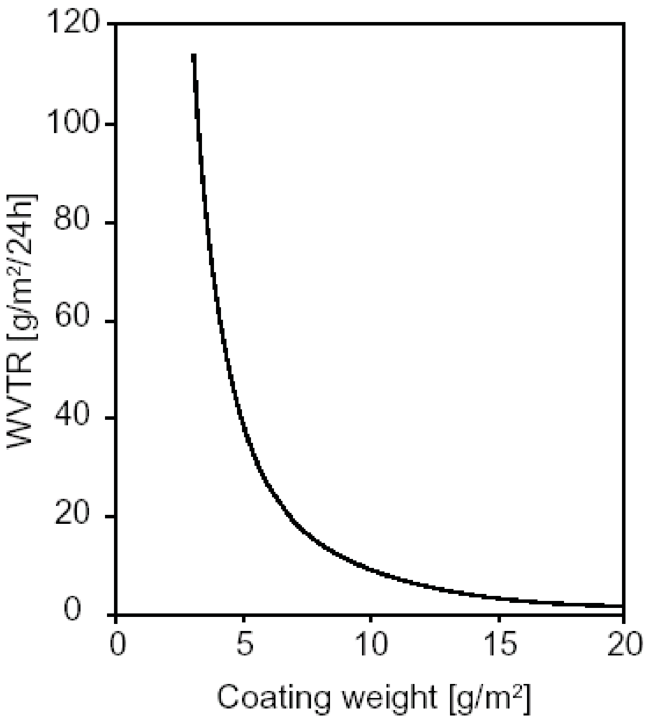





## Water Vapour Transmission Rate (WVTR)

- **Gravimetric Cup – Method, SCAN P22:68 (ASTM E96)**
- **Sample stored in specific test conditions: for example 75% RH ja 25˚C**
- **WVTR [g/m$^2$, 24h]**

Example of how WVTR depends on coating weight




 Ref: Savolainen (1998) 

# Few WVTR values found in literature

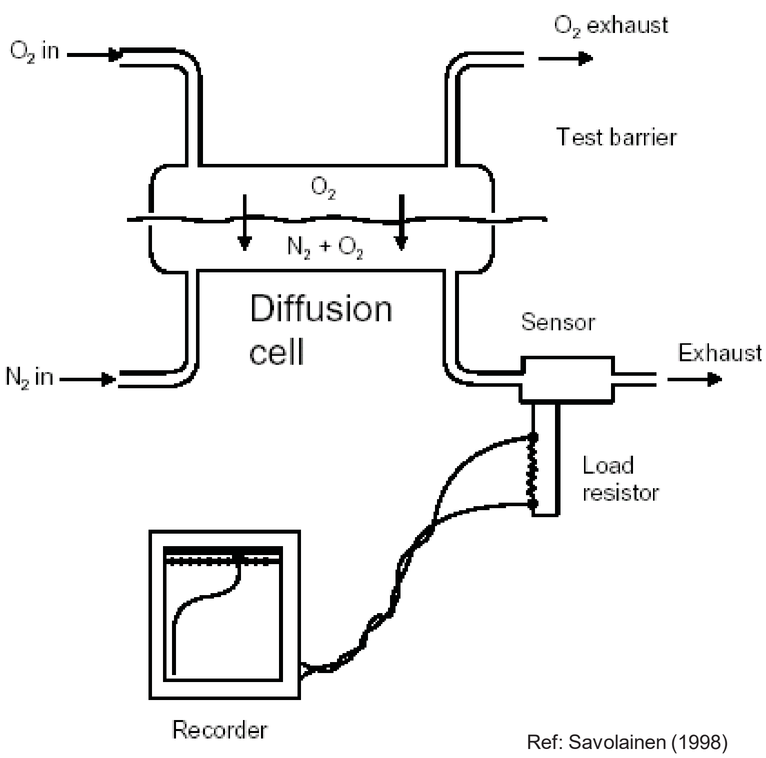
| Material | Test conditions | WVTR | Units | Note |
|---|---|---|---|---|
| LDPE | 37° C, 90% RH | 21.7 | $g/m^2$*day | |
| HDPE | | 4.6 | | |
| PP Unoriented | 38° C, 90% RH | 0.6 – 0.7 | (g mil)/ (100 $in^2$*day) | |
| PP Oriented | | 0.2 – 0.5 | | |
| PS | | 7 - 10 | | |
| PET | | 1 - 2 | | |
| PVC Unplasticized | | 2 – 5 | | |
| PVC Plasticized | | 15 - 40 | | Values depend greatly on plasticizer content |
| Nylon | 37° C, 90% RH | 248 - 341 | $g/m^2$*day | |
| Cellophane | | 18 - 198 | | |
| Cellulose acetate | | 2480 | | |
| PE – vinyl acetate | | 31 - 46 | | |
| Polyvinyl chloride-acetate (plasticized) | | 77.5 - 124 | | |
| Polydimethylsiloxane | ? | 0.01 – 0.006 | $g/m^2$*day | |

[i] * Hallström, B., Gekas, V., Sjöholm, I., Romulus, A. M., *Handbook of Food Engineering: chapter 7 MassTransfer in Foods*, 2nd edition, 2007, p. 471 – 493. Taylor and Francis Group, LCC.
[ii] * Caudill, V., 2005, *Packaging. Bailey's Industrial Oil and Fat Products*, John Wiley & Sons, Inc. DOI: 10.1002/047167849X.bio043
[iii] * Poliskie, M., *Solar Module Packaging, Chapter 2*, CRC Press, p. 21-105. ebook ISBN: 978-1-4398-5074-9. DOI: 10.1201/b10941-4.



## Oxygen Transmission Rate ($O_2$TR)

- Oxygen is brought on the surface side of the sample and the carrier gas on the backside will collect the oxygen that has migrated through the sample
- The volume of the migrated $O_2$ is measured
- OTR [$cm^3$ / ($m^2$, d, bar)]




Ref: Savolainen (1998)

NEW MODEL – AQUATRAN 2
→ 5 x $10^{-5}$ g/m²/d

## MOCON AQUATRAN MODEL 1G

HIGH SENSITIVITY COULOMETRIC WATER VAPOR TRANSMISSION RATE TEST SYSTEM

- Bases on coulometric phosphorous pentoxide sensor
- WVTR range: 0.0005 – 5 g/m²/d
- Test temperature range: 10 – 40 °C
- Relative humidity range: 35 – 90, 100 %
- DIN 53122:2, ASTM F1249

## MOCON OX-TRAN 2/21 MH + SS

STANDARD OXYGEN TRANSMISSION RATE TESTING SYSTEM

- Bases on coulometric sensor
- $O_2$TR range:
  - Unmasked: 0.05 – 200 cm³/m²/d
  - Masked: 0.5 – 2000 cm³/m²/d
- Test temperature range: 10 – 40 °C
- Relative humidity range: 0 (SS), 35 – 90 % (MH)
- Edge leakage adaptors for coated papers/boards
- Package testing adapters
- ASTM D3985 (films), ASTM F1927 (films), ASTM F1307 (packages)

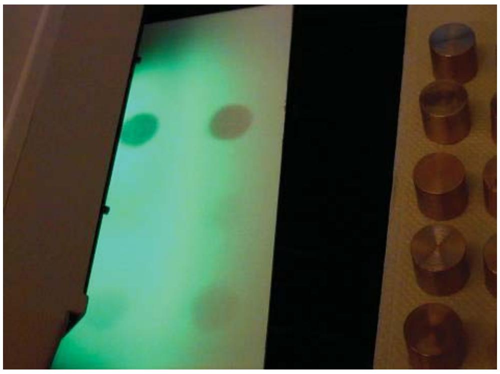



## MOCON PERMATRAN-C 4/41

**STANDARD CARBON DIOXIDE TRANSMISSION RATE TESTING SYSTEM**

- Bases on infrared sensor
- $CO_2$TR range:
  - Standard: 1 – 10 000 cm³/m²/d
  - Masked: 10 – 500 000 cm³/m²/d
- Test conditions: T = 15 – 50 °C, RH = 0 %
- Relative humidity range: 0 (SS), 35 – 90 % (MH)

- **Grease barrier testing** according to ASTM F119-82
- Visual analysis of penetration of test grease, for example olive oil
- Analysis of time in which the grease has penetrated through the sample (hours, days)

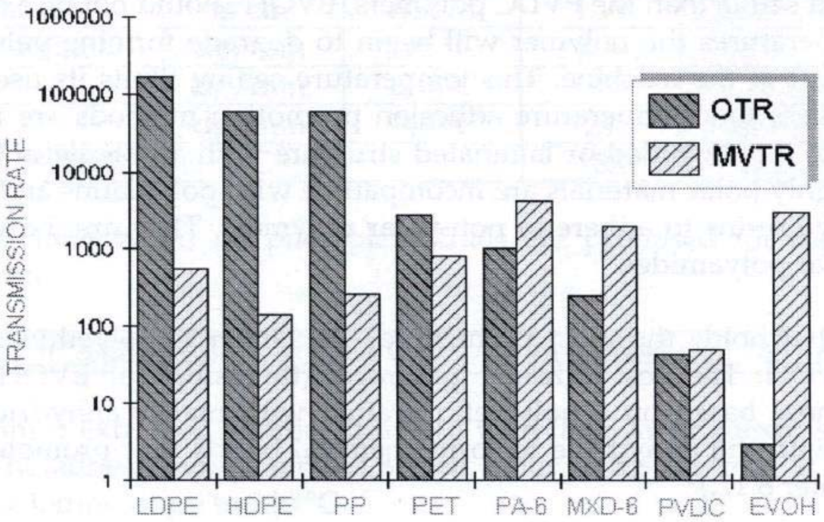




| | Permeability for 1µm (gases: $cm^3/m^2/d$ or water: $g/m^2/d$) | | |
|---|---|---|---|
| **Polymer** | $O_2$ | $CO_2$ | $H_2O$ |
| PVDC | 10–225 | 12–100 | 8–85 |
| EVOH (dry) | 5–24 | 9.8–88 | - |
| EVOH (100 % RH) | 170–575 | - | 360-2100 |
| PA-6 | 200–900 | 400–3 600 | 4 300–8 100 |
| PA-11 | 900 | 4 300 | 1 600 |
| PET | 1 200–2 300 | 2 900 | 500–800 |
| HDPE | $4.4–7.0 \cdot 10^4$ | - | 120–180 |
| LDPE | $1.1–2.0 \cdot 10^5$ | - | 400–600 |
| PP | $6.0–9.5 \cdot 10^4$ | - | 180–300 |
| COC | $1.8 \cdot 10^4$ | - | 20–40 |
| Starch+PCL | 20–40 | - | $3.5-9.0 \cdot 10^4$ |
| Chitosan (dry) | 12 | - | - |
| Chitosan (100 % RH) | $9.3 \cdot 10^4$ | - | - |
| PLA | $2.0–6.0 \cdot 10^4$ | - | 3 000–5 000 |
| Ecoflex® copolyester | $8.0 \cdot 10^4$ | - | 8 500 |
| PHBV | $1.5–3.5 \cdot 10^4$ | - | 1 500-2 500 |
| PCL | $1.0–6.0 \cdot 10^4$ | - | 8 000 |

**WVTR & OTR depend on e.g. polymer, coating grammage (thickness), substrate, conditions**

Fig. 9.1 OXYGEN AND MOISTURE BARRIER OF POLYMERS




OTR : µm-cm³/day/atm./23 °C/50 % RH
MVTR : µm-g/m³/day/38 °C/90 % RH

A high barrier polymer is defined as:

*A polymer that allows an oxygen transmission rate of* **<20 cm³/m²/day-atm. @ 23 °C** *per 25 µm thickness of film.*

Johanna Lahti

TAMPERE UNIVERSITY OF TECHNOLOGY

# Part 4: Nanoscale R2R surface modification and novel thin film technologies

- Flame, corona, atmospheric plasma
- ALD (Atomic Layer Deposition)
- LFS (Liquid Flame Spray)

# Surface treatment methods

- **Ozone** treatment of polymer melt (in extrusion coating)
- **Corona** discharge treatment
- Atmospheric **plasma** treatment
- **Flame** treatment
- **Priming** (i.e. application of adhesion promoter on the substrate)

➢ Each method can have several effects that improve adhesion

➢ A modern extrusion coating line usually has both pre-treatment and post-treatment units

- In addition, there are **several thin layer technologies available** for grafting/coating/surface modification; CVD processes, sol-gel coating, etc.



# Flame treatment

– **Flame treatment is used to change the chemical composition of the surface, increase the surface energy, modify surface topography, or remove the contaminants and weak boundary layers**

– Substrate is exposed to direct flame, which modifies the surface of substrate. In the combustion reaction different thermally activated atoms and molecules, e.g. oxygen ions and atoms, as well as free electrons are formed

– These react with the surface of substrate composing carbonyl, carboxyl and hydroxyl groups among others

– Consequently polarity and oxidation of the surface increases and leads into improved wetting and adhesion

# Flame treatment

- The flame treatment clearly improves adhesion on surfaces of paperboard or polymer
- However, the mechanism behind this adhesion improvement is not necessarily the same
  - In the surface of polymer occurs crosslinking, breaking of the long-chain molecules and some micro roughening
  - In the surface of paperboard micro roughening as well as surface activation takes place. Additionally, the flame treatment removes possible contaminants or sticking fibers from the surface of substrate



# Flame treatment

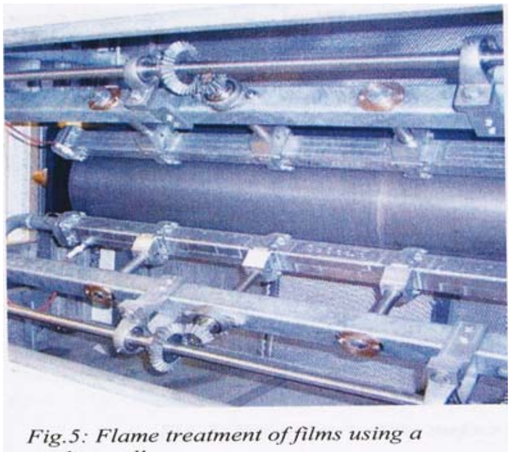


*Fig.5: Flame treatment of films using a cooling roll*

•For obtaining the best possible flame treatment results, burner design and flame treatment parameters must be controlled and optimised

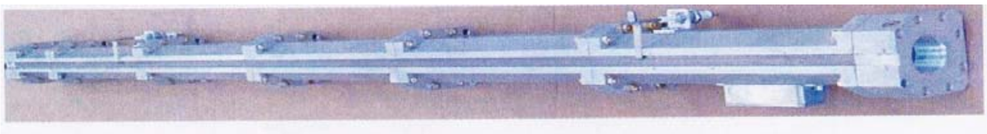
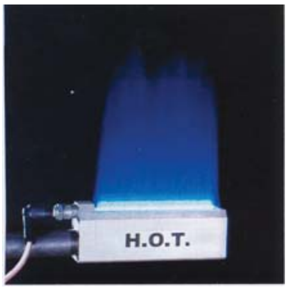
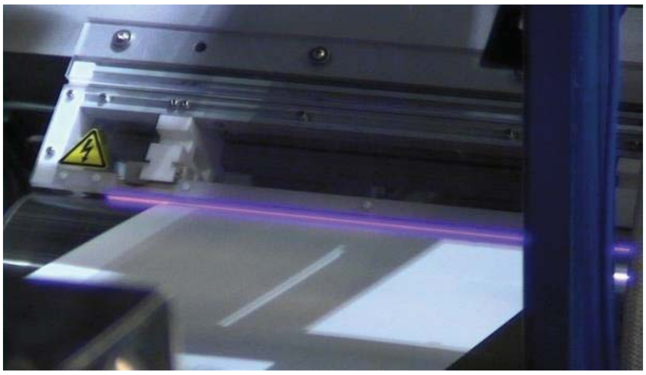


*Fig.6:: Burner used for large web widths*

- **The most important flame treatment parameters are:**
  - The gas rate (output/volume)
  - The air-gas ratio
  - The burner vs. substrate distance
  - The line speed (exposure time)



## Target of corona treatment



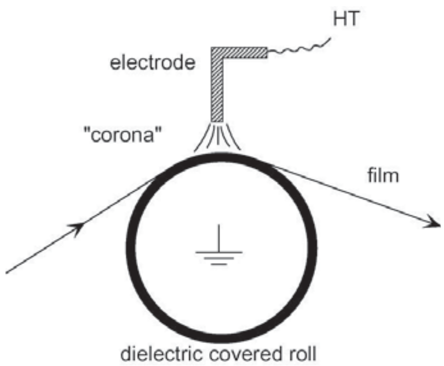
- To activate the surface
- As a pre-treatment, to improve adhesion between substrate and coating
- As a post-treatment, to improve ink adhesion, especially with coated materials
  - Depending on the printing method and ink, the required surface energy level is usually around 30-42 mN/m
  - Thumb rule: surface energy of the substrate should be 7-10 mN/m > surface tension of the printing ink

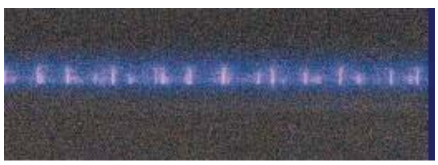


# Principle of corona treatment

•Corona discharge treatment is generally performed in air at atmospheric pressure. The substrate moves over a grounded metal roll covered with an insulating material. A high frequency - high voltage electrode is placed over the substrate forming an air gap between the substrate and the electrode. The corona treatment effect is based on bombarding the surface of the substrate with electrons.

•The gap is small, usually 1.5-2.0 mm, and it must be uniform over the width of the film. With the right power supply, a stable, uniform corona discharge can be established: air between the substrate and the electrode becomes ionised creating a conducting corona. A plasma is formed and a light blue colour can be observed in the air gap.



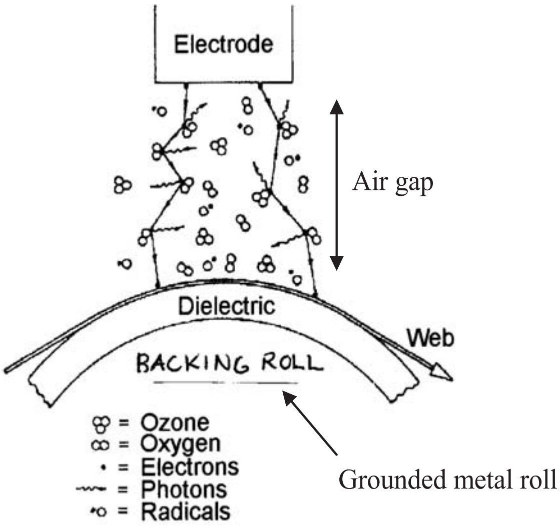



# Effects of corona treatment

1) Chemical changes

2) Physical changes

3) Electrical changes

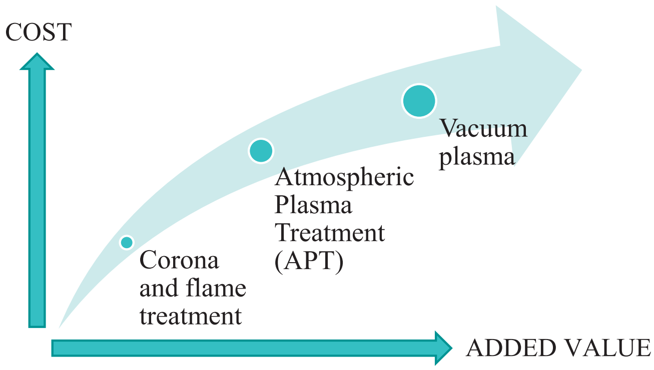


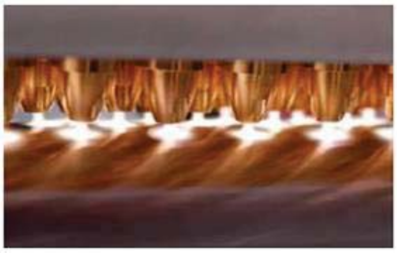

Changes depend on the substrate that is treated (paper/board/coated/plastic, etc.)

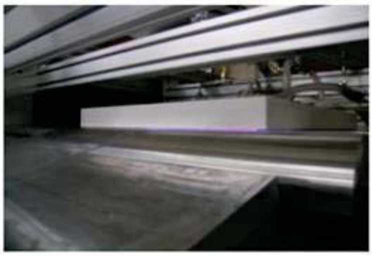


# Plasma surface modification

- Plasma is the fourth state of matter (solid, liquid, gas, plasma), and can be seen in nature e.g. as lightning
- A plasma is a (partially) ionised gas in which ions and electrons are present as well as radicals and molecules in an excited state
- Non-thermal plasmas based on atmospheric Dielectric Barrier Discharge (DBD) are typically used for surface treatment of polymers, metals and textiles





Ref. AFS and VITO

# Plasma treatment

- Plasma treatment
  - As with corona, electrical ionisation of a gas
  - Lower voltage levels than with corona
  - Surface activation and deposition
  - Different process gases (e.g. He, N, Ar)
  - Increase in surface energy and improved adhesion properties

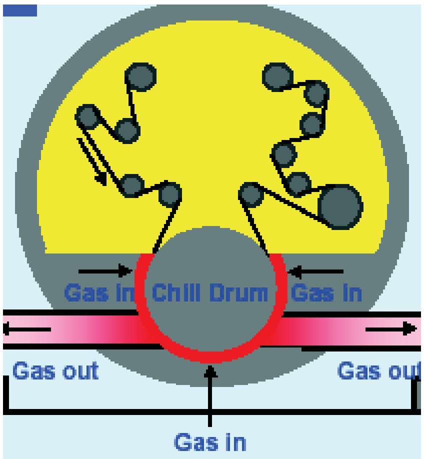
- Atmospheric pressure plasmas
  - Can be located in the converting line similar to corona treaters

- Vacuum plasma (low pressure plasma): pressure 0,01 – 0,1 mbar.



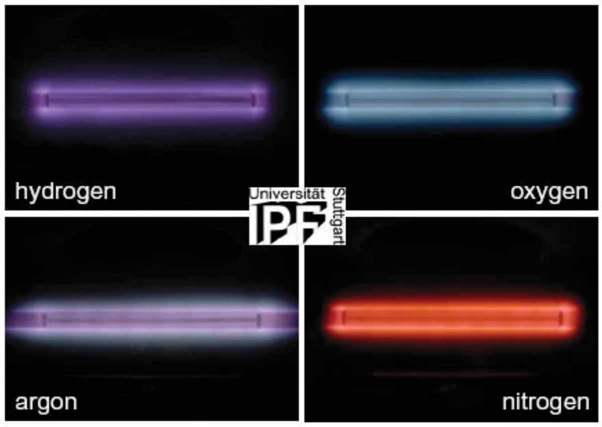
| Atmospheric Plasma Treatment | Corona & Flame Treatment |
|---|---|
| **+ operate in atmosphere (no vacuum/chambers), possibility to select treatment gas → tailored surface chemistry** | + operate in atmosphere → no vacuum or chambers<br>- operate in atmosphere → fixed chemistry (air) |
| **+ high energy densities → effective treatment** | - relatively low energy densities |
| **+ longer lasting treatment** | - decay of treatment level (aging) |
| **+ more uniform treatment (uniform flame)** | - limited treatment uniformity, possible pin holes (corona) |
| **+ no reverse side treatment (no breakdowns through the material)** | - reverse side treatment → blocking problems (corona) |
| **+ on-line, roll-to-roll process** | + on-line, roll-to-roll process |
| - more complex process → control and scale up more difficult | + simple and acknowledged methods |
| - certain treatment gases quite expensive | + relatively low cost and high speeds |

Vacuum plasma / Tetra Pak




Atmospheric pressure plasma

Colour of the plasma flame depends on the process gas






# Plasma surface modification

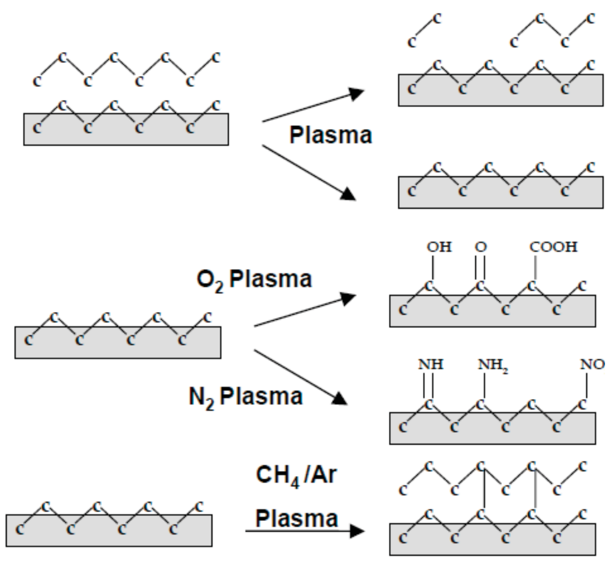
- Plasma activation

Functional chemical groups are created to the surface of the treated material → For packaging materials e.g. to enhance adhesion properties, wettability and printability of surfaces

Cleaning, etching and sterilisation

Activation

Coating

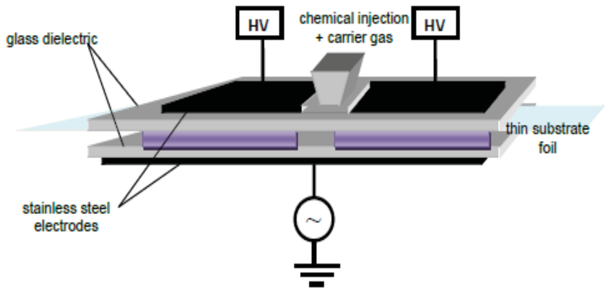



Ref. Vangeneugden, D., 2007

# Plasma surface modification

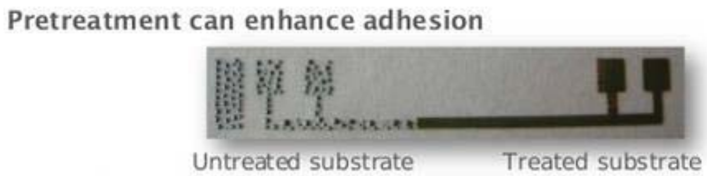
- Plasma deposition

- A completely new surface is created which enables the possibility to create barrier coatings from precursor such as e.g. sol-gels chemistry.
- The desired surface properties can be obtained by injecting the precursor to the plasma discharge.
- Plasma discharge is chemically very reactive environment which causes the precursor to be fragmented into reactive species. These reactive species react with each other and also with the surface to produce a coating to the surface of the treated substrate.
- Depending on the chemistry used, various plasma deposited coatings can be produced, for example with grease/WV/oxygen barrier




Ref. VITO





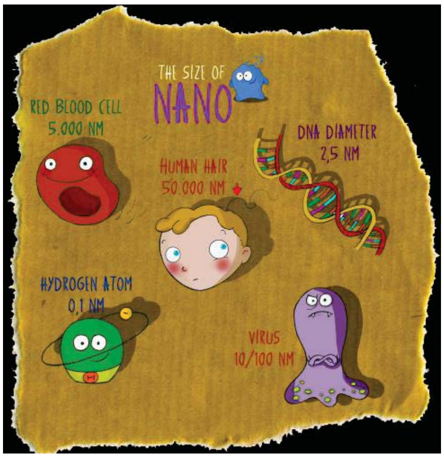

- Example: UV inkjet printability of PP film
  - Argon plasma treatment enhances ink wetting and uniformity of the printed lines
  - In addition, adhesion properties of ink are improved

**Untreated Corona Ar-Plasma**

***PP film / 1 pixel line width / 300 dpi / UV ink***

Ref. Lahti, J. et al. 2011

# Plasma systems can be used for:




– **Chemical functionalisation** (~1-100 nm)
  - O-containing groups
  - N-containing groups
  - F-containing groups
  - SiOx-like coatings
  - Acrylate/acrylic/ester/vinyl…. functionalities

– **Deposition of thin functional coatings** (~10-500 nm)
  - ➢ Adhesion
  - ➢ Release
  - ➢ Antibacterial
  - ➢ Corrosion protection
  - ➢ Reduced friction
  - ➢ Barrier
  - ➢ …..

**Benefits of plasma deposition process:**

- Dry surface treatment
- Cold plasma
- Versatile due to broad range of precursor technologies
- Atmospheric process





# Liquid Flame Spray (LFS) process

Ref. Tuominen, M. et al 2013

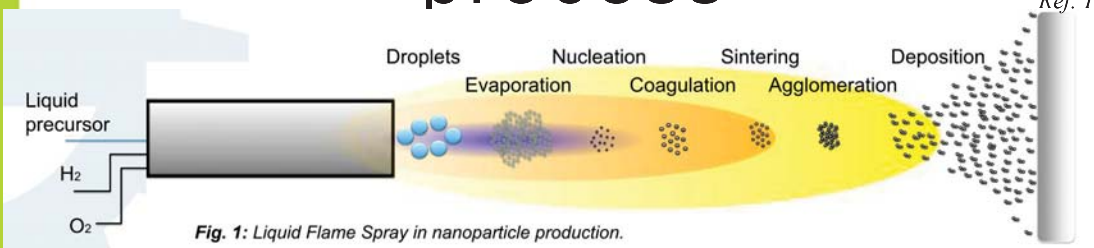
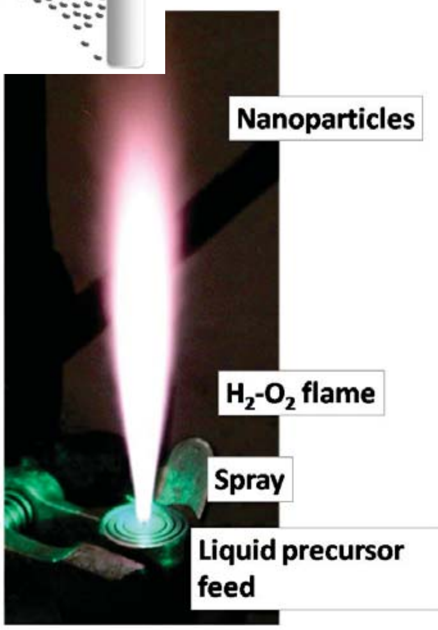



*Fig. 1: Liquid Flame Spray in nanoparticle production.*

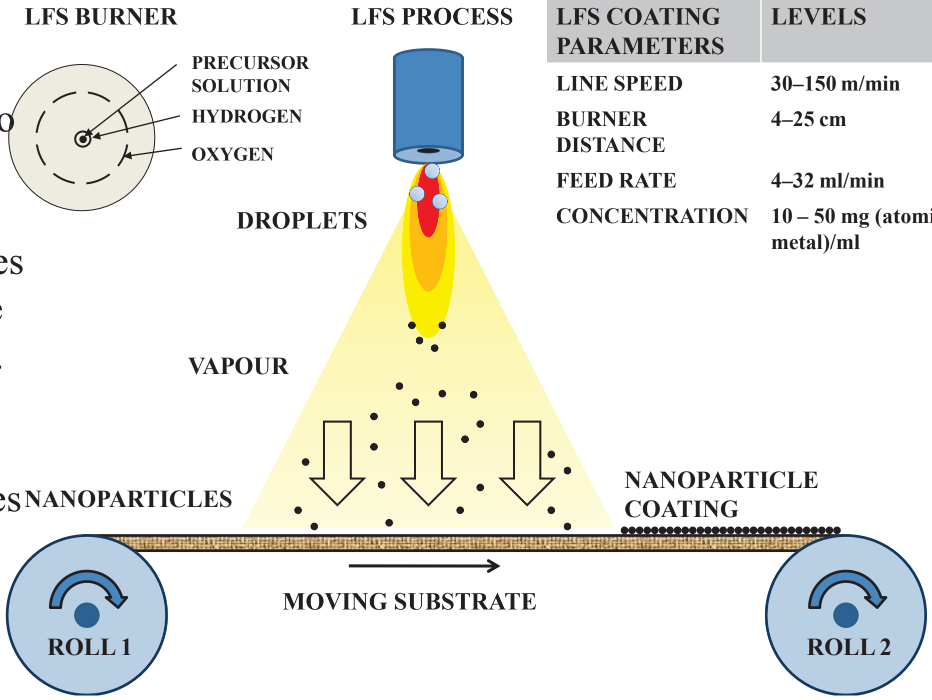
- Generate nanoparticles with flame process, i.e. liquid flame spray
- Particle material: $TiO_2$, $SiO_2$, $ZrO_2$, $Al_2O_3$, Ag, Pd, Pt, Au, oxides of Na, Mg, Sr, Si, Ti, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Mo, Ag, W, Pl, Nd, Pr, Yb, Se … and mixtures/composites
- Particle size range: 2-200 nm
- Develop thin layer -coatings (~20 nm-1 $\mu m$) on e.g. fiber-based packaging materials
- Porous coatings: porosity >90%




**LIQUID FLAME SPRAY**

# Liquid Flame Spray (LFS) process

- Liquid precursor solution is injected into the hydrogen-oxygen flame.
- The solution evaporates and reacts in the flame forming nanoparticles.
- The flame is directed towards the surface where the nanoparticles concetrate creating a coating layer.




| LFS COATING PARAMETERS | LEVELS |
|---|---|
| LINE SPEED | 30–150 m/min |
| BURNER DISTANCE | 4–25 cm |
| FEED RATE | 4–32 ml/min |
| CONCENTRATION | 10 – 50 mg (atomic metal)/ml |



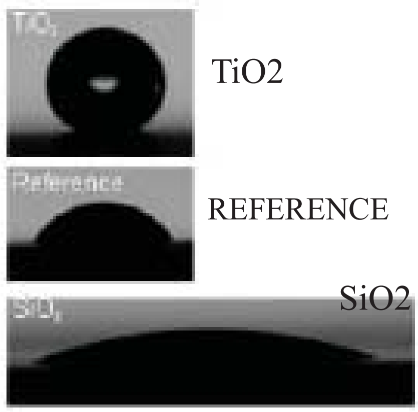
*Ref. Teisala, H., 2010*



# Liquid Flame Spray (LFS) process

- Liquid Flame Spray (LFS) can be used to generate
  - ***superhydrophobic*** CA > 150°(nano-titania, $TiO_2$) and
  - ***superhydrophilic*** CA < 10°(nano-silica, $SiO_2$)

  surfaces onto different substrates like paperboard and paper




- LFS has great potential for industrial scale method because of its continuous nature, low coating amounts (30-50 mg/m2) and high line speeds
- The different amount of carbonaceous material on the $TiO_2$ and $SiO_2$ coatings is the main reason for the opposite wetting behaviour of the surfaces

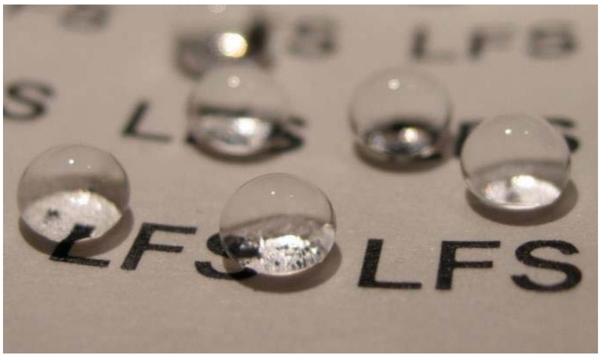


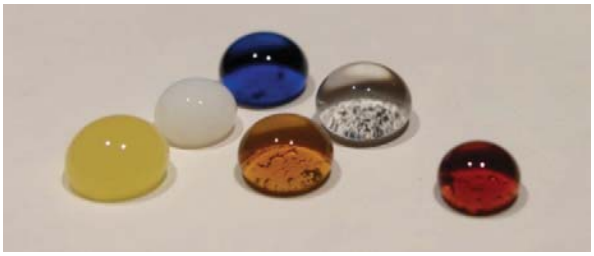
*Ref. Teisala, H., 2010; Mäkelä, J., 2008.*

# Functional nanoparticle coatings using Liquid Flame Spray (LFS)

<u>LFS/$TiO_2$ coating properties:</u>

- Gas permeable (breathable)
- Transparent
- **Multifunctional:**
  - ✓ Superhydrophobicity/(philicity)
  - **LFS/$TiO_2$: >150°**
  - **LFS/$SiO_2$: <10°**
  - ✓ Adjustable wettability by surface stimulation
  - ✓ Self-cleanability



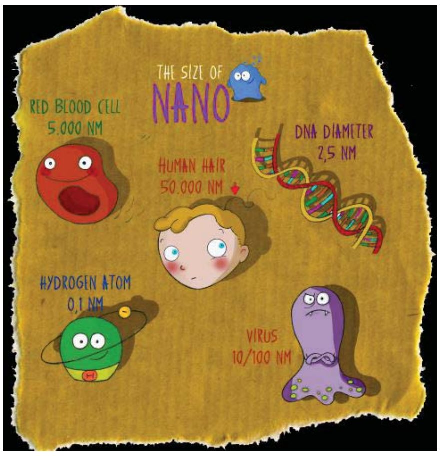



*Ref. Tuominen, M. et al 2013*



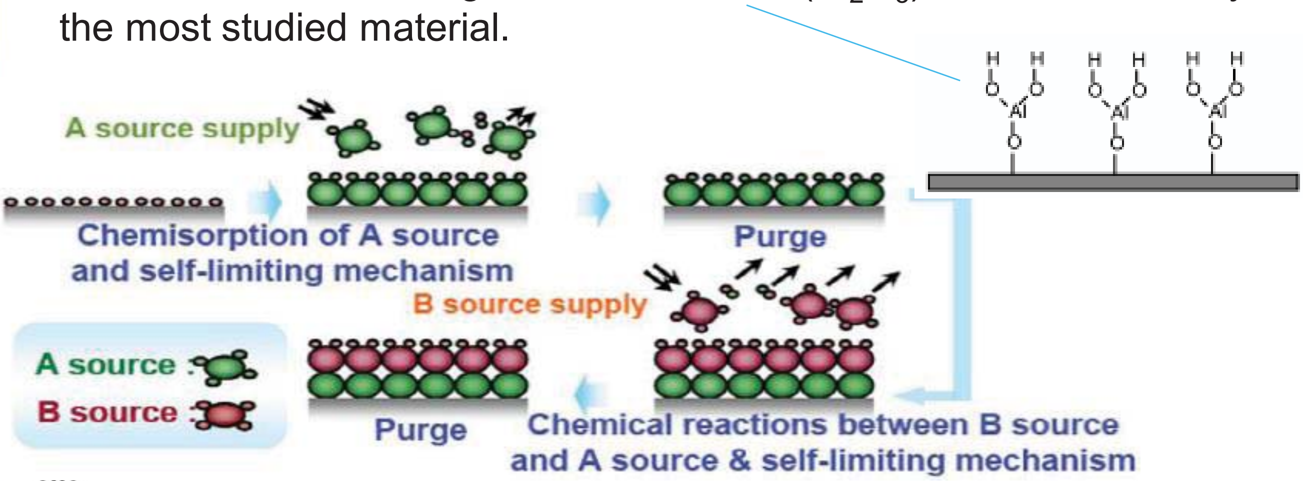
# Atomic Layer Deposition (ALD)

- ALD is a CVD (Chemical Vapour Deposition) process, which enables deposition of highly conformal and uniform thickness thin films with monolayer precision
- <u>Purpose</u>: **thin, tight and stable coating** from gaseous precursors
- <u>Main advantage</u>: **the conformality and uniformity** which can be obtained regardless of the orientation or shape of the substrate; i.e., there are no pinholes in the film
- In ALD process, thin films of material are deposited one atomic layer at a time
- Thickness of a typical ALD layer can vary from 1 to over 100 nm



# Atomic Layer Deposition (ALD)

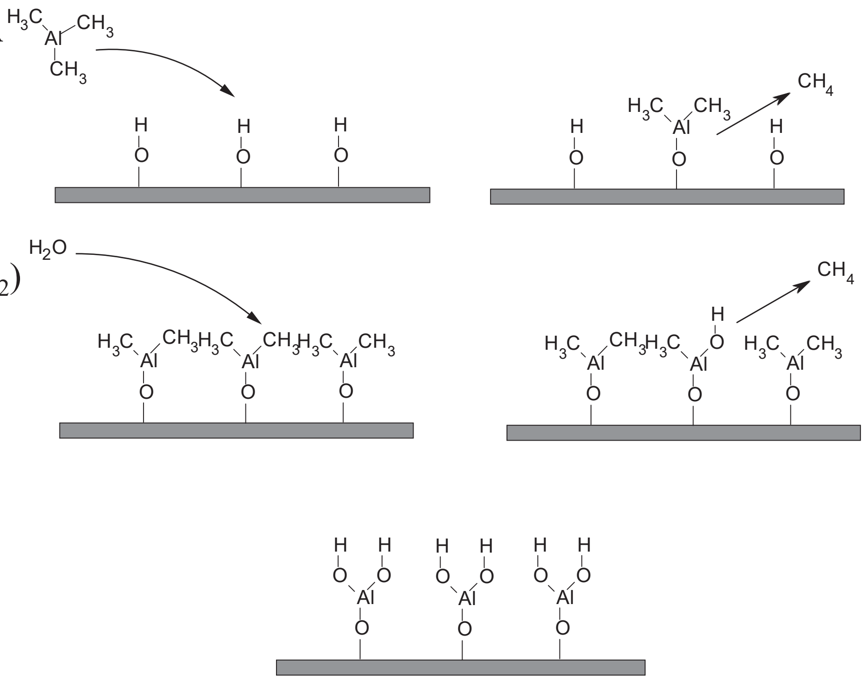
- ALD coating consists of several reaction cycles. One cycle is able to achieve ~0.1 nm layer depending on the coating material and process parameters.
- Typically uses two precursors (TMA, trimethyl aluminium and water) to form film material, e.g. aluminium oxide ($Al_2O_3$), which is currently the most studied material.






# ALD is a chemical vapour deposition (CVD) process based on chemical reactions on the surface of a substrate

- Hydroxyl (-OH) substrate is exposed to **first precursor, TMA** (trimethylaluminum).
- Methane is flushed away from this reaction.



- Dimethyl aluminum (-Al($CH_3$)$_2$) substrate is exposed to **second precursor, water.**
- Methane is flushed away also from this reaction.

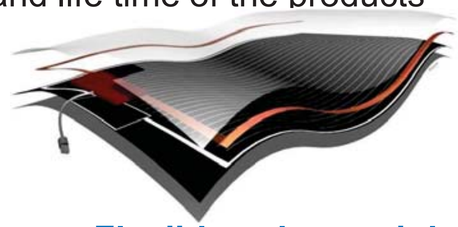
- **The $Al_2O_3$ layer is ready.** The process can now be started again from the beginning.

# NanoMend EU project

NANOMEND
METROLOGY FOR ENHANCED NANO-SCALE DETECTION, CLEANING AND REPAIR

- €7.25million FP7 funded, 4 year long project from Jan 2012, in total 14 partners from Finland, Germany, Switzerland, Netherlands and UK.
- "Enhanced in-line Detection, Cleaning and Repair of Nano-scale Defects for Large Area Substrates„ (NANOMend)

  www.nanomend.eu
- The goal of the project is to bypass the state-of-the-art level of defect detection, cleaning and repair technologies in **fibre-based packaging material** and **flexible solar panel productions**
- Defects within these materials reduce the yield (in production), performance and life time of the products



**Flexible solar modules**

**Food packaging**

TAMPERE UNIVERSITY OF TECHNOLOGY

**Consortium includes 14 partners from Finland, Germany, Switzerland, Netherlands and UK**

NPL National Physical Laboratory

cpi ...the future inspired

IBS Precision Engineering

University of Huddersfield

Fraunhofer IVV

Open your mind. LUT. Lappeenranta University of Technology

Flisom Flexible Solar Modules

TAMPERE UNIVERSITY OF TECHNOLOGY

KITE INNOVATION EUROPE

TNO innovation for life

ISOVOLTAIC

storaenso rethink.

ISRA VISION

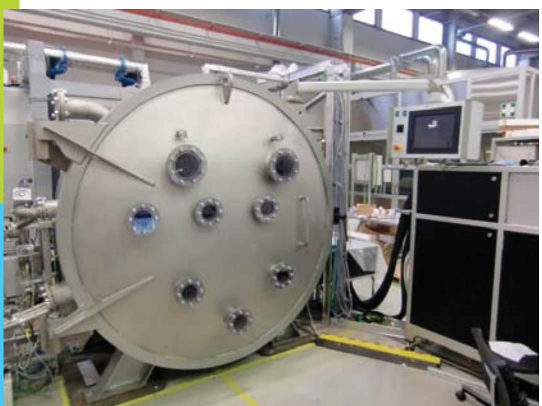
iscent

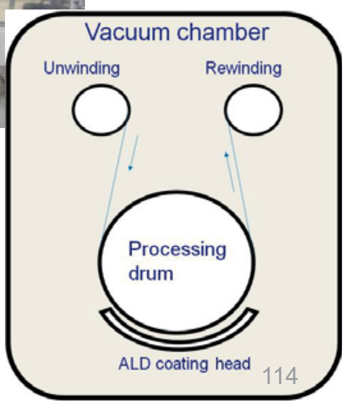
- **NanoMend** was a collaborative, end user led project aimed at pioneering novel technologies for in-line detection, cleaning and repair of micro and nano scale defects on thin films deposited on large area substrates in fibre-based packaging and flexible solar panel productions.
- The aim was to integrate these technologies into systems that work at speeds required for continuous production, thus enabling the new technologies to improve product yield and performance, while keeping manufacturing costs low.
- Defects like pinholes are microholes and like other discontinuity or non-homogeniety they strongly reduce barrier properties of (packaging) materials
  - Pinholes in material or coating layer can restrict or even prevent the usage of the material in certain applications
- **Role of TUT and LUT was research and demonstration of detection and cleaning systems relating to production of packaging materials.** Furthermore, target was to study use of **(R2R) ALD technology** in production of packaging materials and to create improved properties.




# Roll-to-Roll Atomic Layer Deposition (R2R ALD)

- A new R2R ALD process opens up a possibility to perform high-throughput ALD processing for flexible substrates





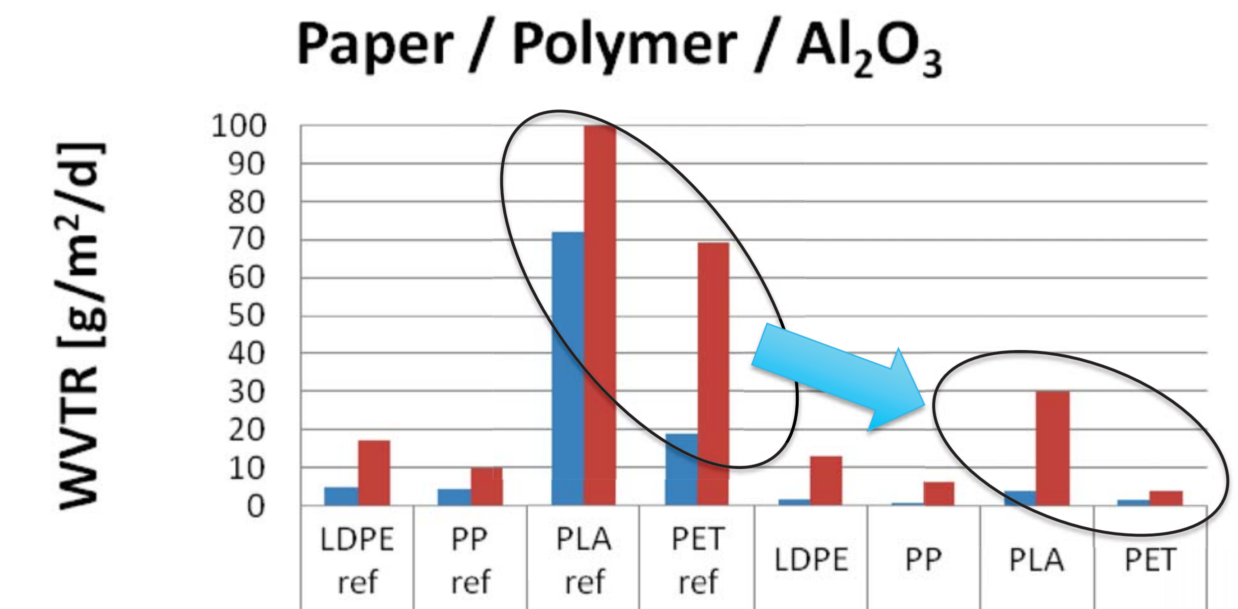

**Beneq WCS 500 Roll-to-Roll ALD system at LUT in Mikkeli (Finland)**
Process description available in YouTube

# ALD (Atomic Layer Deposition) as part of a package

- The targets for ALD technology as part of a packaging can be:
  - **Decrease the amount of other materials by extra ALD layer** (if the barrier properties of the structure is the reason for thicker layer).
  - **Replace the whole layer in the package** (e.g. aluminium foil in ultimate case)
  - To create hydrophopic / hydrophilic –surface
  - Improve optical properties of the surface
- Concerning of barrier properties, the ALD process on moving substrate has been a success. The oxygen and water vapor barrier of paper / polymer / $Al_2O_3$ -structures has improved significantly. In addition, UV barrier properties have been achieved.



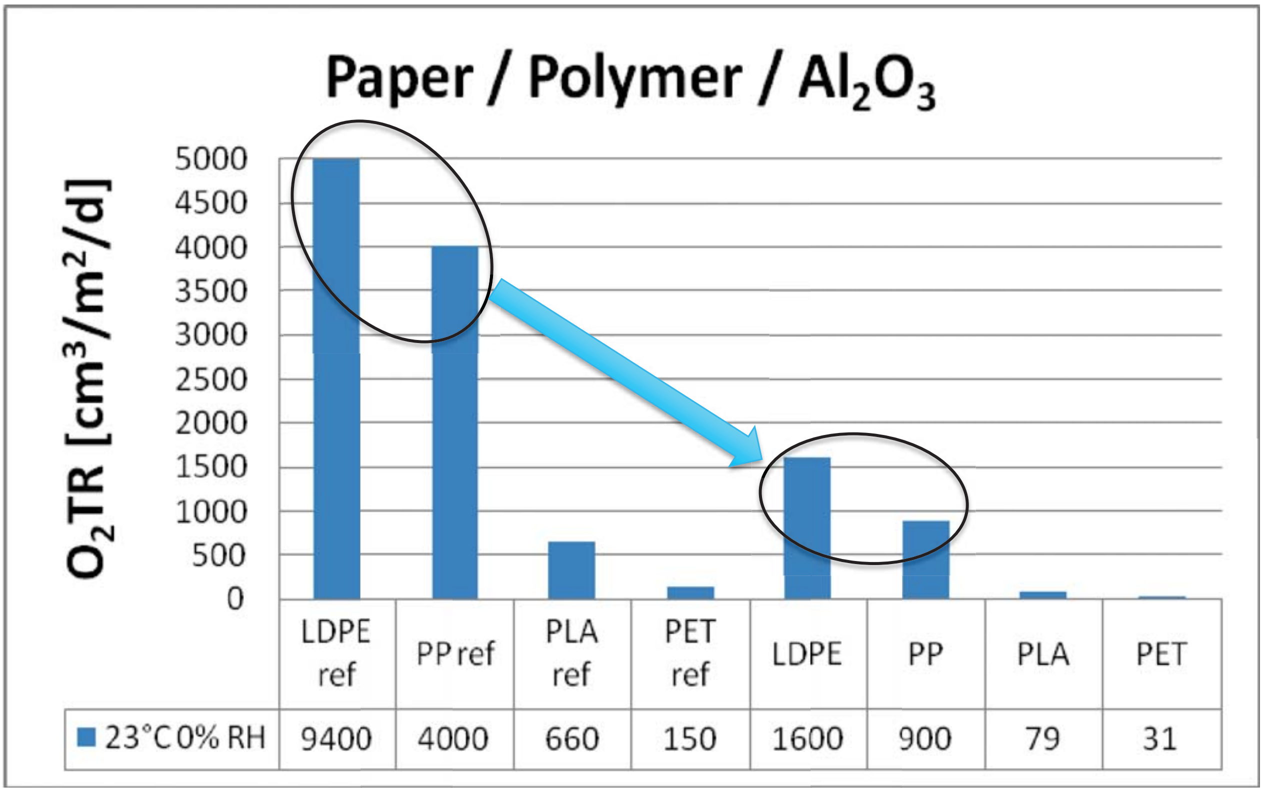
EXAMPLE: **Water vapour barrier improvement**




| | LDPE ref | PP ref | PLA ref | PET ref | LDPE | PP | PLA | PET |
|---|---|---|---|---|---|---|---|---|
| 23°C 50% RH | 4,6 | 4,2 | 72 | 19 | 1,4 | 0,5 | 3,8 | 1,4 |
| 38°C 90% RH | 17 | 10 | 290 | 69 | 13 | 6 | 30 | 4 |

 Ref. Johansson, P., 2010 

## EXAMPLE: Oxygen barrier improvement






## Acknowledgements & Further information


- Research work presented has been funded by EC FP7 programme and Finnish National Funding Agency TEKES


Tekes

- www.nanomend.eu
- www.tut.fi/plasmanice
- www.tut.fi/mol
- www.actinpak.eu/

Plasma NICE SEVENTH FRAMEWORK PROGRAMME NANOMEND

# Thank you for your attention!

**Dr. Johanna Lahti**
**Senior Research Fellow**
**Tampere University of Technology**
**johanna.lahti@tut.fi**



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## 14. Advanced Screen Printing

### Fernando Zicarelli Fernández, Asada Mesh

### Biography

2011 - Now: Europe's new business development manager for Asada mesh – Spain
Introducing Europe´s customers to Asada´s latest mesh technology
Screen printing technology advisor

2009 - 2011: Metallization expert at epfl in Neuchâtel – Switzerland
Developed high efficiency heterojunction solar cells

2007 - 2009: Director of process development at eoplex technologies – USA
Developed 3d screen printing components

1990 - 2007: Various development positions – USA
Business developer of v-screen mask technology (5 years)
Development of screen mask technology (7 years)
Engineer of hybrid thick film circuits (5 years)

### Abstract

n/a

# Summer School 2016

## at

## WCPC

## Swansea University

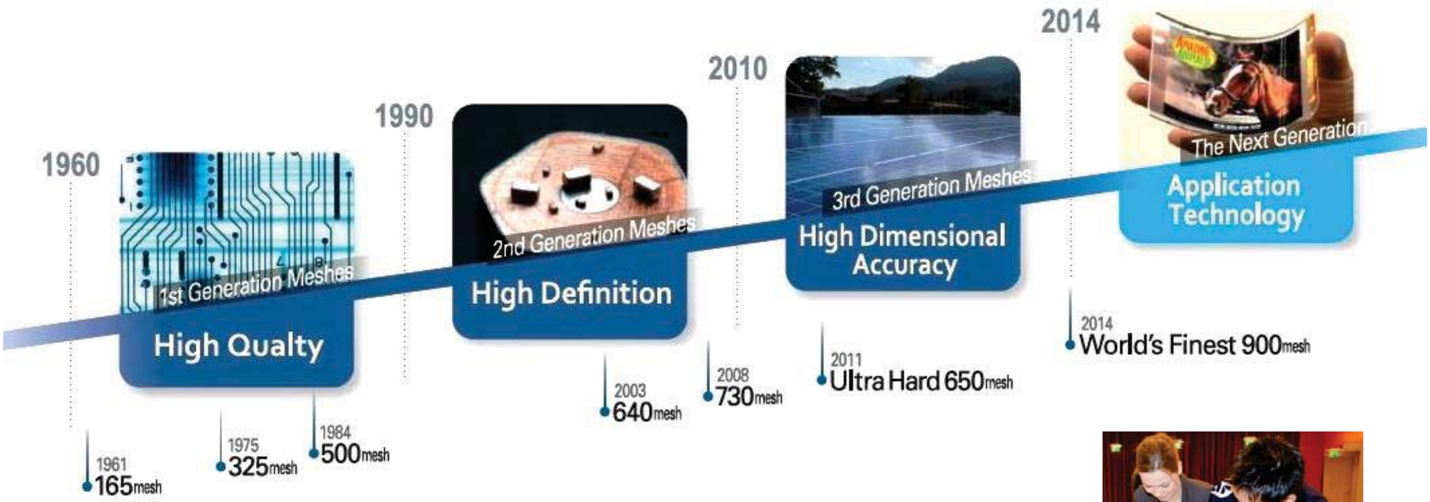
WCPC

Swansea University
Prifysgol Abertawe

icmPrint

## Roadmap for Advanced Screen Printed Microelectronics

WCPS // JULY 11th – JULY 15th




ASADA MESH CO.,LTD.

30 micron
Hand Print

# Company Overview

ASADA MESH CO.,LTD.

## Asada Mesh Co., Ltd

Founded in: **1940**

Employees: **258** (as of May 1, 2015)

Scope of Business:
**Manufacturing of woven wire mesh**
for Screen printing
for Filtering, sieving etc…

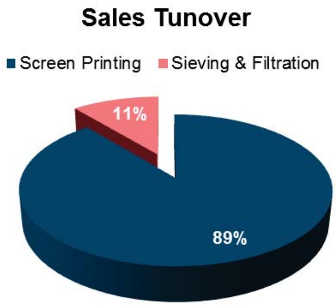


Osaka Headquarters


Kagoshima Plant, Japan


Suzhou Plant, China


Handloom




# Contents:

ASADA MESH CO.,LTD.

1. Open Innovation Hub
2. Stainless Mesh & Screen Printing
3. Ultra-Hard HS-D-mesh
4. The Latest Screen Printed Electronics

# Contents:

ASADA MESH CO.,LTD.



# Open Innovation Hub

ASADA MESH CO.,LTD.

At OIH, we provide the latest technology of the world's finest metal mesh made from high quality materials.
By transcending the boundaries between various fields, we will contribute to bringing people together to create new technology and Innovation.

OPEN INNOVATION HUB
ASADA MESH CO.,LTD. R&D Center

**Asada Mesh Co., LTD. R&D Center** (aka: **Open Innovation Hub**)

**Total technical screen printing support** from Screen Selection, Screen-Making, Screen Printing Optimization and analyzation.
Counselling in the choosing of the best mesh based on field and usage, and in the development of new products.

We look forward to having you here.

Up to 1000mm Size Screens

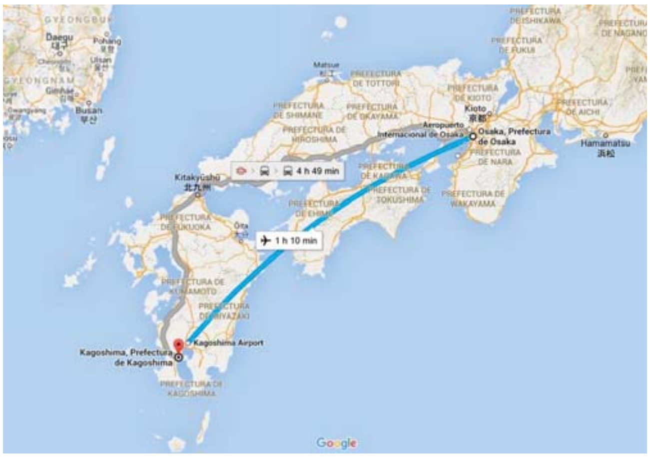
4 Printing Machines

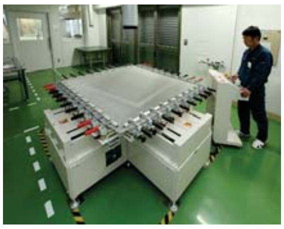
Asada Mesh New R&D Center

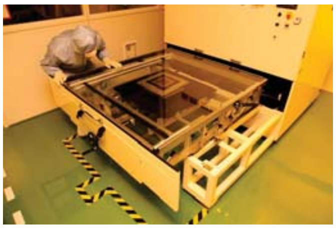
# Open Innovation Hub

ASADA MESH CO.,LTD.

OPEN INNOVATION HUB
ASADA MESH CO.,LTD. R&D Center





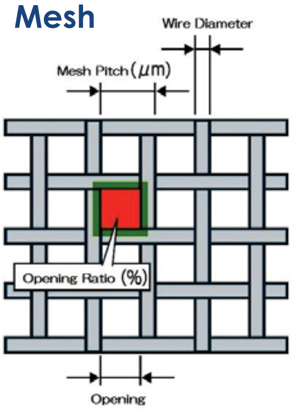
Asada Mesh New R&D Center

# Understanding Mesh, Screens and Printing:

ASADA MESH CO.,LTD.

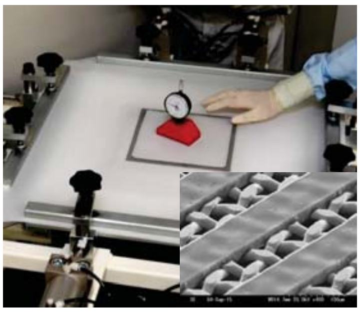


## Mesh



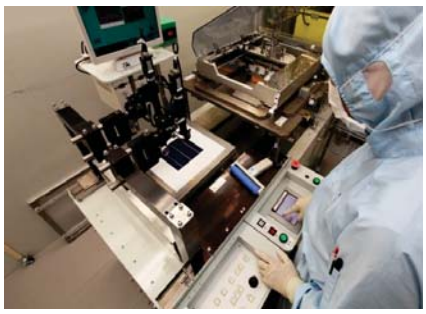

**Determined by**
- Strength
- Opening Ratio
- Thickness
- Mesh Count

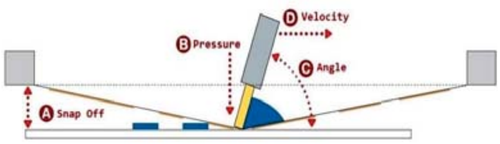
## Screen



**Training program of learning**
- Stretching Method
- Appropriate Tension
- Trampoline (Poly + SUS)
- Emulsion Coating(Flatness)

## Print



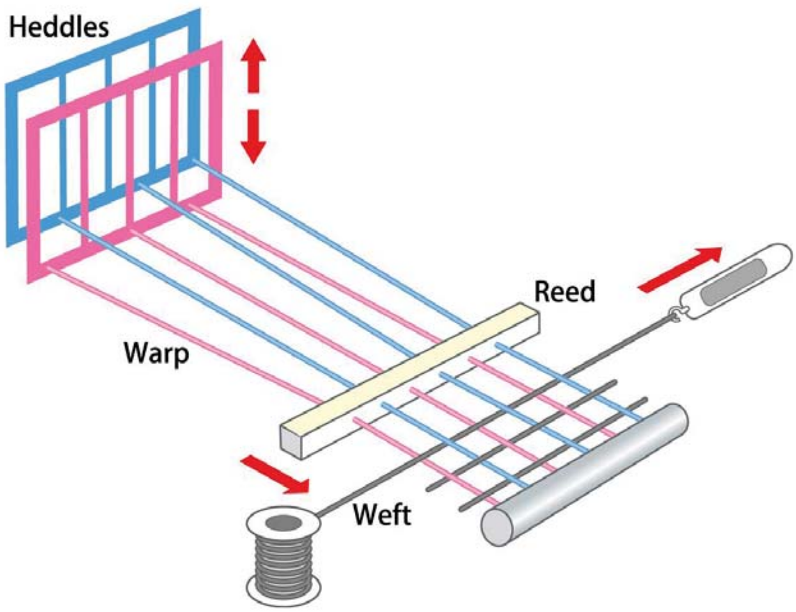



**Understanding of**
- Squeegee & Scraper Type
- 4 Printing Conditions

# Contents:

ASADA MESH CO.,LTD.



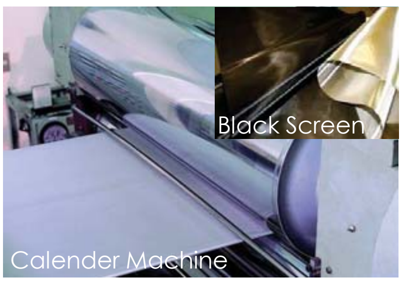



Reed

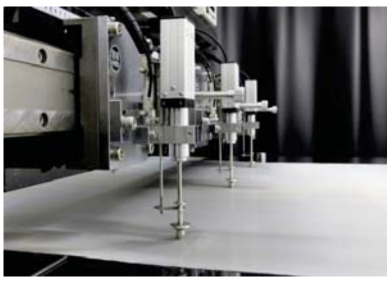
20000 wires are needed for 500/40".

3. Heddles & Reed Threading

4. Adjustment & Weaving




5. Value-Added Process

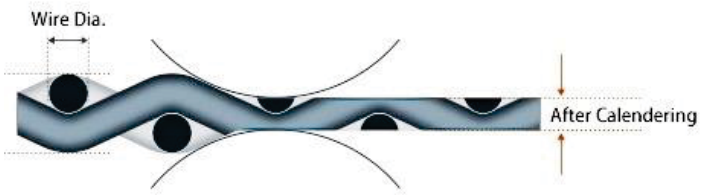


6. Quality Inspection

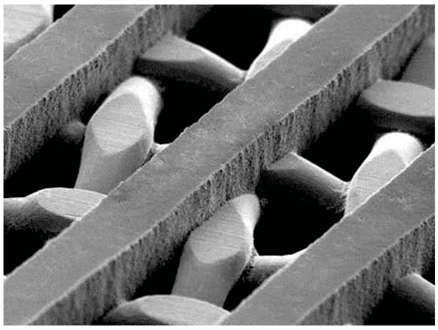
# Process of Screen Mesh Making

ASADA MESH CO.,LTD.

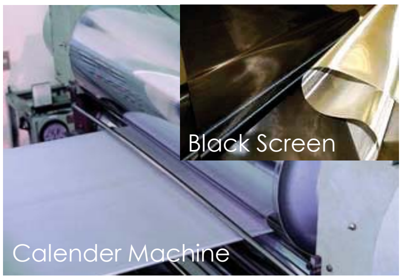
**Calender Machine**



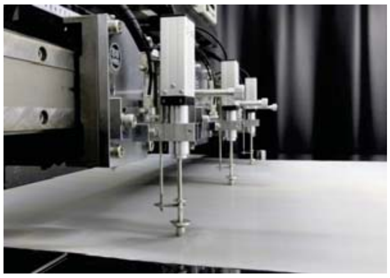

**Precise Resolution Exposure**



4. Adjustment & Weaving




5. Value-Added Process

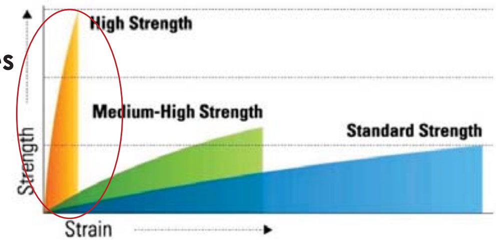


6. Quality Inspection

# Wire Hardness and Opening Rate

ASADA MESH CO.,LTD.

**Type of Material Wires**




***Standard*-Type *BS***

*From 200 to 500mesh*
*Opening Rate : 40%*

**Basic Standard Strength**
**Stainless Steel Woven Wire Cloth**

As a standard mesh for screen printing, it has been adopted for wide use such as fine line printing and thin deposit printing for MLCC.

Standard Strength

***Hardmesh*-Type *MS***

*From 250 to 730mesh*
*Opening Rate : 40%*

**Medium-High Strength**
**Stainless Steel Woven Wire Cloth**

Mesh tensile strength has been improved by 30% greater than the BS-Standard. Higher printed resolution has been achieved through the development of 730 and 640 mesh.

Medium-High Strength

***Supermesh*-Type *HS* & *S-HS***

*From 230 to 380mesh*
*Opening Rate : 60%*

**High Strength**
**Stainless Steel Woven Wire Cloth**

By using the stainless steel wire of high strength and low elongation, wires were woven at an open ratio of 60%. Thus, the transmittance of the printing paste has been improved.

High Strength

# Mesh Strength

ASADA MESH CO.,LTD.

Thinner wires must be selected to weave high meshes.
The higher mesh count is, the smaller the strength index will be.

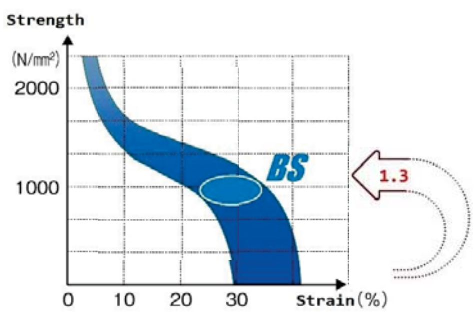
| Spec. | Wire.Dia | Mesh Count | Strength Index |
|---|---|---|---|
| BS-200/40 | 40 | 200 | 1.26 |
| BS-325/28 | 28 | 325 | 1.00 |
| BS-400/23 | 23 | 400 | 0.83 |
| BS-500/19 | 19 | 500 | 0.71 |
| MS-640/15 | 15 | 640 | 0.73 |
| MS-730/13 | 13 | 730 | 0.63 |

$$\left(\frac{1.3}{1}\right) = 1.3 \quad \left(\frac{13}{28}\right)^2 = 0.22 \quad \left(\frac{730}{325}\right) = 2.25 \quad \boxed{0.63}$$

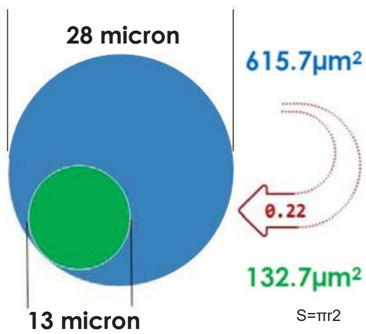
**Strength Index of BS325/28 =1.00 (Industry Standard)**

**Wire diameter** has a significant impact on **Mesh Strength**.

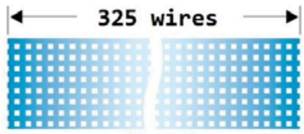
**Wire Strength**




**Cross Section**

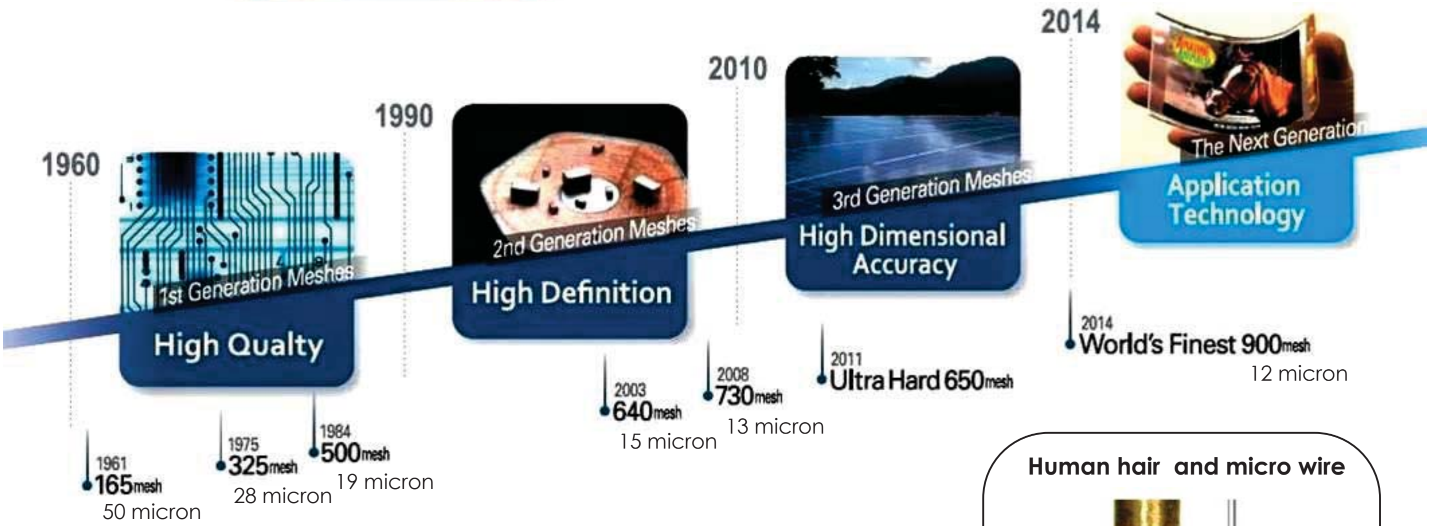



**Mesh Count**



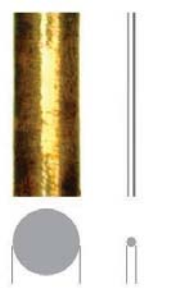

# From past to present

ASADA MESH CO.,LTD.

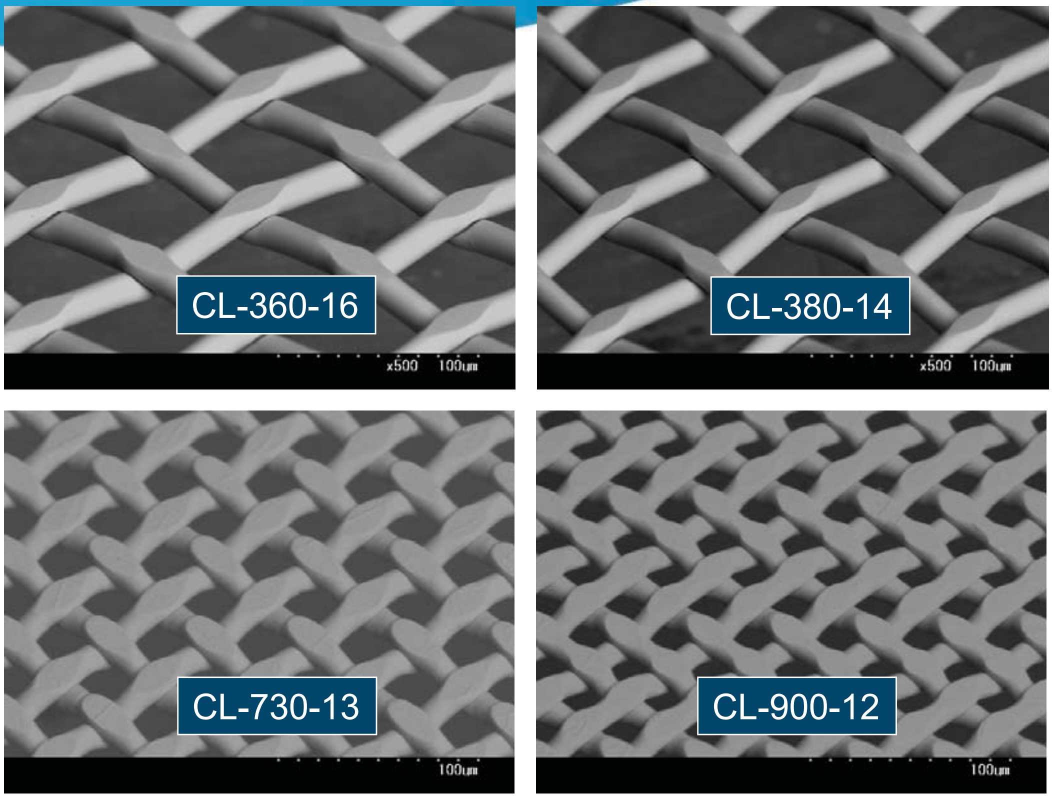



Stainless Mesh technology advanced rapidly in the last 50 years.
We are now introducing 900 which is 5 times finer mesh count than 165 developed in 1961.
However; there is only one technical challenge for high meshes to overcome.

**Human hair and micro wire**



# Mesh Counts under High Magnification




ASADA MESH CO.,LTD.

# Stainless Mesh & Screen Printing

## Advantage of high mesh count screens

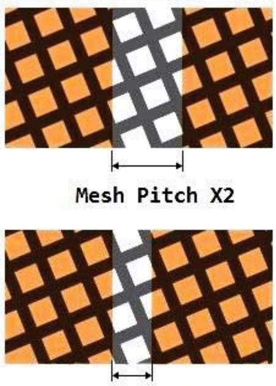
ASADA MESH CO.,LTD.

**Experiment of 50 micron Fine Line Printing**
325mesh/28 vs. 500mesh/19

**High Mesh Screen is necessary to achieve high resolution fine lines.**

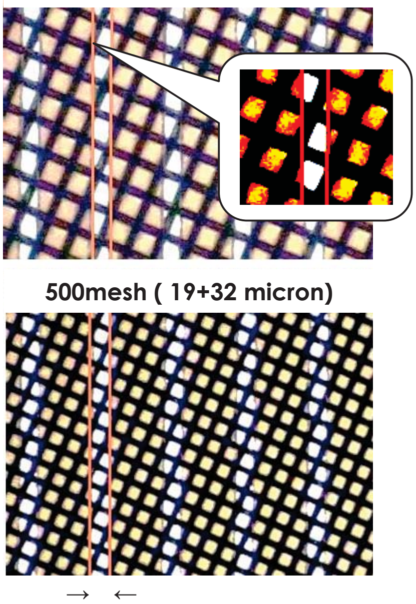
**A Standard Recommends**

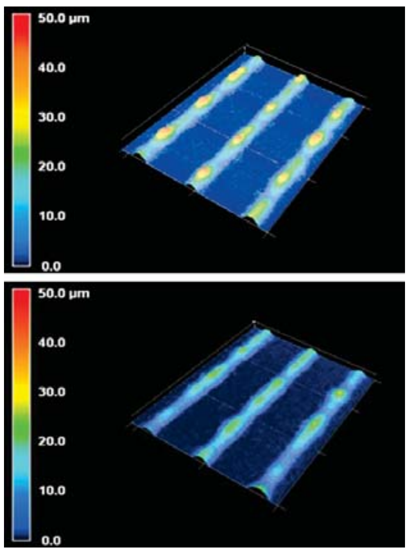
[ Emulsion Opening ]




Printable Line Width is from 0.8 to 2.0 of Mesh Pitch

325mesh ( 28+50 micron)




・Frame : 450mm ・Substrate : Si
・Trampoline ・SQ :200mm/sec

# Contents:

ASADA MESH CO.,LTD.



# Special Structure of HS-D Mesh

ASADA MESH CO.,LTD.

**Supermesh**-*Type* **HS-D** ★★

**Ultra-Hard "Non-distortion" Stainless Steel Woven Wire Cloth**

Tensile strength of Supermesh HS-D is over 3 times greater than BS-Standard. Produces more stable and dimensional accurate print plus it has an expected longevity of 2x-3x conventional meshes. Screen printing potential will be further enhanced.

*360, 500 and 650 mesh*

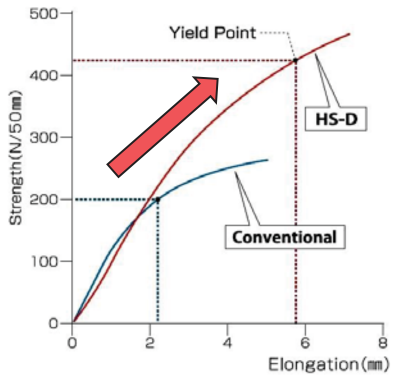
*Opening Rate : 40%*

**High Strength** 3.0

# Experiments of HS-D Mesh

ASADA MESH CO.,LTD.

## Strength and Strain of Wires

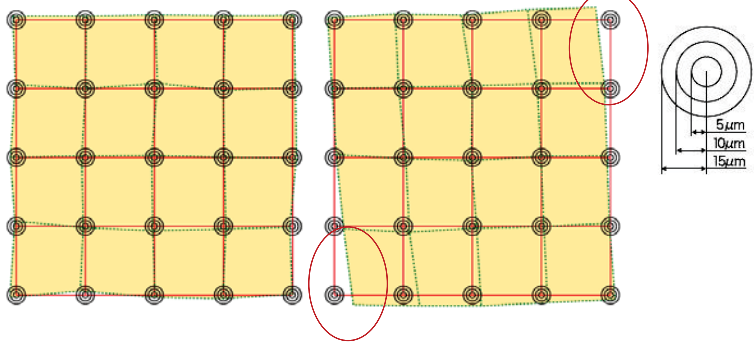



## Comparison of Screen Distortion

Dimensional Accuracy Test 300 prints

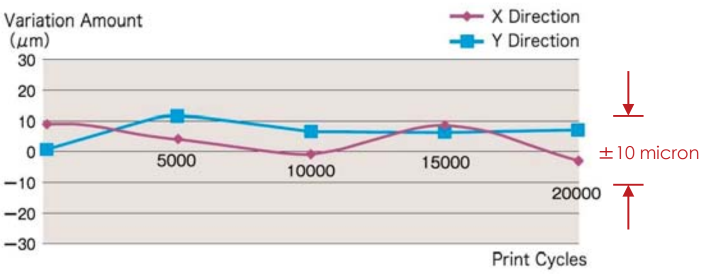
- Frame : 550mm□
- Pattern : 200mm□
- Snap Off : 3.8mm

HS-D Screen vs. Conventional




## Experiment of HS-D Screen Distortion

Dimensional Accuracy Test – 20000 prints




HS-D mesh doesn't cause plastic deformation even after 20000 cycles with a high snap off distance. Variation between 2 axes is within ±10 micron.

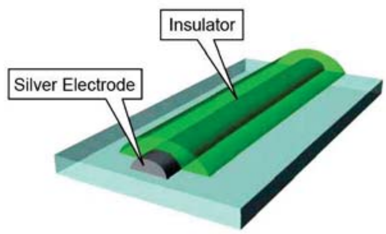
# Changing the Industry Standard by Ultra Hard HS-D Screen

ASADA MESH CO.,LTD.

## 3 Advantages of HS-D Mesh

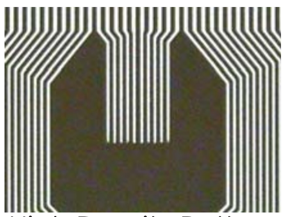
### High Dimensional Accuracy

Yield Point is extremely high so that it achieves high dimensional accuracy. Makes it possible to produce Multi-Layered PE devices with HS-D mesh.




### High Resolution

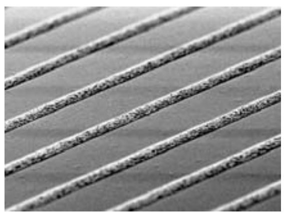
Super High Viscosity Paste can be used with high Snap-Off distance.
Fine and high-density mixed pattern can be printed on a Low absorbability PET film.



High Density Pattern

### Fine Pattern

High Mesh Count – 500 and 650 mesh have been developed and less than 30 micron is now printable.
A High Strength Screen achieves longer Screen life.



30 micron on PET

# Contents:

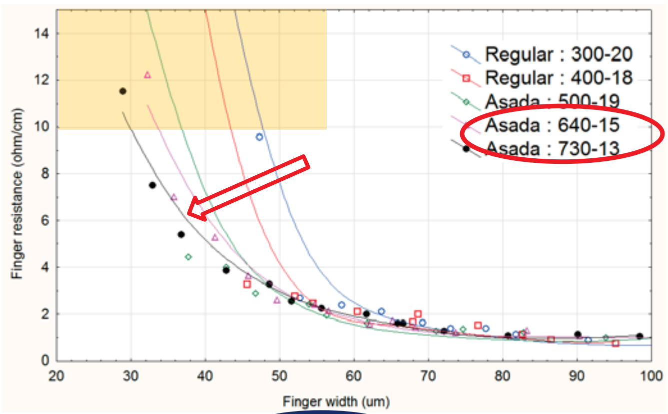
ASADA MESH CO.,LTD.



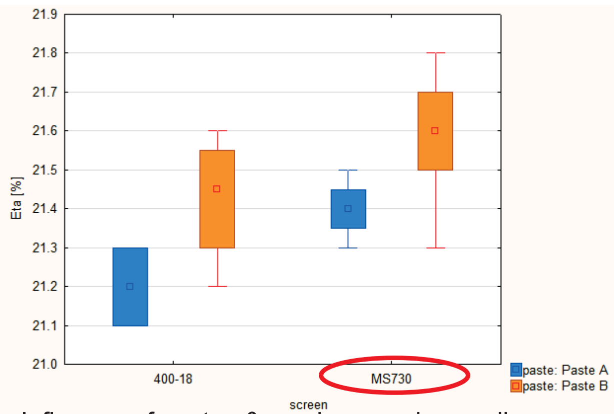
## Screen printed Ag fingers for High Efficiency Solar Cells

MEYER BURGER

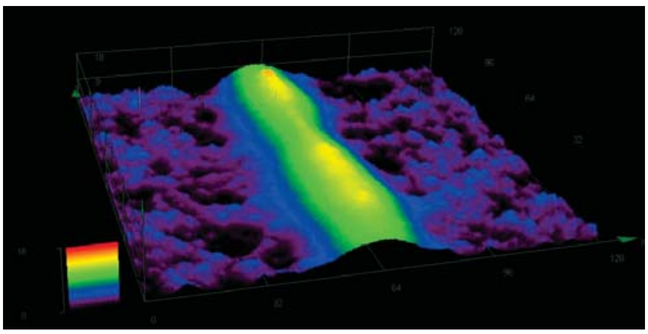
- Based on high count Asada meshes narrower fingers can be screen printed (figure on right)
- Applied on solar cells, an increase up to 1%$_{rel}$ on cell efficiency was reached thanks to Asada meshes
- < 35um wide fingers are uniformily printed on textured solar cell surface thanks to high mesh count. Finger heights are more uniform with less peaks and valleys




Finger width and resistance function of mesh count used




Influence of pastes & meshes used regarding cell performances



Confocal image of screen printed fingers with MS730

# Screen Printed Electronics

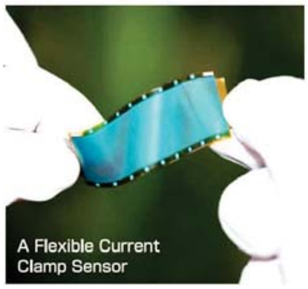
for real-time monitoring and control of the power system

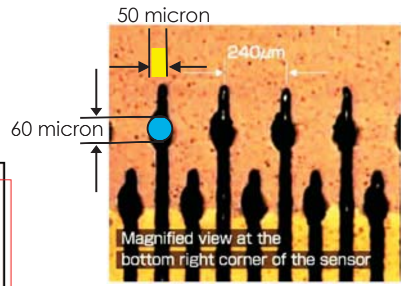
ASADA MESH CO.,LTD.

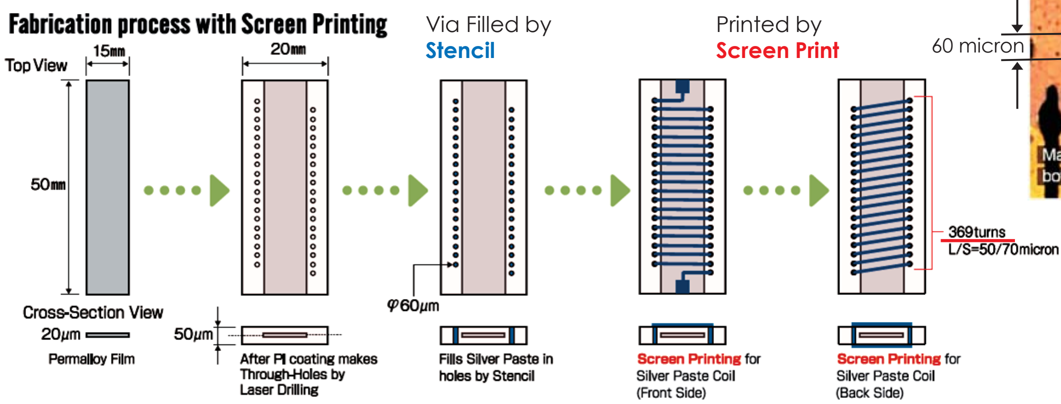
## Flexible MEMS

Fabricating a Low Cost Flexible Thin Film Current Sensor

This flexible current sensor with 369 turns silver paste coil (L/S=50/70 micron) is produced by Screen Printing.
Ultra Hard **HS-D mesh** with **high dimensional accuracy** achieves silver coil circuit printed on front and back side.




Smart grid is the latest trend in the global power system. It is important to develop a mass production technology of small size and inexpensive sensors.

This research has been conducted with the support of the National Institute of Advanced Industrial Science and Technology.

# Screen Printed Electronics

ASADA MESH CO.,LTD.

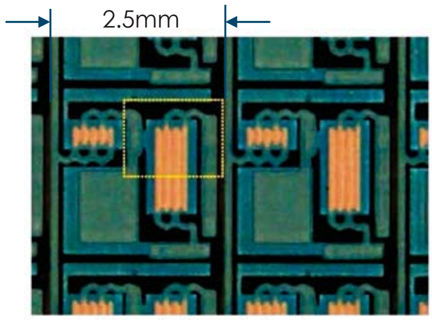
## Organic Transistors – Printed Electronics

2.5mm pitch "2T1C" Large Organic Transistor Array

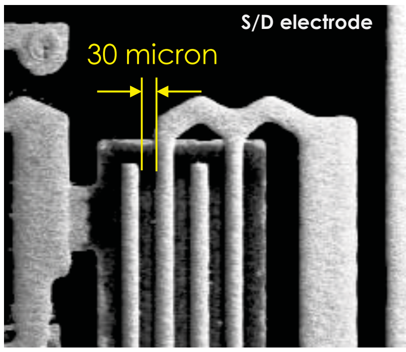
A 2.5mm pitch, "2T1C" Large Organic Transistor Array is produced only by Screen Printing on PEN film.
Gate and S/D electrodes of **30 micron channel length** are printed by HS-D650 mesh with high viscosity paste.

**6 screens performed highly accurate alignment and made multi-layered structure.**
1.via-fill 2. back side electrode 3. gate electrode
4. gate insulator 5. S/D electrode 6. Passivation mask

Screen Printing is the most effective for manufacturing back plane of PE devices.

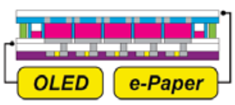


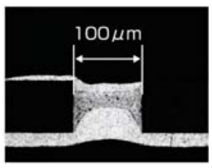
Large Organic Transistor Array




### Example

TFT back plane for organic Electro Luminescence Display or E-paper
Various Flexible Sensors



Via-Fill

Support of
The University of Tokyo
Someya Group

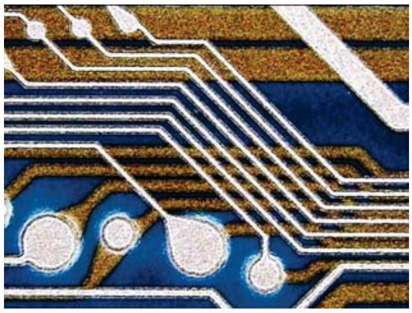
# Screen Printed Electronics

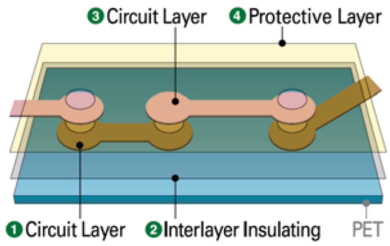
ASADA MESH CO.,LTD.

## A Single-Sided / Multi-Layer Substrate

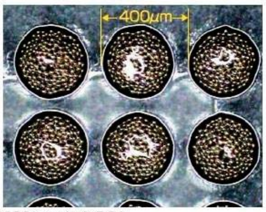
Multi-Layer Printed Circuit Board

Screen Printing relies on a unique principle of depositing paste in a screen mask openings onto a substrate with a rubber squeegee and excels in printing on a rugged substrate.
Since PE devices require multi-layers, Screen Printing is ideal for PE manufacturing process.


**Excels in printing on a Rugged substrate**



**Achieves multi-layered Structure**



400μm pitch BGA

Low melting Small particle
**Solder Paste**

### Surface Mount Device

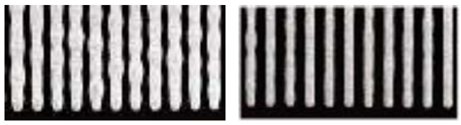
Screen Printing instead of Stencil realizes consistent paste deposition +/- 20%.
**Low temp solder paste allows mounting components on PET film.**

Reduces Manhattan Phenomenon


- Frame : 550mm□
- Mesh : HS-D360/25/CL41or 59
- Line Width : 200 micron
- Paste : Tatsuta Electric Wire & Cable

# Decorative Screen Printing

ASADA MESH CO.,LTD.

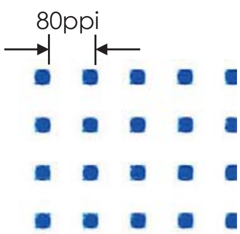

**Conventional paste causes bleeding easily(Left).**

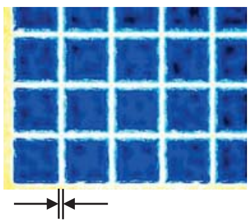
## High Definition Decorative Screen Printing

Achieved with a new designed Concept Paste

Low viscosity paste, which has been used for decorative printing for years, cannot be used for high definition printing because it causes bleeding easily.
High quality and high definition printing can be achieved in combination with a high viscosity paste and HS-D mesh, solving the problems of "bleeding" and "delayed peel off" issues.

**GRADATION PATTERN**
on a PET film





25 micron Gap

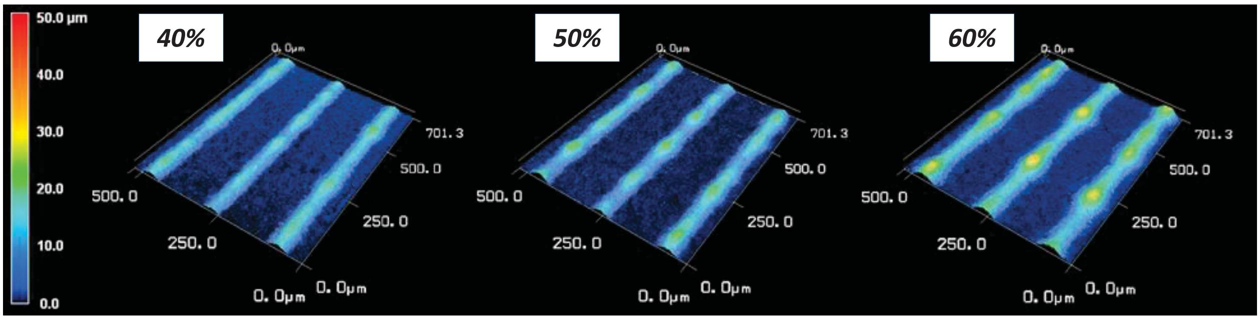
100 Pa・S - **30 times higher viscosity paste** than conventional **reduced the bleeding leve**l to less than 8 micron setting **a higher snap-off distance**. High density grid pattern is printable.

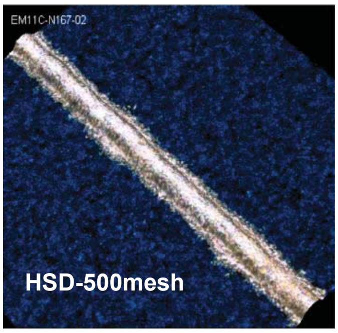
- Frame : 550mm□
- Mesh : HS-D500/19/CL25
- Paste : Teikoku Printing Inks Mfg.Co.,Ltd.

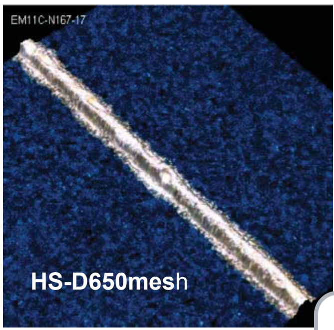
# Screen Mesh with 40%, 50% and 60% Open Area

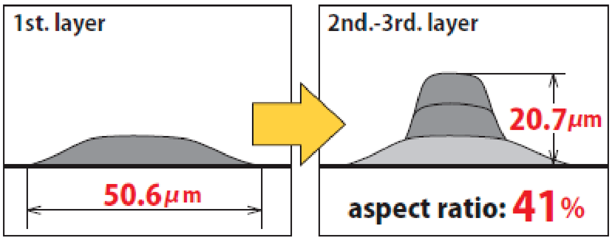
ASADA MESH CO.,LTD.

*Using 40% Open Area Mesh shows how the shape of Line becomes more "Uniform" when compared with 50% and 60%.*



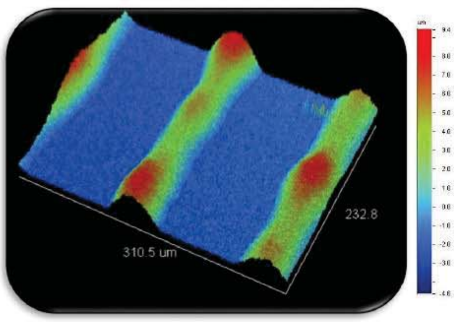




*Screen: HS-D500/19/CL25/EOM20 & HS-D650/14/CL23/EOM15*
*Frame-Size: 450mmx450mm Wafer: 6" of polycrystalline Silicon cells*
*Snap-off: 1.5mm SQ speed: 200mm/sec Paste: DD-1200N-167KEL*

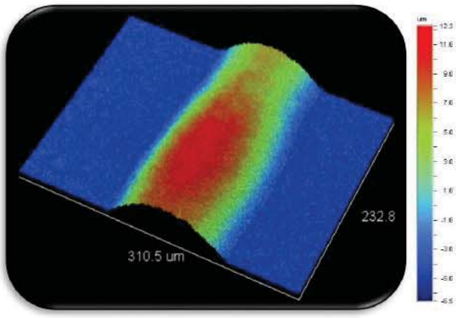
# Practical Session pictures obtained by Sarah-Jane Potts and Dr. David Beynon

## ASADA 290 Mesh

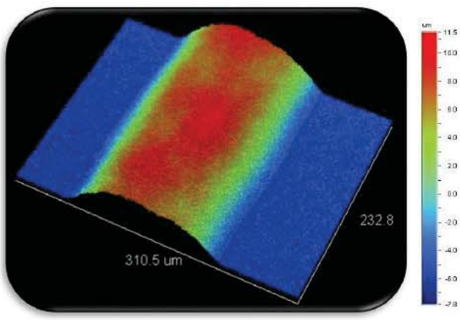
**Settings:**
**Press**: DEK 248 – frame size 583mmx583mm outer
**Squeegee** – Trelleborg Unitex diamond profile (70-75 shore A hardness)
**Ink** - SunChemical - CXT0667
**Print pressure** – 11kg
**Snap off** – 1.9mm
**Print speed** – 70mm/s
**Clean up solvent** – Sericol screen wash (final clean with IPA)




**50 µm line track**
Average true width: ~ 62 µm




**100 µm line track**
Average true width: ~ 134 µm



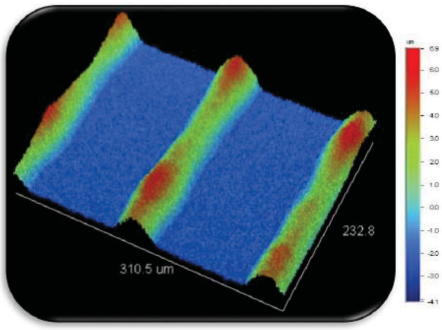

**150 µm line track**
Average true width: ~ 171 µm

Images and measurements were produced using the Veeco NT9300 Wide Area White Light Interferometer with the 20x lens

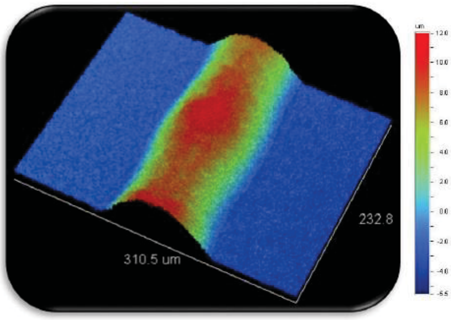
# Practical Session pictures obtained by Sarah-Jane Potts and Dr. David Beynon

## ASADA 400 Mesh

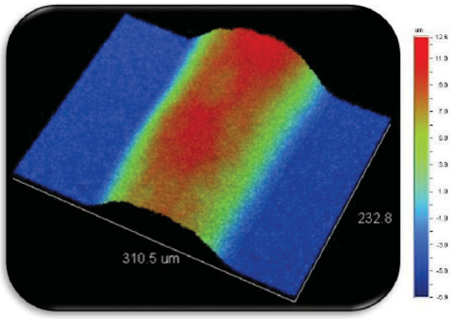
**Settings:**
**Press**: DEK 248 – frame size 583mmx583mm outer
**Squeegee** – Trelleborg Unitex diamond profile (70-75 shore A hardness)
**Ink** - SunChemical - CXT0667
**Print pressure** – 11kg
**Snap off** – 1.9mm
**Print speed** – 70mm/s
**Clean up solvent** – Sericol screen wash (final clean with IPA)




**50 µm line tracks**
Average true width: ~ 56 µm




**100 µm line tracks**
Average true width: ~ 123 µm



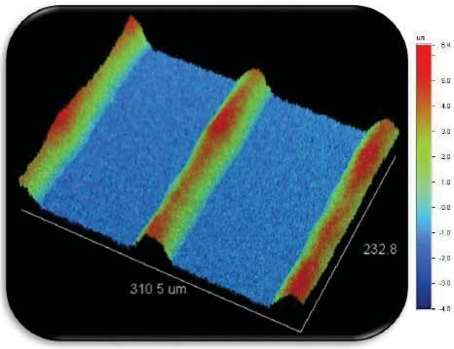

**150 µm line tracks**
Average true width: ~ 165 µm

Images and measurements produced using the Veeco NT9300 Wide Area White Light Interferometer with the 20x lens

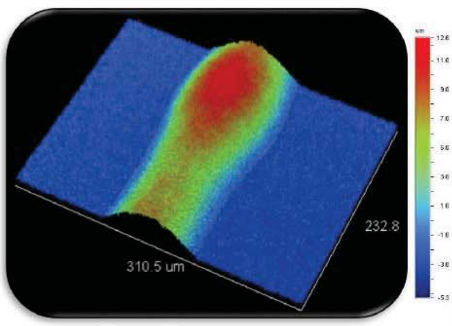

# Practical Session pictures obtained by Sarah-Jane Potts and Dr. David Beynon


## ASADA 500 Mesh

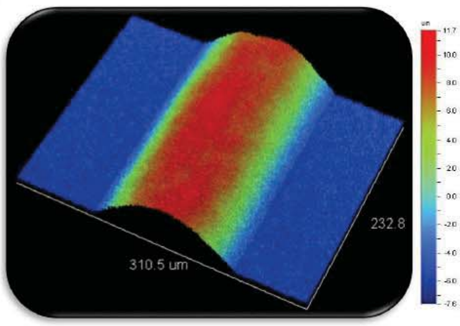
**Settings:**
**Press**: DEK 248 – frame size 583mmx583mm outer
**Squeegee** – Trelleborg Unitex diamond profile (70-75 shore A hardness)
**Ink** - SunChemical - CXT0667
**Print pressure** – 11kg
**Snap off** – 1.9mm
**Print speed** – 70mm/s
**Clean up solvent** – Sericol screen wash (final clean with IPA)




**50µm line track**
Average true width: ~ 49 µm




**100µm line track**
Average true width: ~ 119 µm




**150µm line track**
Average true width: ~ 156 µm

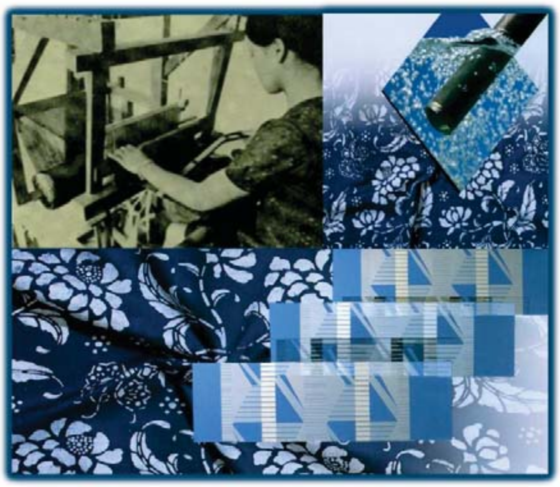
Images and measurements produced using the Veeco NT9300 Wide Area White Light Interferometer with the 20x lens

# Screen Print Forever 2016!

ASADA MESH CO.,LTD.

OPEN INNOVATION HUB
ASADA MESH CO.,LTD. R&D Center

Thank you very much for your attention!!



WCPC July 11th-15th, 2016

# 2016 Asada Mesh Screen Printing Workshop – Barcelona

(October 3rd-4th)


+

University of Terrassa

**Final Agenda:**

- **Ph.D. Cecilia Wolluschek Perri from Navarra´s Functional Print Cluster; "An example of innovative business collaboration in Functional Printing".**
- **Mr. Art Dobie from Ikonics: "Advances in Flexible Substrate Technology for Improved Resolution and Accuracy of Screen Printing Ag Conductors".**
- **Mr. Sergiu Pop from Yingli Solar: "Progress in Front Contact printing for the Next Generation of Mono p-type Cells".**
- **Prof. Tim Claypole from Swansea University: "Raising the bar in Screen Printing".**
- **Ph.D. Tomas Syrovy from University of Pardubice: "Fine Line Printing for Sensor Applications".**
- **Mr. Bavo Muys from Agfa: "Conductive Inks for Functional Printing; less is more".**
- **Mr. Sousuke Nabeshima from Asada: "Update in the latest products from Asada Mesh".**
- **Prof. Gunter Hubner from University of Stuttgart: "Challenges for screen printing of zinc air batteries".**
- **Mr. Armand Bettinelli from CEA/INES: "Advanced PV Research using Screen Printing Technology".**
- **Prof. José María Canal from Catalonia's Polytechnic University: "Improving the criteria for Fabrics prepared for High performance Screen Printing with conductive pastes".**
- **Mr. Grégoire Staelens from Gene´s Ink: "State of the art of Conductive Nano inks for Screen Printing".**

ASADA MESH CO.,LTD.

## 15. Colour Measurement

Tim Claypole, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a

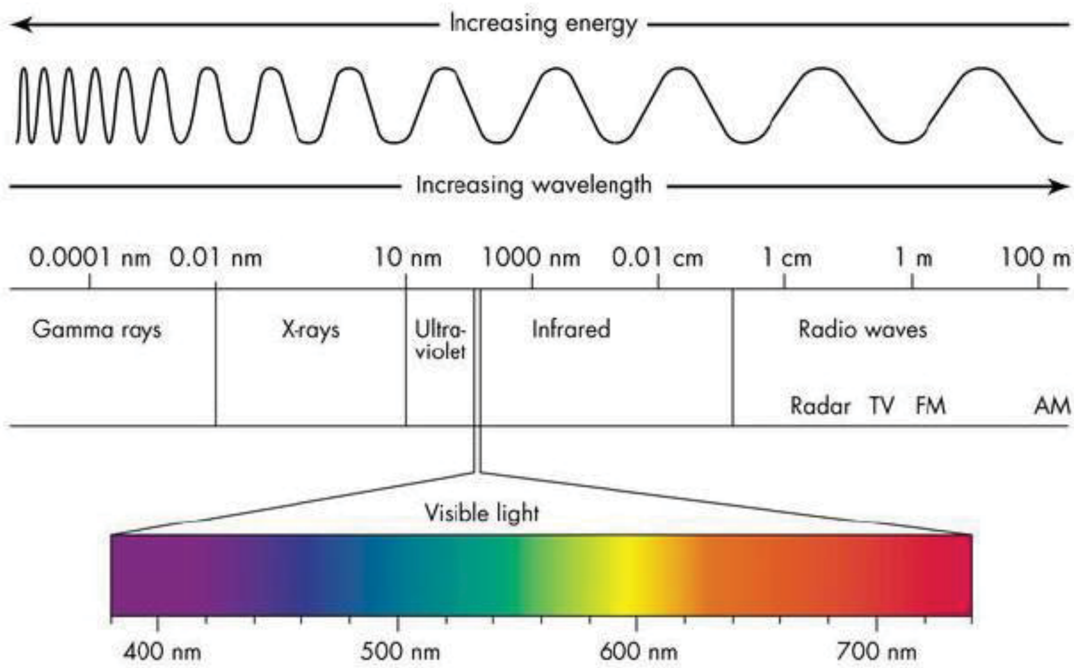

## Welsh Centre for Printing and Coating

# Colour Perception and Measurement

Tim C. Claypole

## What is a colour?

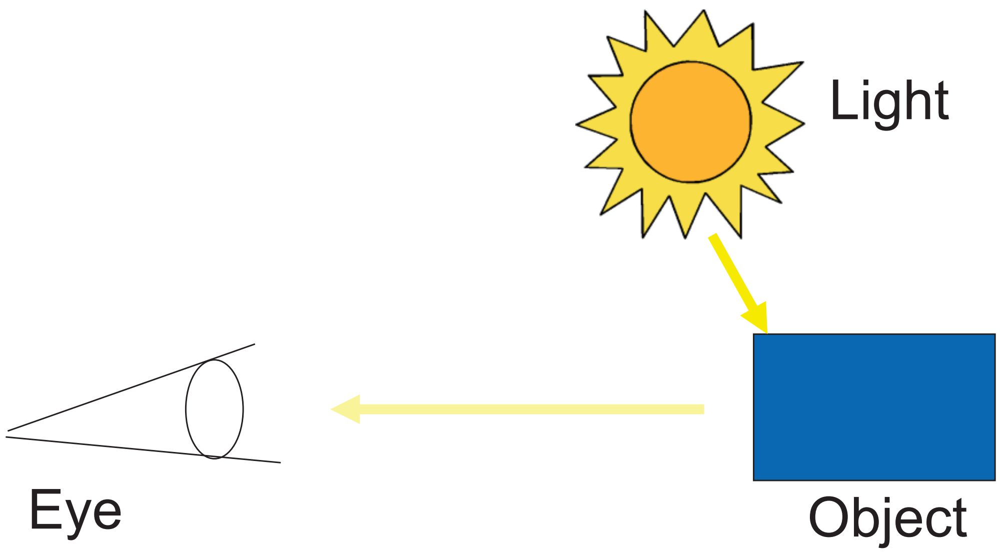
"Visible electromagnetic waves"






## What is a colour?

- Colours are an "interpretation" of reality
  - Depends on lighting, experience, individual

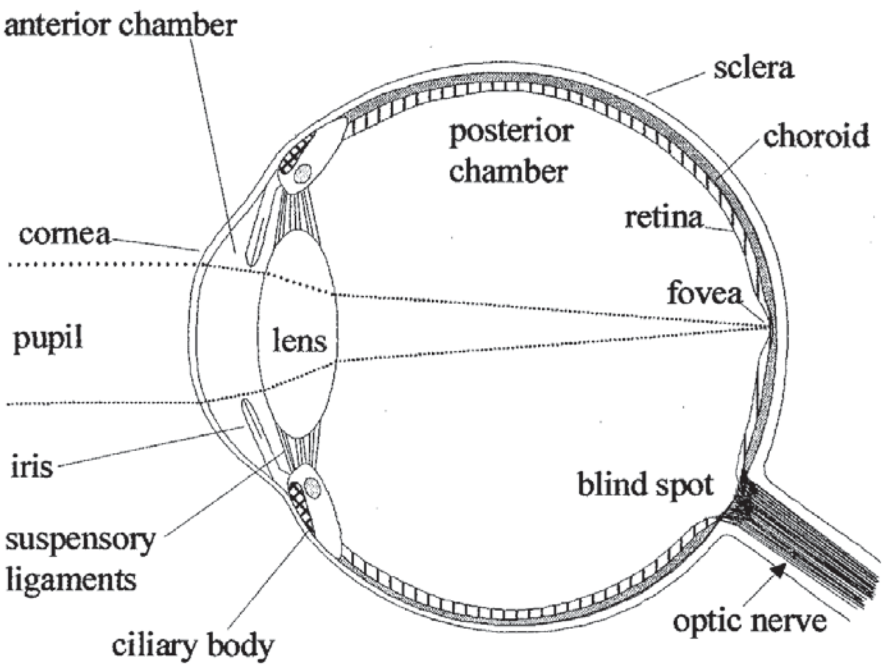


## Visual colour perception

- “Estimated humans can distinguish between 10 million colours”, Wyszecki and Styles
- In the eye
  - Colour detected by cones
  - Light stimulates chemicals
  - Detect red, green, blue
  - Night vision by rods



## Eye schematic




WCPC Swansea University Prifysgol Abertawe icmPrint

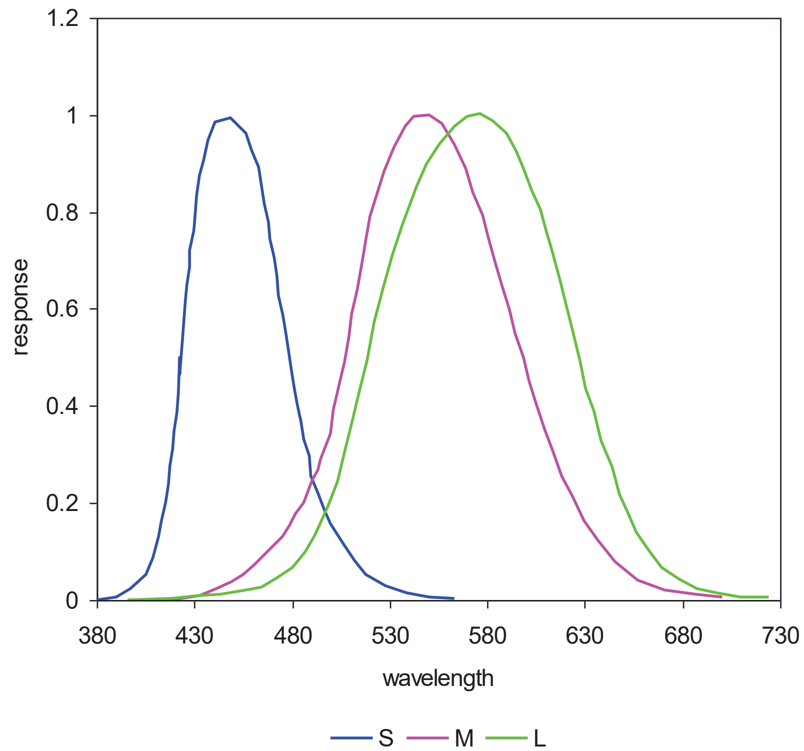
# Colour constancy

- Colour recognition
- Varying levels of illumination
  - Eye will "adapt"

  - Scotopic - low illumination
  - Photopic - high levels of illumination
- Consider changes
  - 1,000 scale change moving from daylight to room



# Spectral sensitivity of the eye



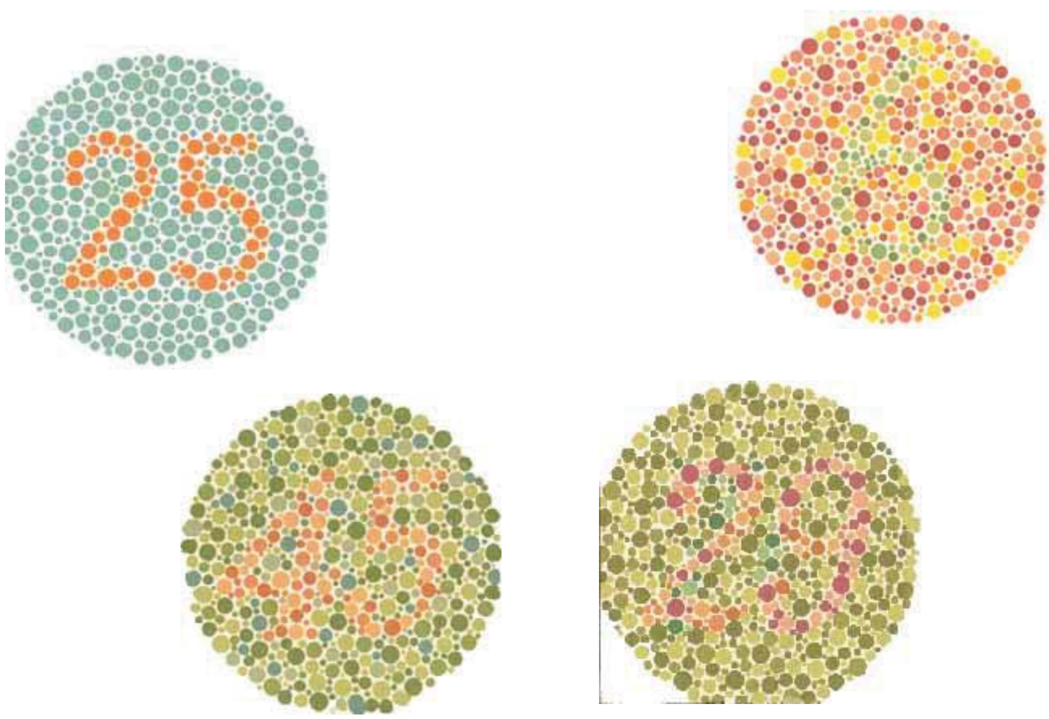
# Colour defective and colour blindness

More prevalent in males

| | |
|---|---|
| Deuteranomaly | 4.9 |
| Deuteranopia | 1.1 |
| Protanomaly | 1.0 |
| Protanopia | 1.0 |
| Tritanopia | 0.002 |
| Cone monochromatism | v. rare |



# Tests for colour defective vision



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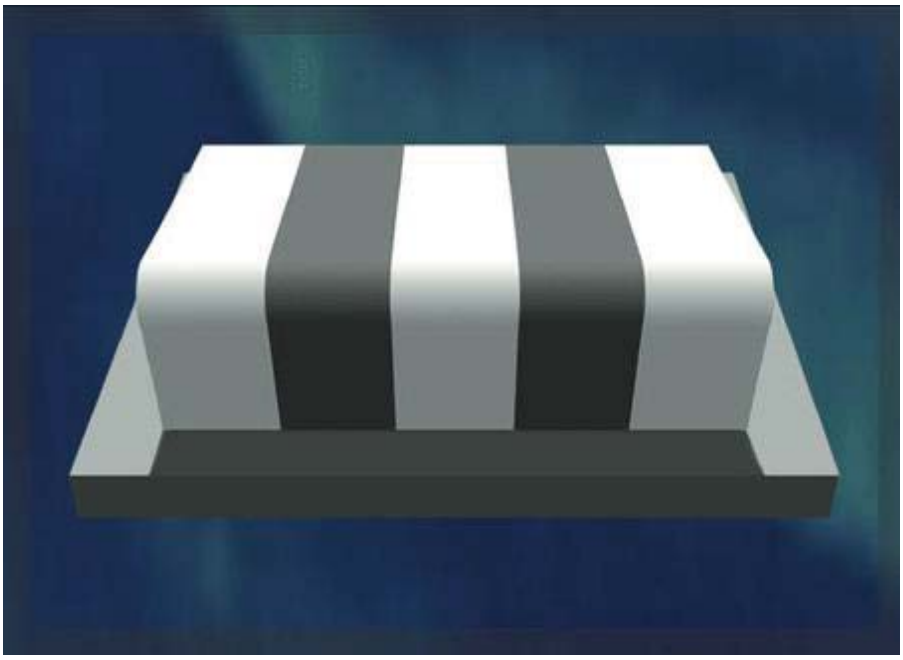
## What is a colour?

- What colour are the bands?

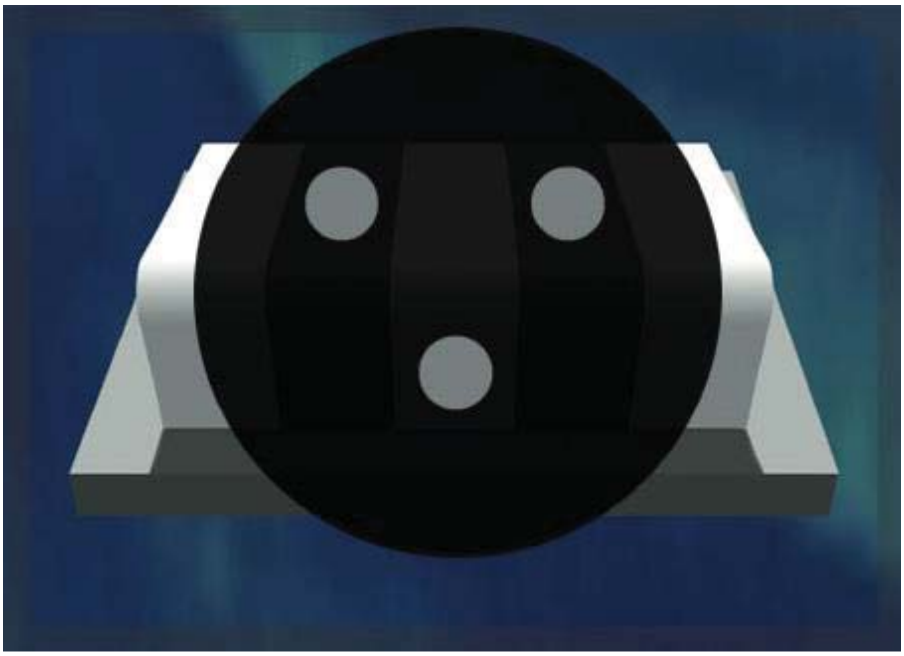


R.Beau Lotto
http://www.lottolab.org



## What is a colour?

- What colour are the bands?




## The shirt is white?

FINANCIAL TIMES

EUROPE Thursday September 18 2008

Global banks in crisis

Full coverage of the market turbulence: NEWS Pages 2-6 COMMENT Page 15
LEX Page 18 MARKETS Pages 34-36 ONLINE www.ft.com/crisis

Newspaper of the year

World Business Newspaper

News Briefing

**EDF considers bid for Constellation Energy**

Page 19

**EU shoe duty plea**

Page 11

**Nato talks on Russia**

Page 8; Lex, Page 18

**Syrian Airbus hopes**

# Credit panic hits historic levels

**The day in summary**

One-month US Treasury bill yield

**Global markets**

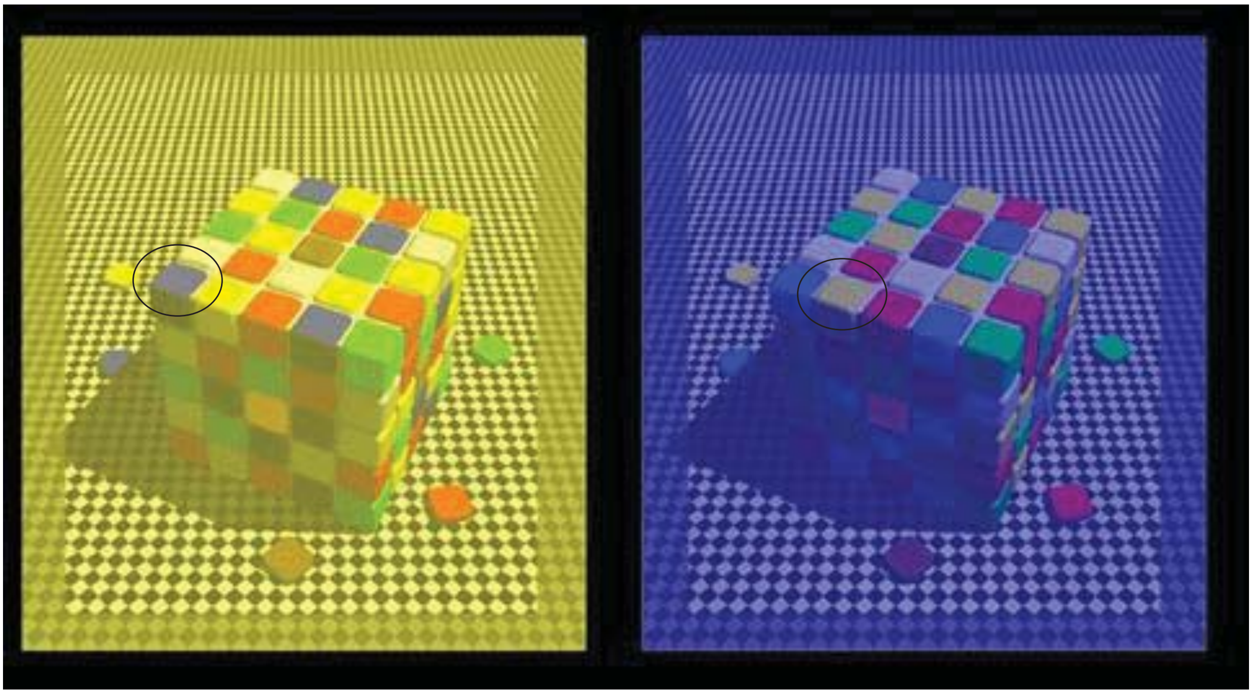
| | |
|---|---|
| Three-month Treasury bill yield | 0.06% |
| FTSE 100 | ▼-2.25% |
| S&P 500 | ▼-2.59% |

Pages 34-36

HBOS

## What is a colour?

- What colour are the tiles?



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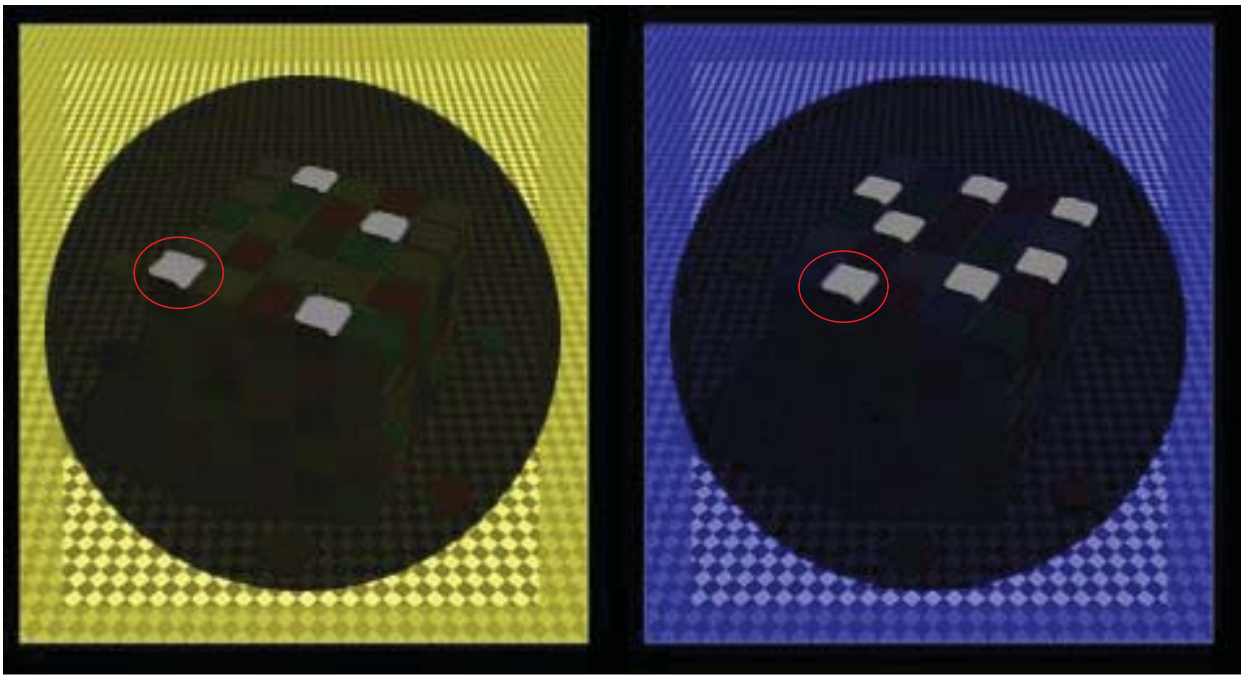
## What is a colour?

- Masking the surrounding....



Images by R.Beau Lotto
http://www.lottolab.org

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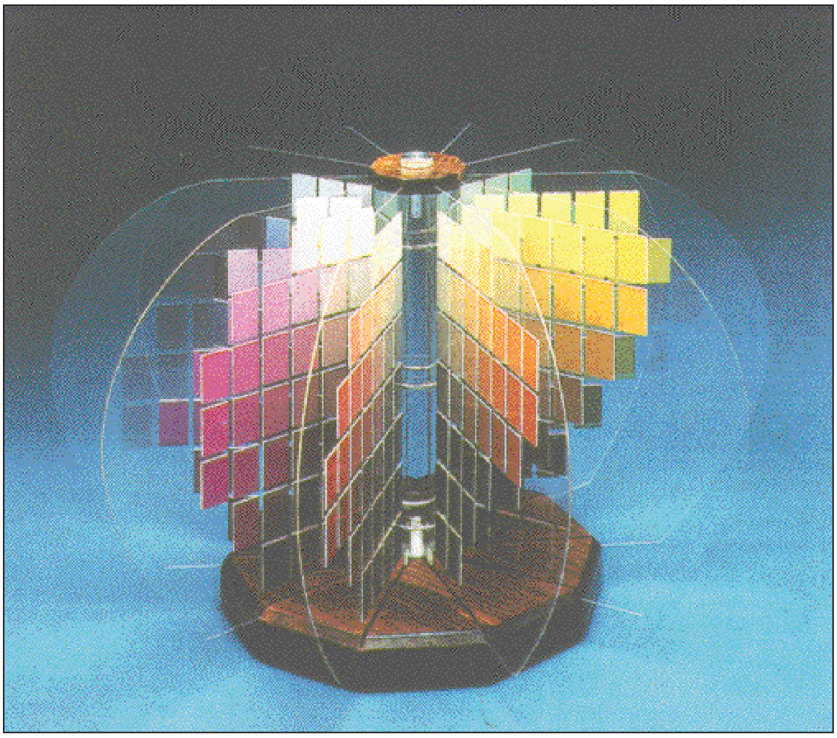
# Colour Atlas

- To communicate colour development of colour atlas or colour books
- Various methods have been devised
  - Munsell
  - Natural Colour System

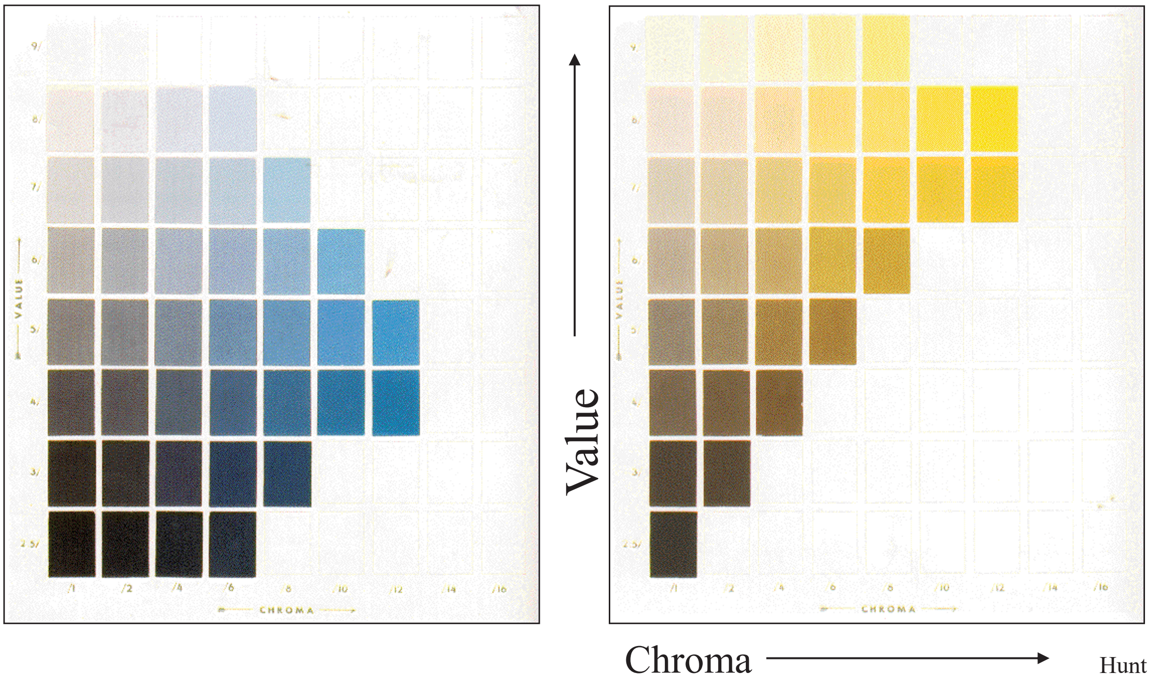


# Munsell Colour Tree



X-Rite

# Munsell – Constant Hue page, Hunt

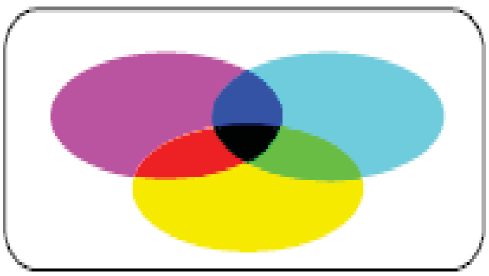





# What is a colour?

- 3 basic colours (RGB or CMY) combines creating the range of colours

Additive: Monitors (RGB)



Subtractive: Printing (CMY)

- Why add black ink (K) ?

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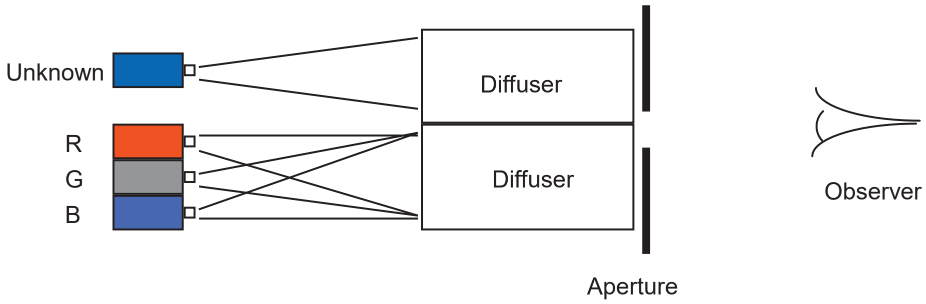
# Colour matching experiments

- Experiments to evaluate the amount of light needed to match
- Three lights adjusted for match
- Negative values can be attained as in some cases to match light had to be added to the sample

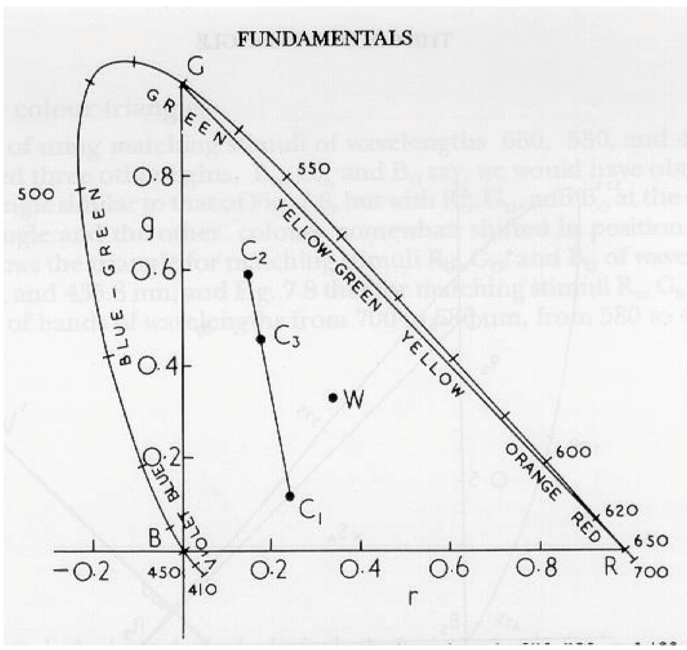



Guild and Wright, 1920's

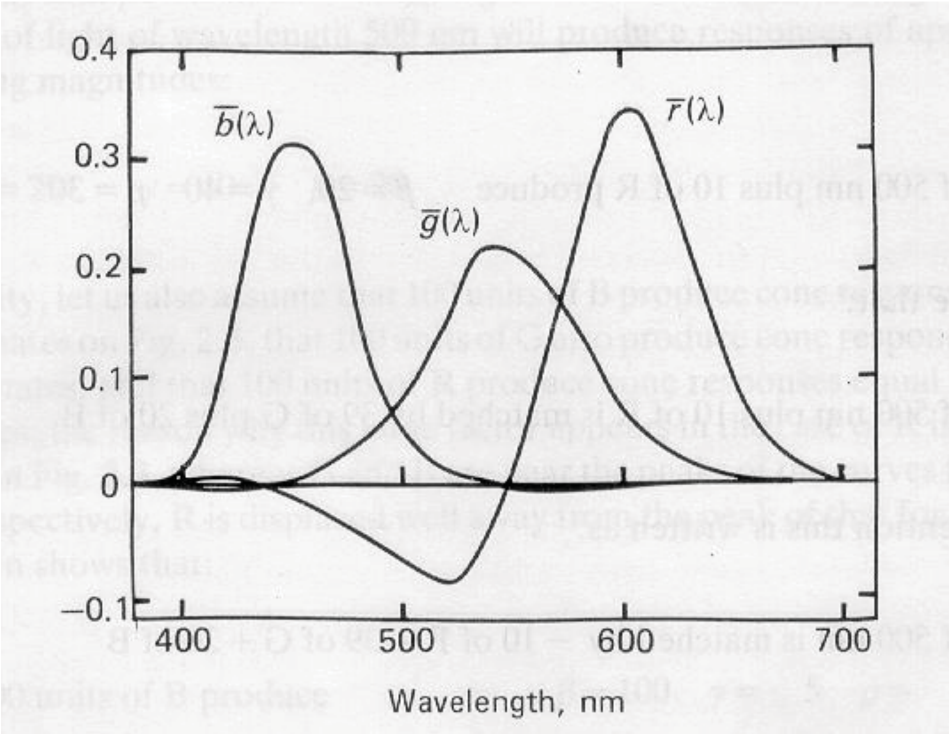


# Colour matching experiments

- Negative numbers in some cases
- Not able to mix all spectral colours
- Example of red green mix



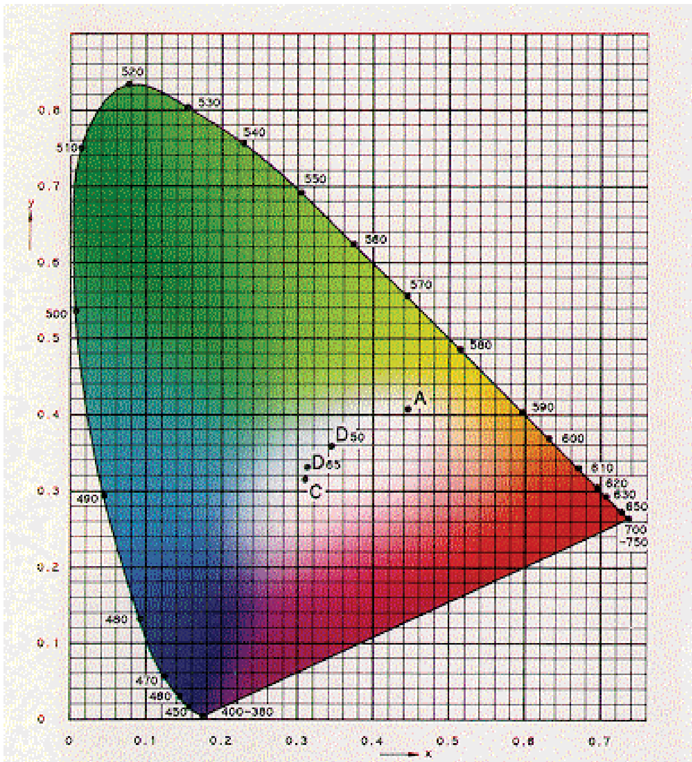
# Colour matching functions – RGB






# CIE xy colour space

- CIE 1931,
  - Commission Internationale de l'Éclairage
- To overcome the negative numbers
- CIE XYZ
  - calculated from the reflectance spectrum
  - Weighted ordinate system commonly used




X-Rite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# Colour Spaces – CIE 1976

- Improved colour spaces
- CIE L*a*b* and CIE L*u*v*
- Improved lightness scales, with improved linearity with respect to visual assessment
- Use of CIE L*C*h representation for ease of visualisation with C* (strength/saturation) and hue angle h for colour

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# CIE L*a*b* colour space

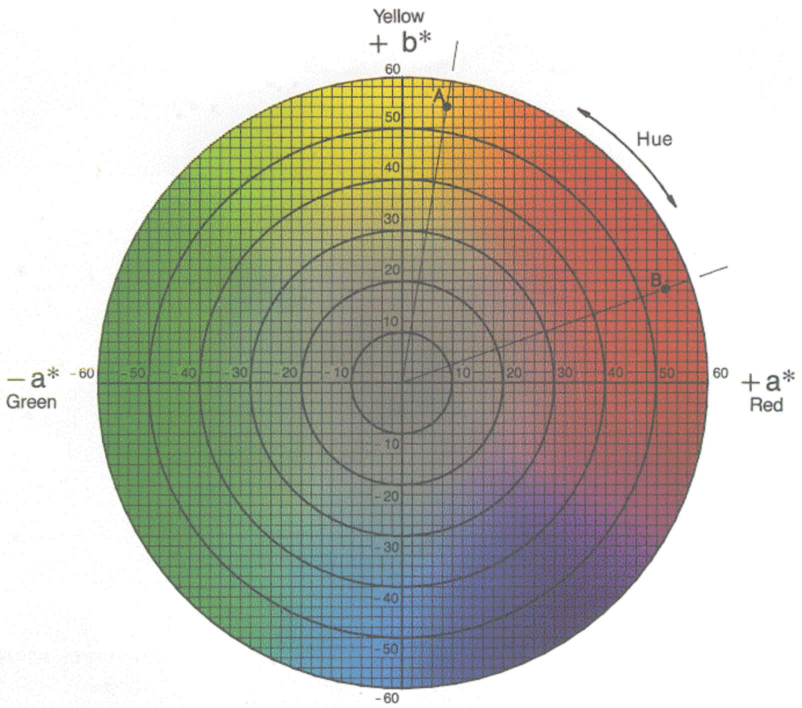


Figure 7: CIELAB Color Chart

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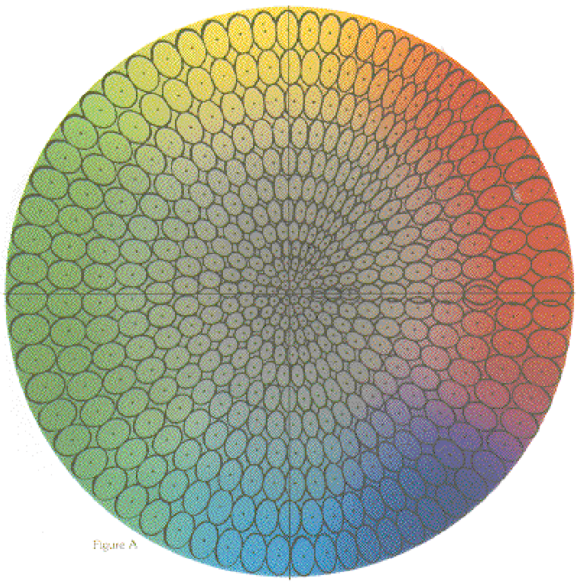
## CIE colour difference formulae

- Colour difference between CIE colour space values
- Visual differences should give approximately similar delta E values



$$\Delta E^*_{ab} = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2}$$

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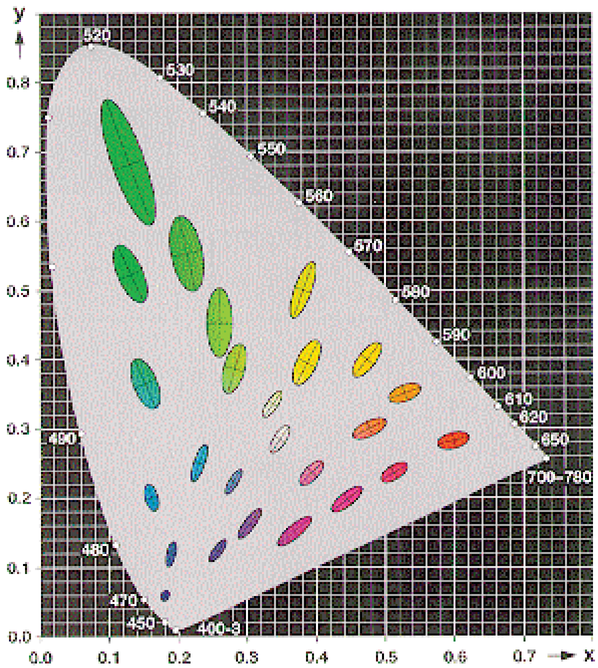
## Visual perception




Heidelberg

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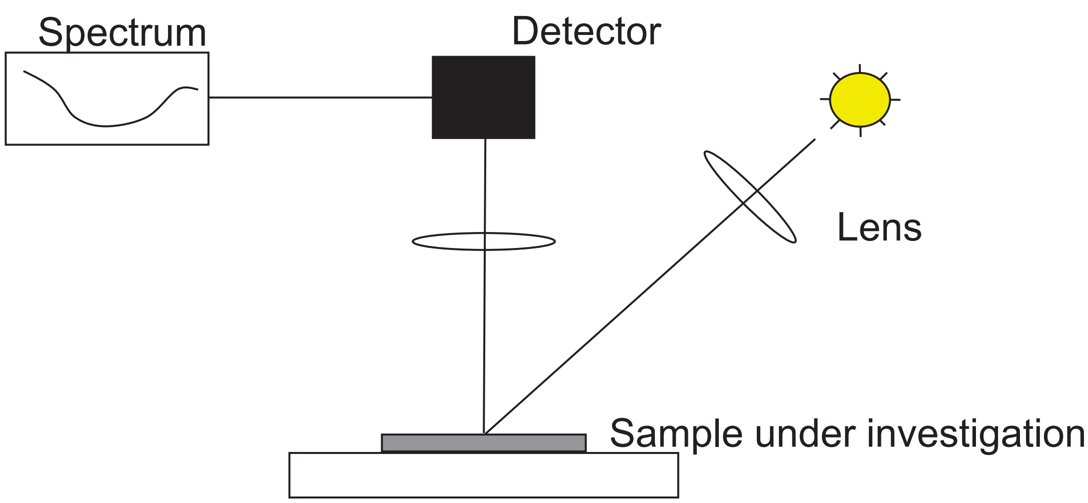
# Spectrophotometry

- Control light source
- Measures remission spectrum
- Different optical configurations
  - 0/45
  - Integrating sphere
- Calculates tristimulus data



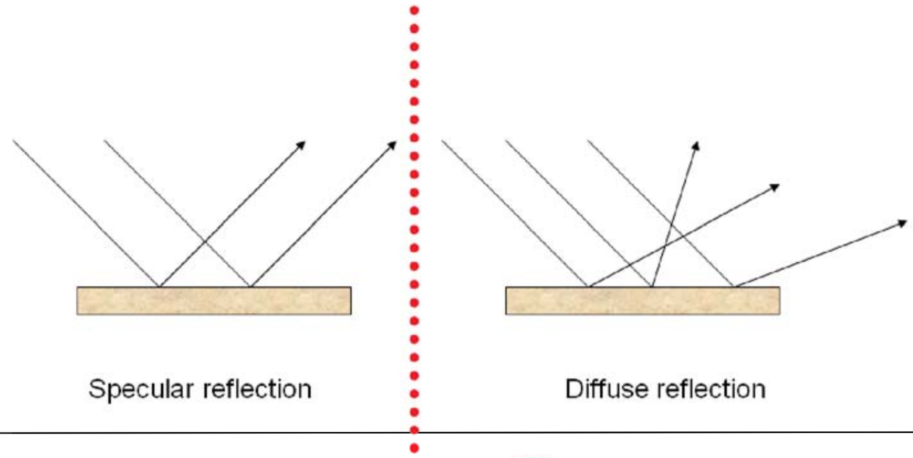
# $45^0/0^0$ spectrophotometer




- Optics set at $45^0$ and $0^0$ to substrate
- Stabilised light to illuminate the sample
- Collected light back to give a spectrum

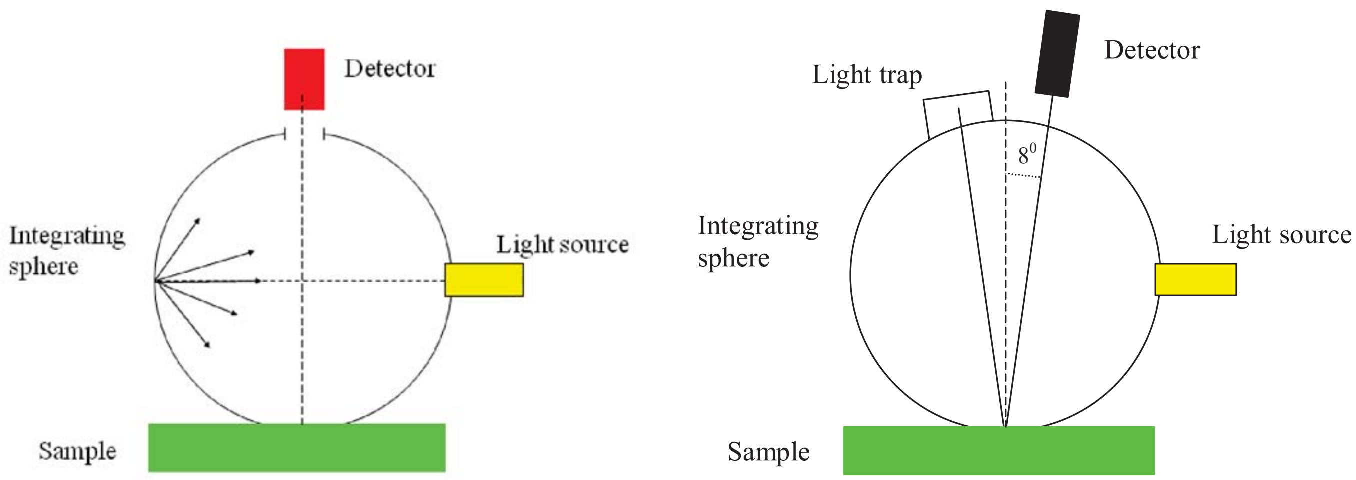
# Spherical spectrophotometer

- Different optical configuration
- Diffuse and specularly reflected components of the scattered light
- Ideal for the measurement of metallic samples and those with direction surface effects






# Spherical spectrophotometer



## Spectrophotometers

- $45^0/0^0$ instruments
  - Reflectance spectrum
  - Spectrophotometry
  - Densitometry
- Spherical instruments
  - Reflectance spectrum
  - Spectrophotometry



## Lighting

- The light under which an object is viewed effects the colour
- Objects need to be viewed under same lighting conditions
- Defined under CIE standards

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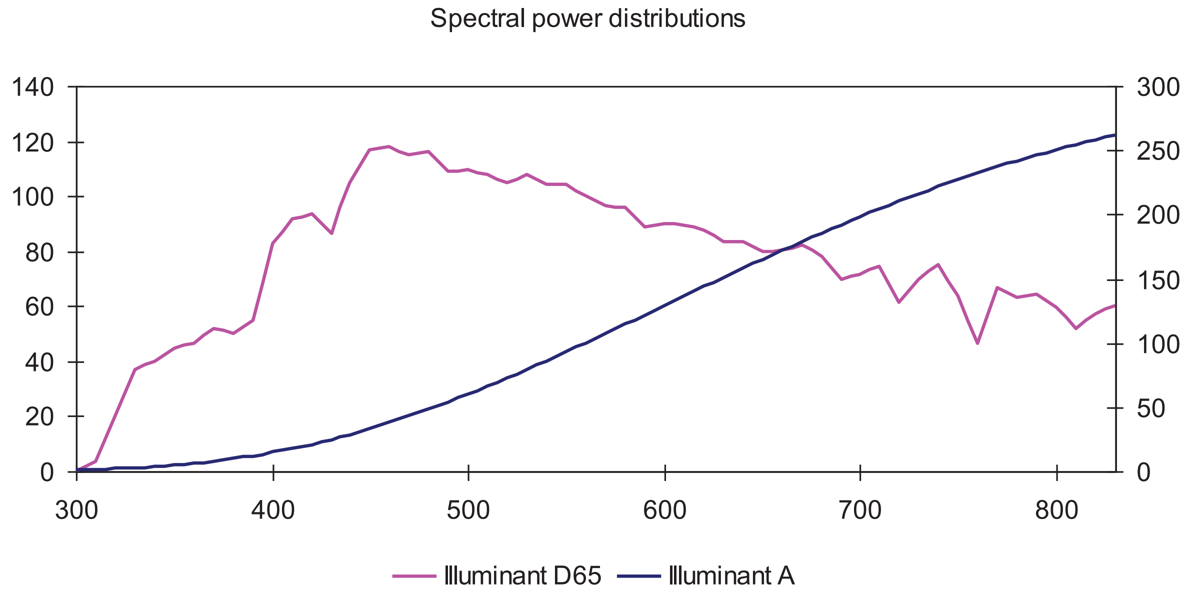
# Illuminant lighting




# Metamerism

- Object colours will appear different under various lighting conditions
- Objects with different spectral responses can appear the same
- These can be identified using instrumentation

# Fluorescence

- When a sample emits light at a different wavelength to the incident light
- Analyse using
  - Double monochromators
  - Two-mode method
  - Filter reduction
  - Luminescence weakening
- Practical considerations
  - Illumination standardisation
  - Stability of samples
  - Illumination and viewing
  - Spherical coatings non fluorescent



# Whiteness

- Important for many industries including paper, textile and paint
- Luminance
- Chromaticity changes
- CIE standards

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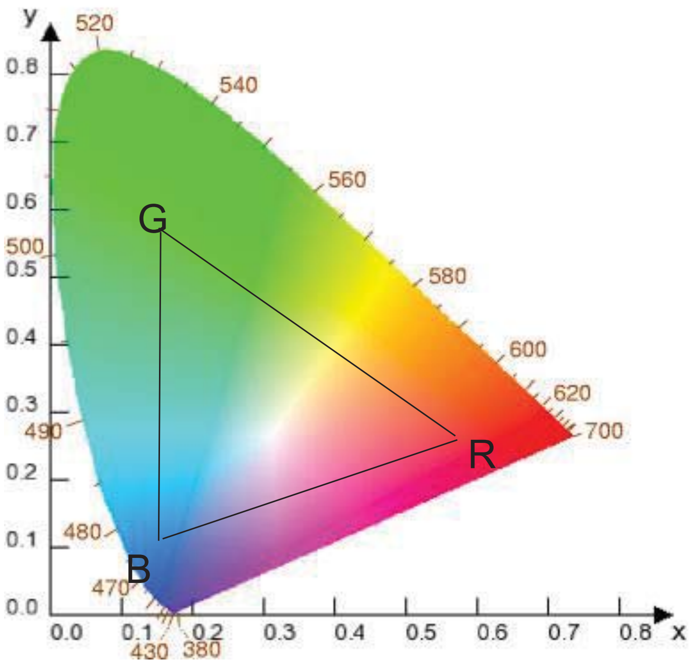
## Possible error sources

- Thermochromism
- White calibration
- Instrument geometry and illumination
- Sample preparation
- Polarisation



## What is a colour?

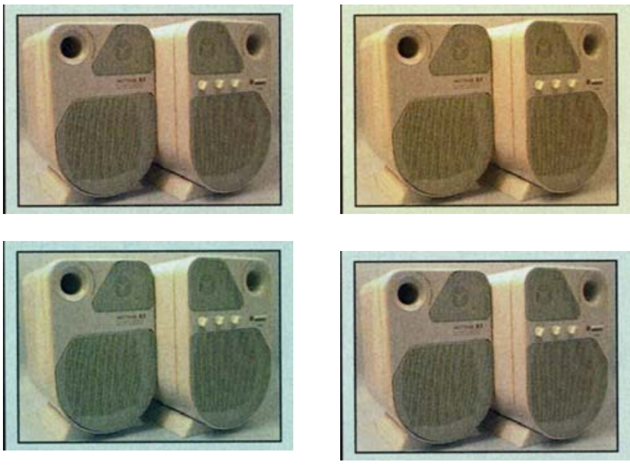
- Are 3 colours enough to recreate all colours?




Gold, silver ?

## What is a colour?

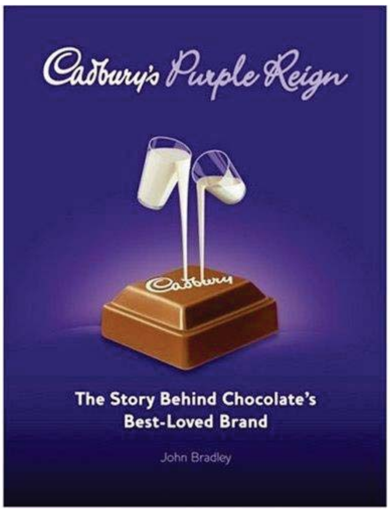
- In printing, we can introduce “spot colours”
  - Solution to gamut limitations
  - Process control – one colour is easier to control than 3 or 4!





## What is a colour?

- Special spot colours:




- Colours protected by patents!

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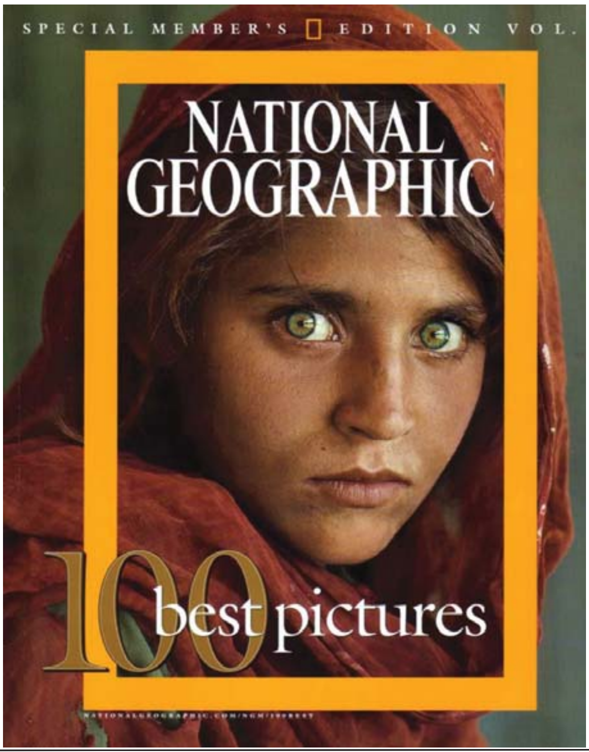
# What is a colour?

- High quality 6 colour printing : a better gamut






# Closure

- Colour comprises light, material and viewer
- The eye is a good comparator
  - Poor colour memory
  - Many people have colour vision defects
- Sphectrophotometers measure one aspect of colour
- Are 3/4 colours enough?
  - Emissive Displays use RGB
  - Reflective use CMYK
  - Spot colours
  - Special effects

## 16. PAPER AS SUBSTRATE FOR PRINTED ELECTRONICS

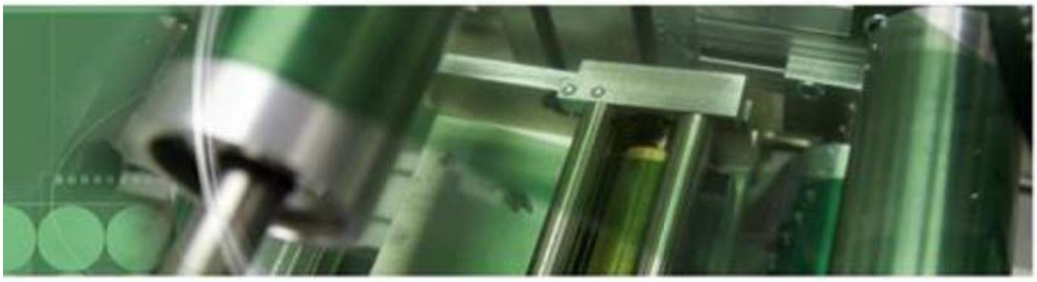
MARTTI TOIVAKKA, ABO AKADEMI UNIVERSITY

### BIOGRAPHY

Martti Toivakka is currently a full professor and head of the Laboratory of Paper Coating and Converting at Åbo Akademi University, Finland (www.abo.fi/lpcc). He received his doctoral degree in chemical engineering in the area of paper chemistry in 1998. His research group is a member of the Academy of Finland appointed Center of Excellence for Functional Materials, which develops functional materials and demonstrates devices for printed intelligence. His research interests include novel coating and surface treatment methods for natural fiber-based products, printing as a fabrication method and use of paper as a substrate for printed electronics. He has (co-)authored over 130 peer-reviewed scientific publications in international journals and conferences.

### ABSTRACT

Mass-produced paper electronics (large area organic printed electronics on paper-based substrates, “throw-away electronics”) has the potential to introduce the use of flexible electronic applications in everyday life. While paper manufacturing and printing have a long history and are considered among the greatest inventions of mankind, they were not developed with electronic applications in mind. Modifications to paper substrates and printing processes are required in order to obtain working electronic devices. This should be done while maintaining the high throughput of conventional printing techniques and the low cost and recyclability of paper. Influence of paper properties on printed functional devices, and possibilities to improve compatibility with printed electronics is discussed. Examples demonstrator devices printed with a custom built roll-to-roll hybrid printer are shown.



# Paper Electronics

## Paper as Substrate for Printed Electronics and Sensors

Martti Toivakka
Laboratory of Paper Coating and Converting
Center for Functional Materials
Åbo Akademi University

## Paper Electronics = Disposable Printed Electronics on/in Paper with Commercial Potential


Electro-magnetic blocking, De Barros et al.

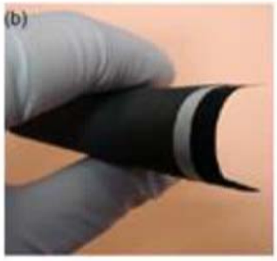
Incontinence detection, Sensible Solutions Sweden AB

Patient adherence tracking
Pharma DDSi, StoraEnso

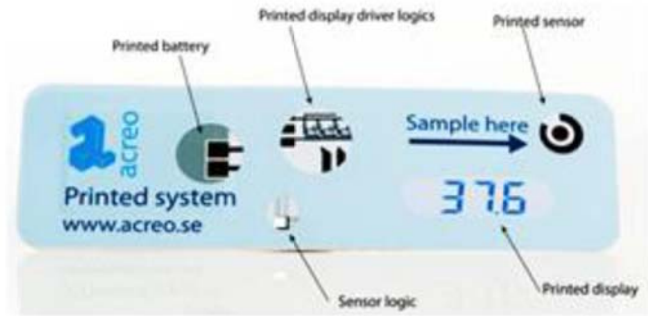
Self-cooking soup packaging
Fulton Innovation

# Product Concepts Based on Electrochemistry

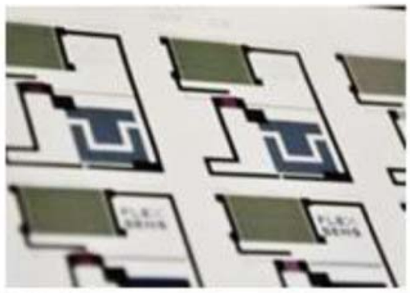

"Zero-Cost Diagnostics"
G.M. Whitesides



Li-ion paper-batteries,
Jabbour et al.




Printed bio-sensing platform, Acreo



Gas sensor on paper,
Peltonen et al., FunMat/FlexSens



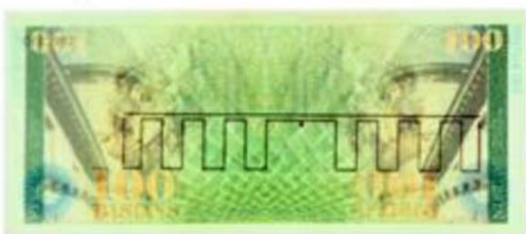
# Hybrid Products

Confidex


- Combine, e.g. silicon-based RFID-chips with printed antenna:
  - Contactless smartcards and tickets
  - Product tracing and copy protection

Powercoat® Alive

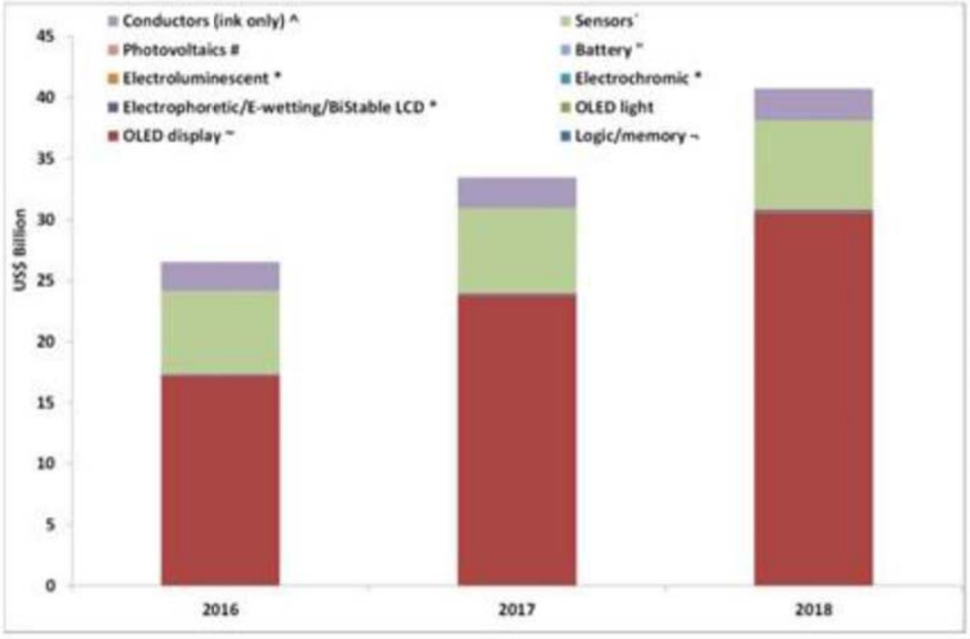
NDSU, 2015



Walki® Pantenna

## Market Prediction for Printed Electronics

IDTechEx Nov 2015



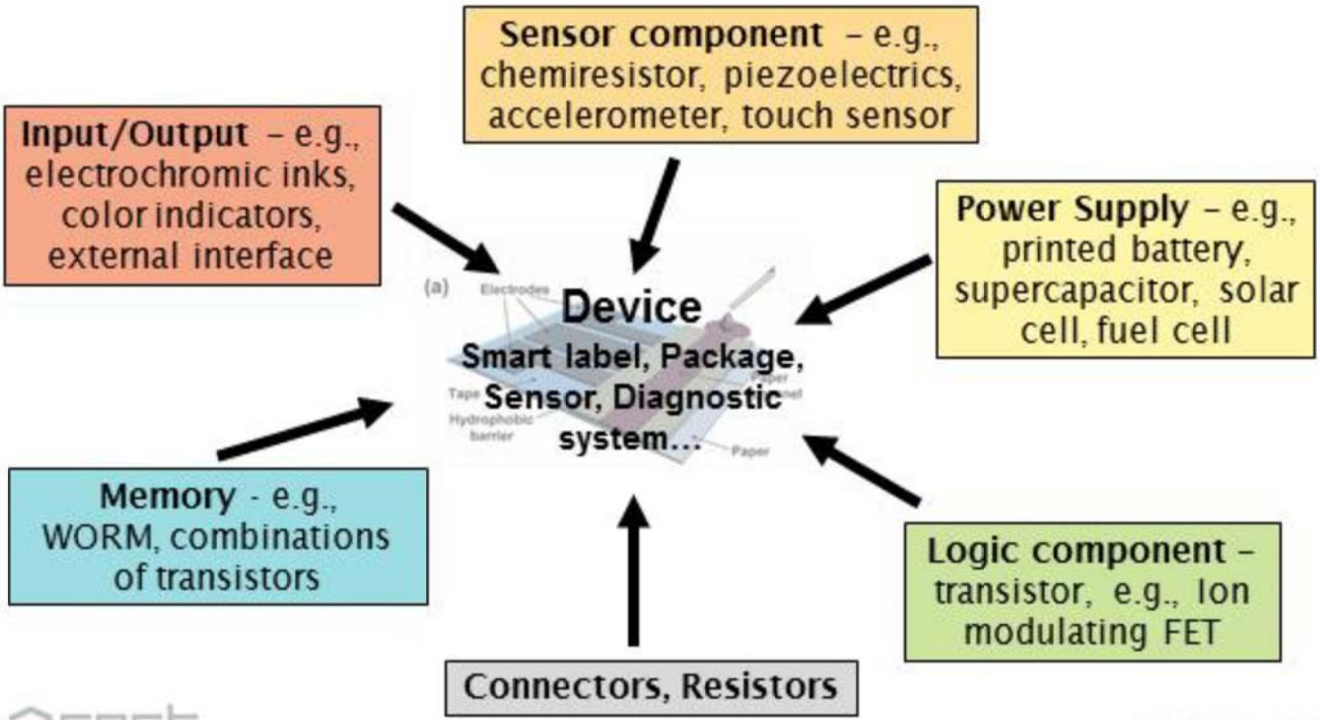



## Advantages of Using Paper as Substrate for Printed Electronics

- Low cost and large existing product base
- Biodegradability, compostability, ease of disposal → one-time use, "throw-away electronics"*
- Mechanical properties: stiffness, foldability
- Adjustable printability of functional materials
- High temperature tolerance → inexpensive infrared sintering
- Transparency by using nanopaper (=nanocellulosic films)
- Biocompatibility beneficial for biological applications

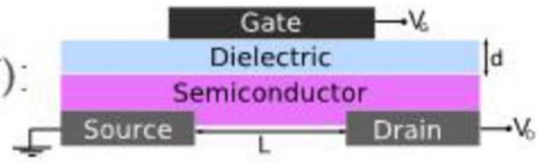
* Aliaga et al., The influence of printed electronics on the recyclability of paper: a case study for smart envelopes in courier and postal services. Waste Management 38:41–48, 2015

# Paper Electronics – from Components to Devices and Products






# Example: Low-voltage Printed Transistor on Paper



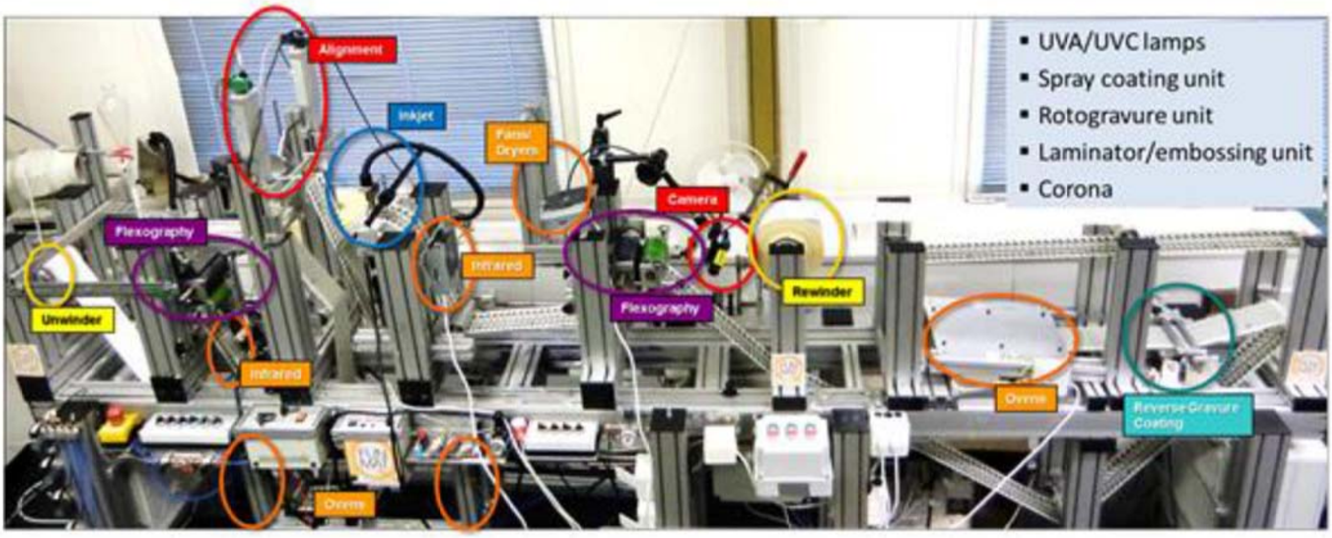

HIFET (Hygroscopic Insulator FET):

- **Source and drain**
  - AgNP-ink: Inkjet printed and IR-sintered (10 s)
- **Organic semiconductor**
  - P3HT: Inkjet printed
- **Dielectric** (hygroscopic insulator)
  - PVP: Reverse gravure coated
- **Gate contact**
  - PEDOT:PSS: Inkjet printed or drop cast

FUJIFILM Dimatix, Inc

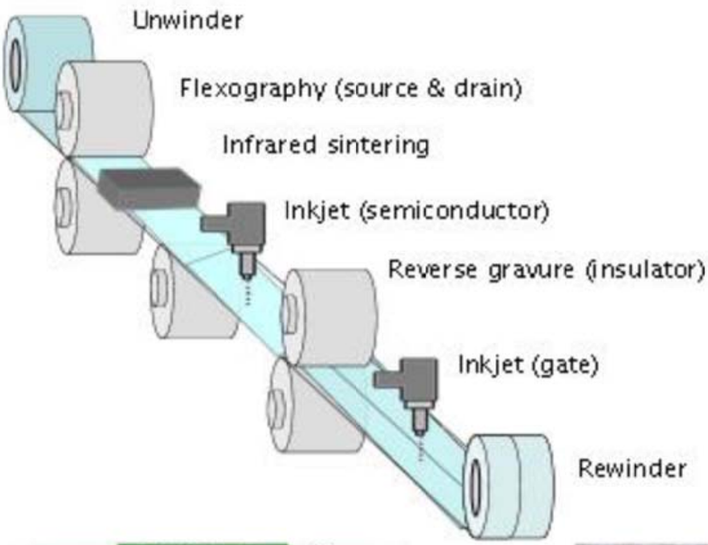
Mini-Labo, Yasui Seiki Co.

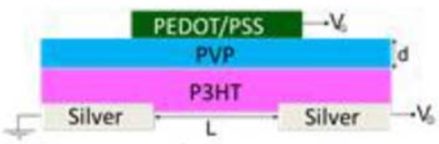
# "FunPrinter" – Custom-built Hybrid Printer for Functional Materials





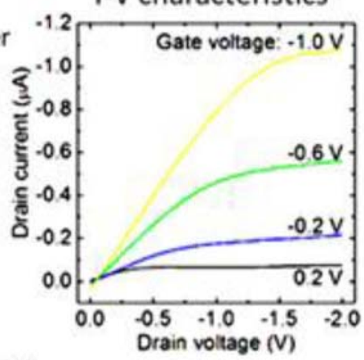

# R2R-printed Transistors on Paper



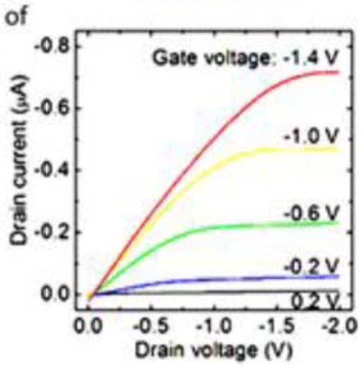




I-V characteristics

Immediately after manufacturing




After 4.5 months of storage in room atmosphere



# Towards Logic Circuits on Paper

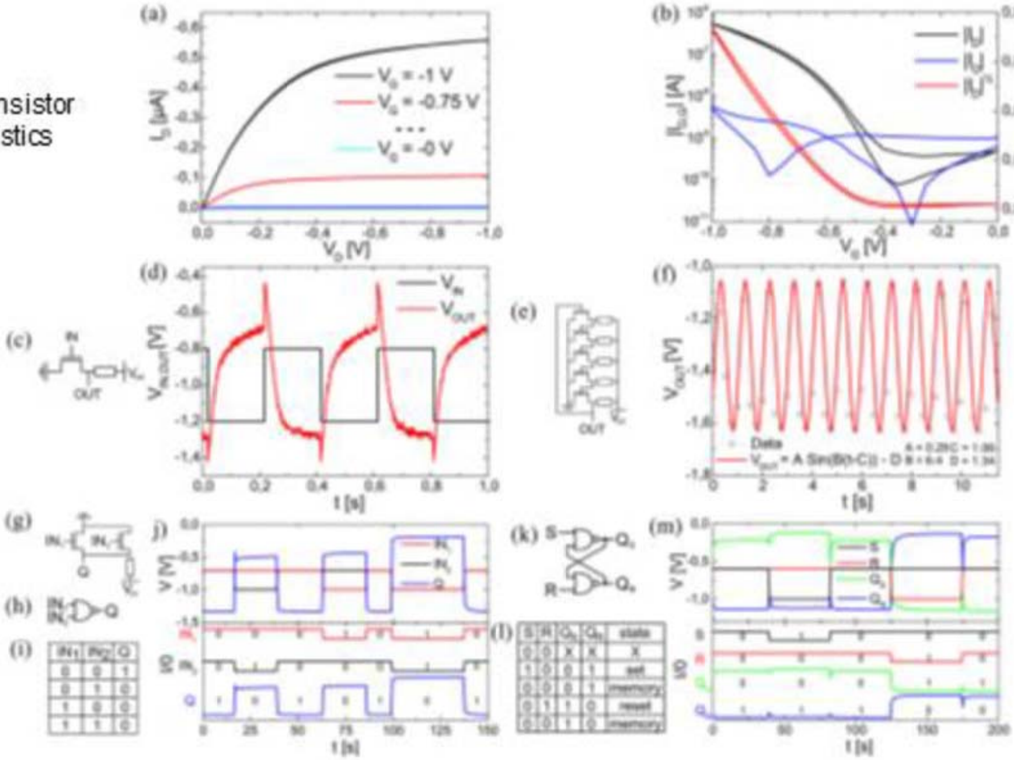
CSorb transistor characteristics

Inverter

Ring-oscillator

NOR-gate

SR-latch

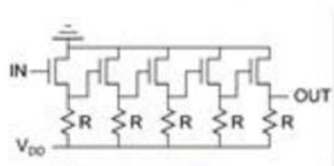


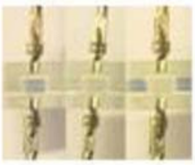

Pettersson, F., *Paper- and Membrane-Based Ion-Modulated Electronics*, 2015, PhD thesis, Åbo Akademi



# Proof-of-concept Devices on Paper

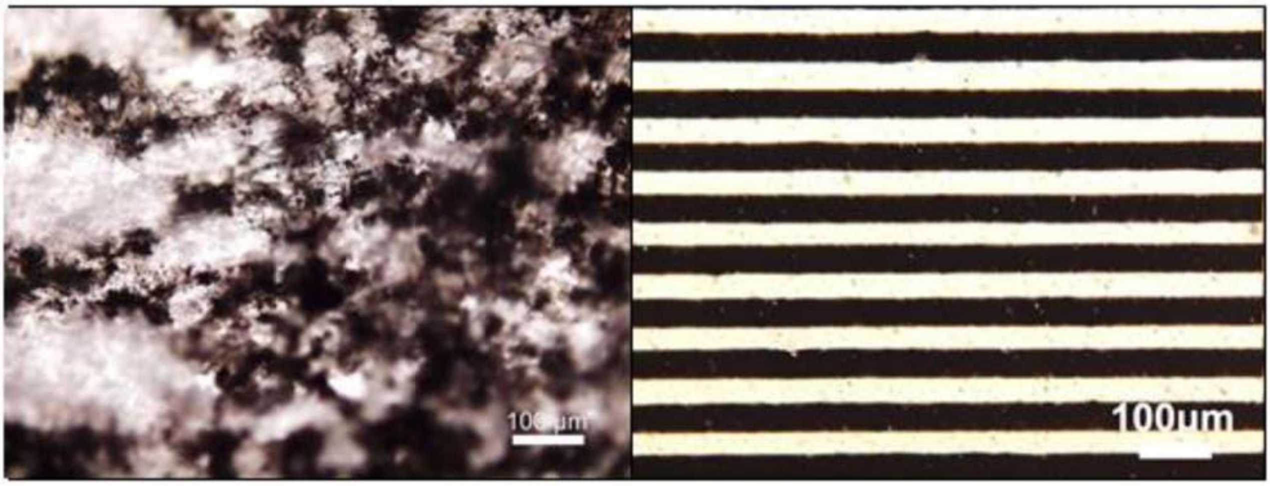
- Transistors
- Ring oscillators
- 1-bit memory
- Electrochromic pixels
- Light-emitting electrochemical cell
- Ion-selective electrodes
- Hydrogen sulfide sensors
- Oxygen sensors
- Printable circuit for gas sensors
- Reaction arrays
- Digital microfluidics



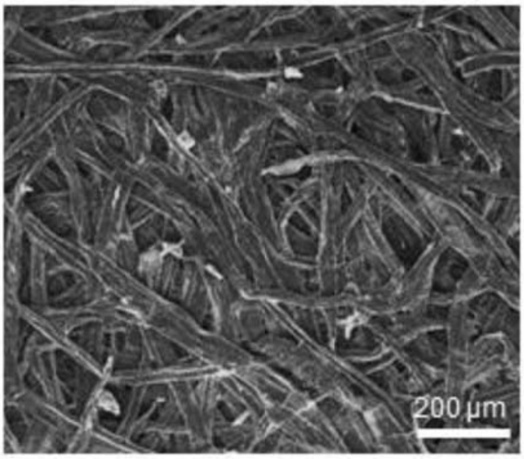
# Challenges of Printing Electronics on Paper

- Paper & printing not developed for electronics



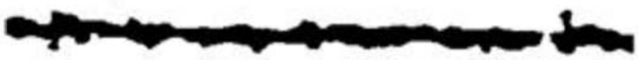



# Functional Printing on Uncoated Paper



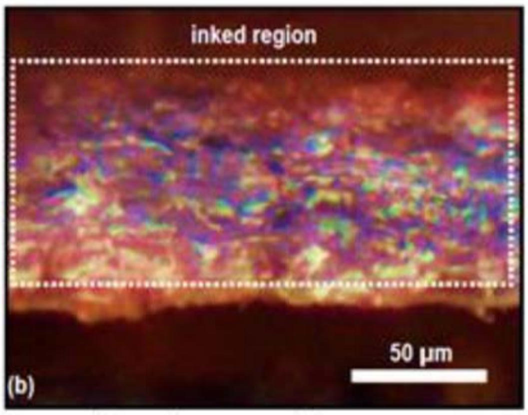

- Poor performance due to:
  - high surface roughness
  - uncontrolled spreading
  - uncontrolled absorption

**Inkjetted Particulate Silver Ink**



R. Bollström et al., 2013.

**Inkjetted PEDOT:PSS-SWCNT Ink**




P. Angelo et al. NPPRJ 27(2):486, 2012

## Challenges of Using Paper as Substrate for Printed Electronics

- High surface roughness and porosity, large pore size
- Hygroscopicity and poor dimensional stability
- Poor long time heat resistance
- Complex surface chemistry
- Poor barrier properties
- Dusty material not allowed in clean room environment used by printed electronics manufacturers

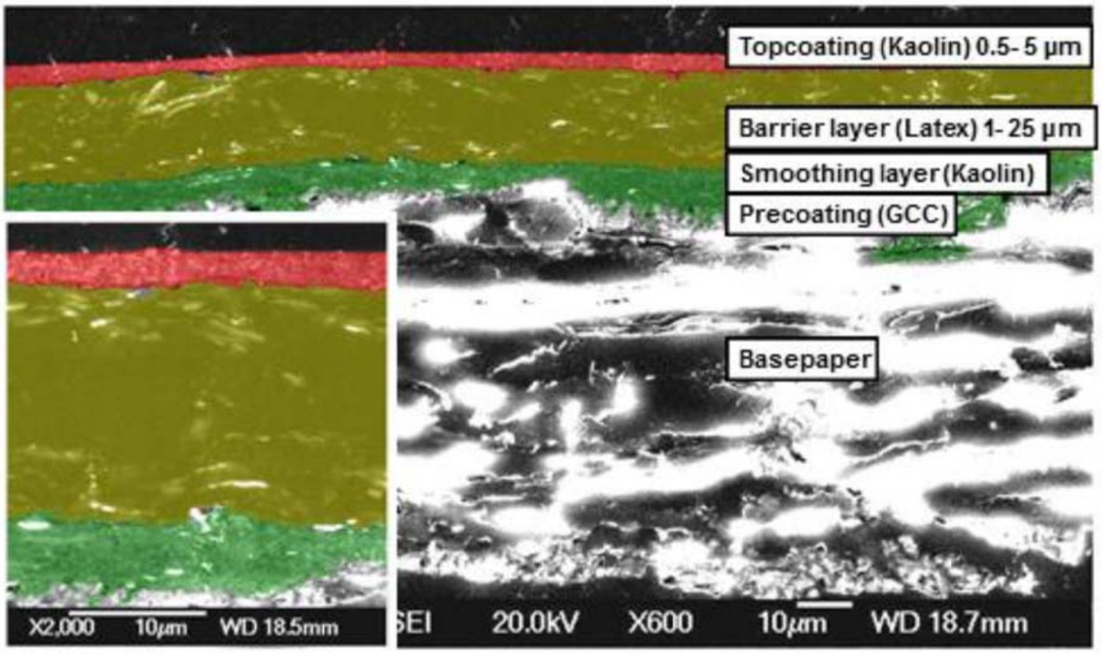


## Making Paper Compatible with Printed Electronics

- We need to **measure and control surface properties of the substrate**: roughness, (surface) porosity, wettability, chemical activity/inertness, barrier properties, mechanical properties, dimensional stability, humidity

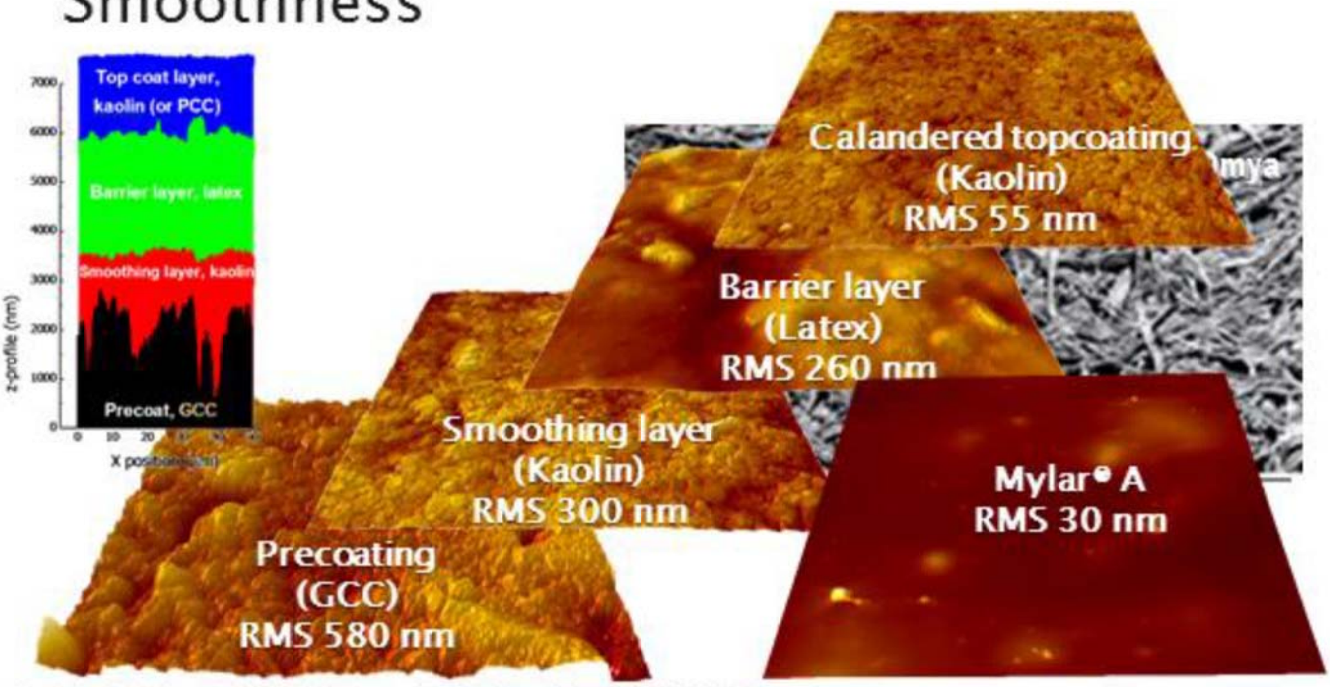
- Surface treatment methods to improve printability:
  - **Existing**:
    - surface sizing
    - pigment coating
    - dispersion coating
    - extrusion coating
    - corona treatment
  - **Novel methods**:
    - plasma activation/coating
    - nanoparticle deposition
    - sol-gel coating
    - atomic layer deposition
    - chemical vapor deposition

# Example Substrate Concept For Paper Electronics




R. Bollström, A. Määttänen, P. Ihalainen, M. Toivakka, J. Peltonen: **Chinese patent (ZL 201080006446.5), European patent (2392197)**
R. Bollstrom, D. Tobjörk, A. Määttänen, P. Ihalainen, R. Österbacka, J. Peltonen, M. Toivakka,: **Org. Electronics, 10, 1020 (2009)**

# Printed Electronics Requires Surface Smoothness




J. Järnström, P. Ihalainen, K. Backfolk, J. Peltonen: **Applied Surface Science 2542 (2008) 5741**
R. Bollström, A. Määttänen, P. Ihalainen, M. Toivakka, J. Peltonen: **Chinese patent (ZL 201080006446.5), European patent (2392197)**
R. Bollstrom, D. Tobjörk, A. Määttänen, P. Ihalainen, R. Österbacka, J. Peltonen, M. Toivakka,: **Org. Electronics, 10, 1020 (2009)**

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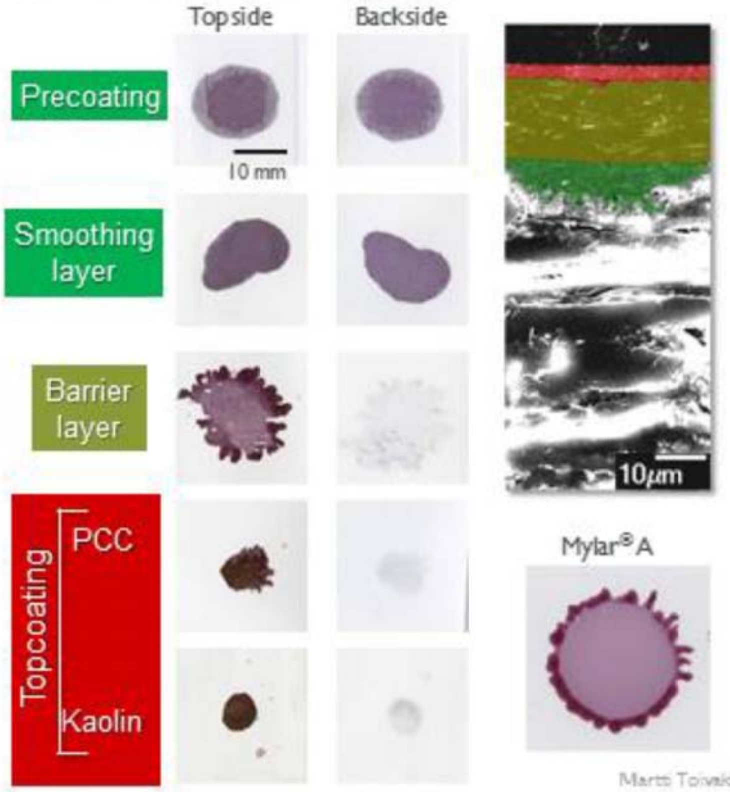
M.Toivakka/Åbo Akademi

# Barrier Properties and Solvent Resistance

**Acetone**
**Toluene**
**IPA**
**CB**
**DCB**
**THF**
**DMSO**
**DMF**
**Xylene**
**Acetic acid**
**HCL**
**NaOH**

Drop size
5µl

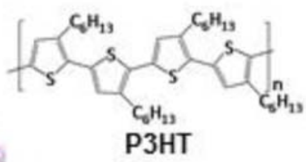
P3HT in DCB

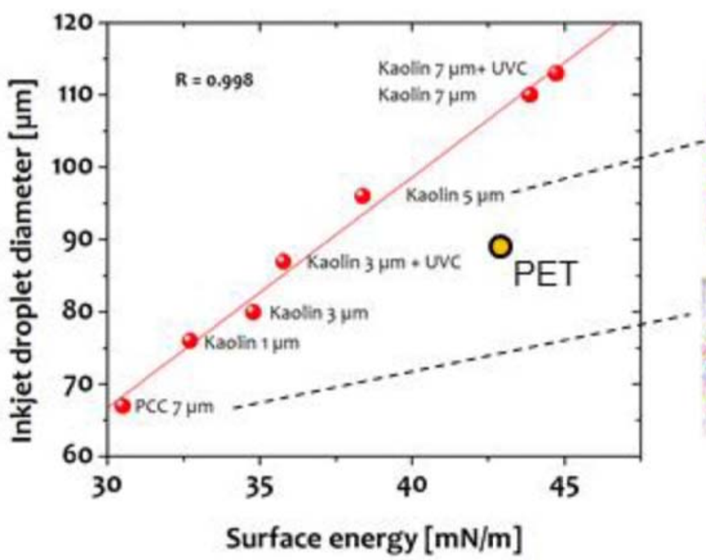


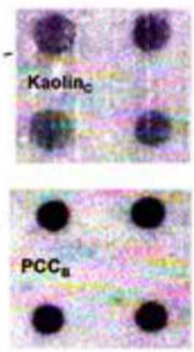


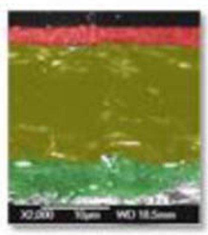

# Improved Inkjet Printability Through Control of Wettability

Ink: 0.5 wt.% P3HT in o-dichlorobenzene (o-DCB), V = 10 pl



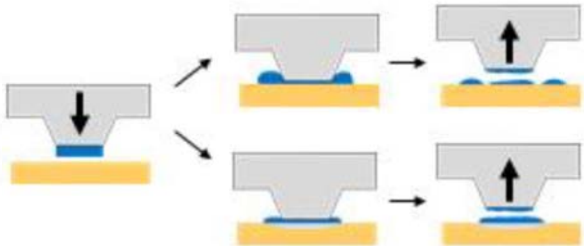



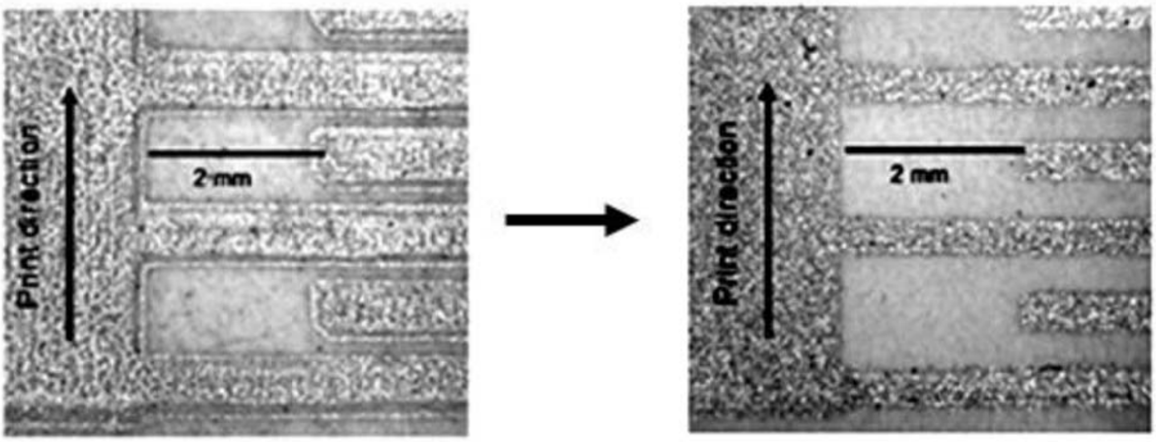



Määttänen, A., Ihalainen, P., Bollström, R., Toivakka, M., & Peltonen, J. (2010). *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 367*(1-3), 76–84.

# Elimination of "Squeeze" in Flexography





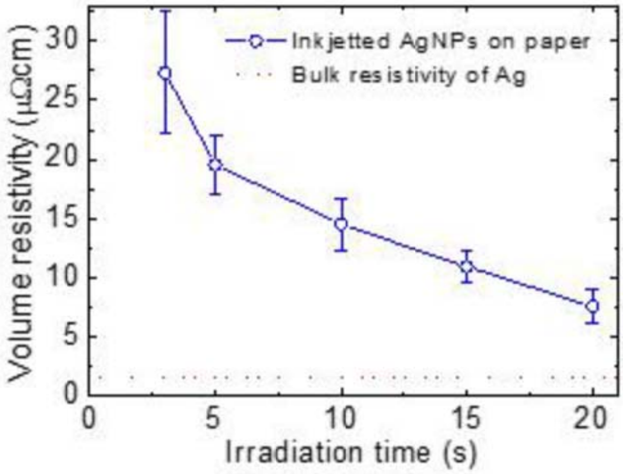

Low surface porosity

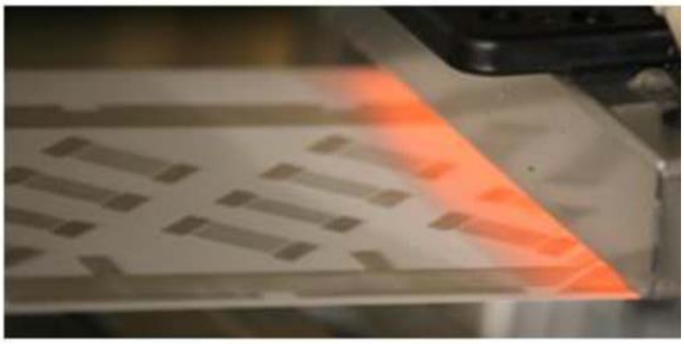
High surface porosity



# Infrared Sintering of Ag-nanoparticles

- Especially suitable on paper: high diffuse reflectance, low thermal conductivity and high thermal stability of paper
- Volume resistivity of inkjetted Ag below 15 μΩcm



D. Tobjörk, H. Aarnio, P. Pulkkinen, R. Bollström, A. Määttänen, P. Ihalainen, T. Mäkelä, J. Peltonen, M. Toivakka, H. Tenhu, R. Österbacka (2012), *IR-sintering of ink-jet printed metal-nanoparticles on paper*, *Thin Solid Films*, **520**(7), 2949–2955.

# Fabrication of Solution Processable Devices on Paper

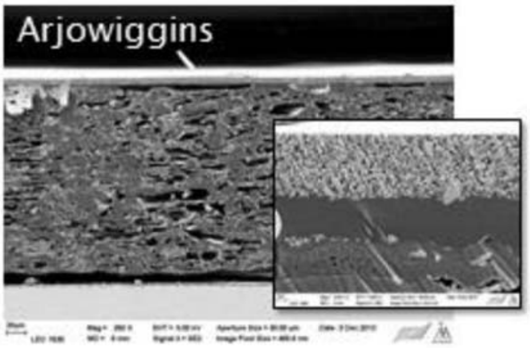
- Success of fabrication (printability) is determined by <u>compatibility</u> of **ink – printing method – substrate**:
  - **Inks (solution processable functional materials)**:
    - Conductive particulate inks, e.g. nanoparticle/micron-size silver, carbon, gold, copper...
    - Conductive polymer inks, e.g. PEDOT:PSS, PANI...
    - Semiconducting inks, e.g. P3HT, PQT...
    - Insulators, e.g. PVP, PMMA...
  - **Printing / coating method**:
    - Inkjet, flexography, rotogravure, screen printing...
    - Reverse gravure, spray, slot, curtain...
  - **Substrate**: Paper or board, with adjustable physico-chemical surface properties

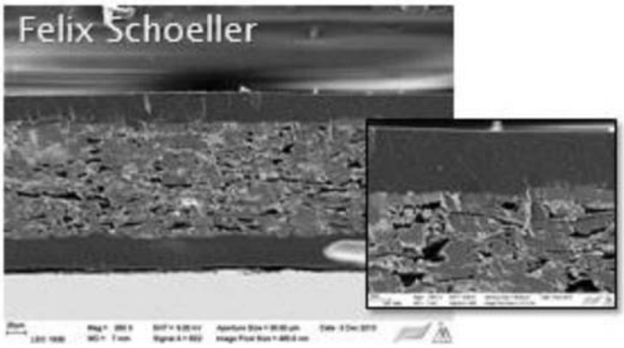


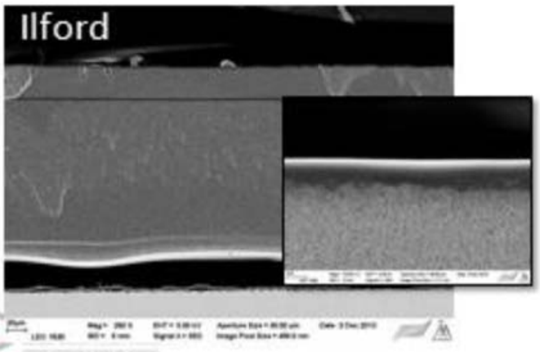
# Paper as a Substrate for Printed Electronics and Functionality

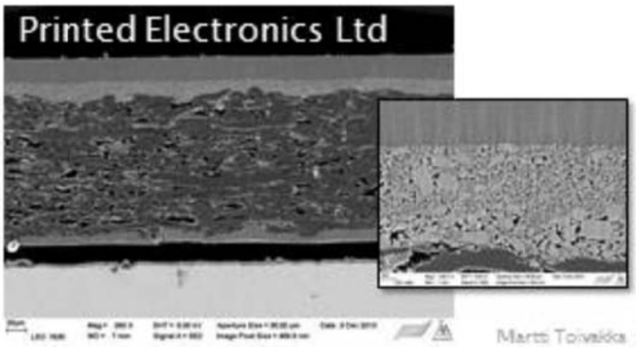
- No universal "Paper for printed electronics" exists (excluding perhaps plastic coated paper)
- Device(s) to be fabricated, i.e. end-use application, determine which paper properties must to be measured and controlled:
  - Barrier properties, surface roughness, surface energy, surface porosity, dimensional stability, thermal resistance...
  - ...while maintaining the low cost and recyclability
- Devices often need to be adapted for paper
- Device fabrication directly in/onto paper challenging in existing converting and printing processes:
  - →separate production of devices/components (on paper/silicon/plastic)
  - →Integration in/onto products, e.g., as stickers

# Commercial Papers for Printed Electronics






# Conclusions and Outlook for Paper Electronics

- Printed transistors, simple circuits and numerous other devices as well as sensors can be fabricated on multilayer coated specialty paper
- Simple products based on conductive lines already on market
- Numerous challenges remain, including shortage of profitable business cases and market ”resistance”, scale-up issues, expensive materials and processes, non-existence of suitable hybrid printer facilities (paper not allowed in clean rooms)
- High commercialization potential for low-cost “large area” applications, simple sensors for biological, biomedical and chemical applications (paper-based microfluidics / diagnostics)

http://www.abo.fi/lpcc

http://www.funmat.fi/

## 17. Inks & formulation

Chris Phillips, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a


# Guide to Printing Ink Manufacture

# Content

1. What influences the choice of ink and formulation
2. Print processes & process considerations
    - Particle size importance in printing
    - Rheology
3. Ink components
    - Pigments
    - Polymer
    - Solvents
    - Additives
4. Ink manufacture
    - Mixing
    - Milling



# What influences choice of ink

- Functional or decorative application
    - Graphic
    - Functional
        - Conductive, insulating, dielectric etc.
- Which printing process?
    - Thickness, resolution, run length
- Viscosity and particle size limitations
- Product life
    - Rub or scuff resistance
- Health and safety considerations
    - Less aggressive solvents or water based

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# Process requirements

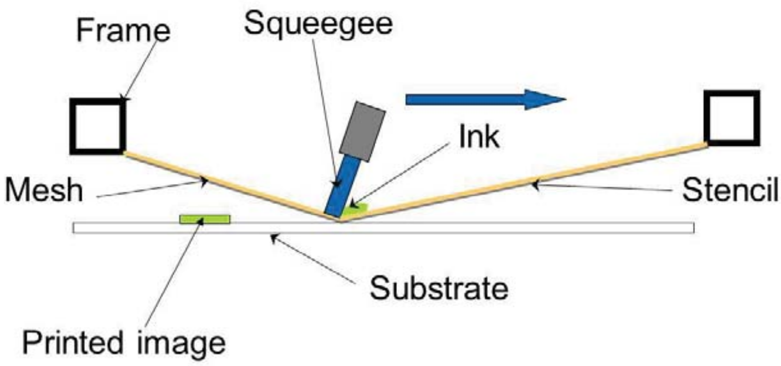
## Different inks for different processes

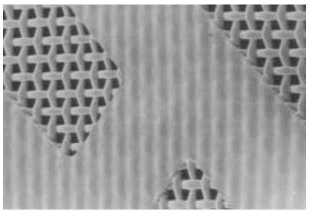
- Screen
- Stencil
- Lithography
- Letterpress
- Flexography
- Gravure
- Spray
- Aerosol jet
- Inkjet
- Slot Die
- Curtain coating

| Printing process | Percentage Pigment | Viscosity* (Pas) | Film Thickness (μm) |
|---|---|---|---|
| Letterpress | 20 - 30 | 1 - 50 | 1 - 6 |
| Lithography | 20 - 30 | 10 - 80 | 1 - 6 |
| Gravure | 10 - 30 | 0.05 - 1 | 1 - 12 |
| Flexography | 10 - 40 | 0.1 - 40 | 1 - 10 |
| Screen | 5 - 50 | 0.1 - 40 | 1 - 50 |
| Ink Jet | Very low | 0.05 – 0.1 | 1 - 6 |

*Indicative single value

# Print processes - Screen



- Thick paste inks
- Thick deposit
  - High loading
  - Good for functional applications
- Predominant method for printed electronics
  - Low cost, simplicity
- Short run length

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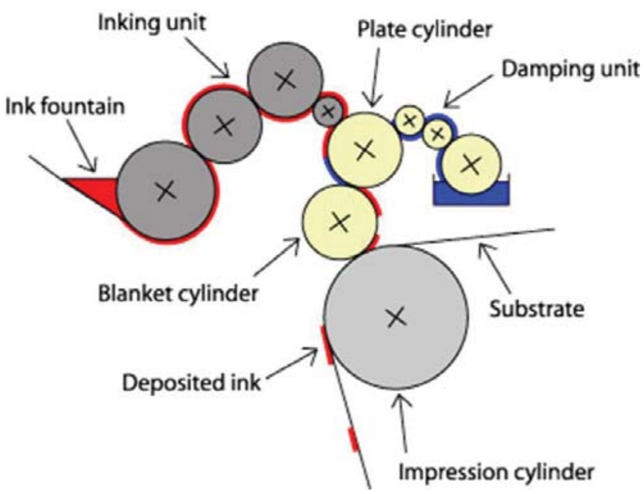
# Print processes – Offset Lithography




- Very thick paste inks
- Oily and hydrophobic
- Long run length
- Currently limited use in functional printing
  - Water in process

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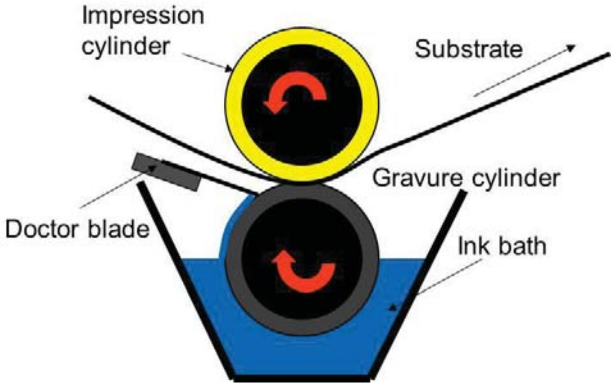
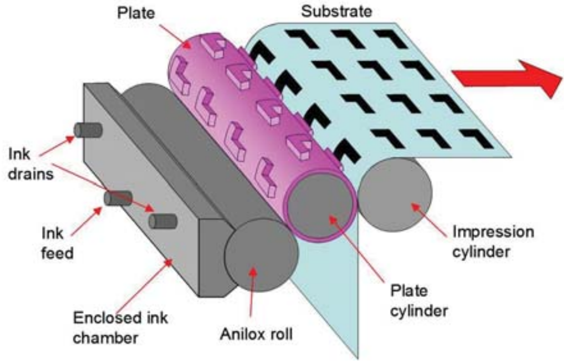
# Print processes – Gravure and Flexo

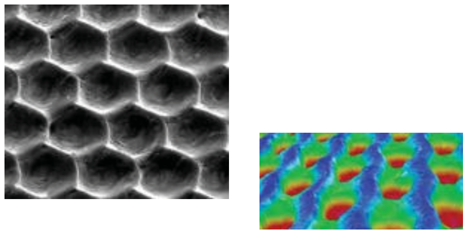
Gravure




- Liquid inks
- Mid to long run lengths
- Flexo growing interest for functional applications

Flexography



Anilox cells

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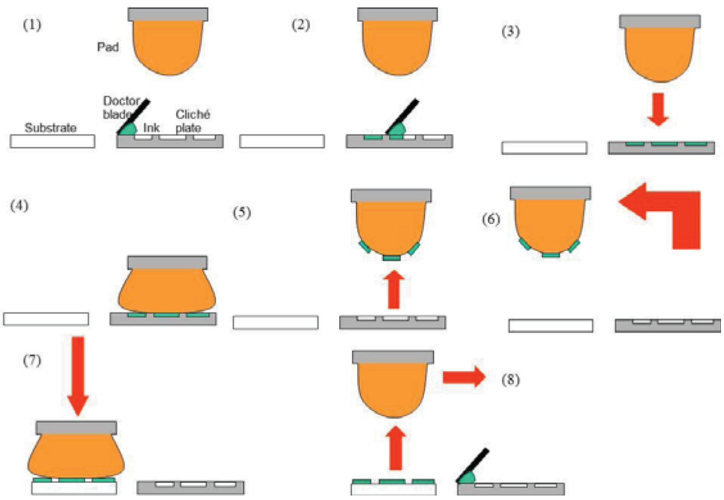
# Print processes - Pad




- Low viscosity ink
- Fast solvents to encourage ink surface to be “sticky”
- Currently limited use in functional printing
    - Useful for non-flat surfaces

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# Print processes - Ink jet

- Very low solid content
- Small particles
- Narrow viscosity and surface tension window
- Popular research equipment for functional applications
  - Efforts to improve volume production

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# Particle size ranges

- Lithography < 5 µm
  - *inks dry through oxidative cure (cold set) or hot air*
- Gravure < 5 µm
  - *fast drying, UV curing, Hot air, IR etc.*
- Flexography < 5 µm
  - *fast drying, UV curing, Hot air, IR etc.*
- Screen – Particulate size defined by the screen mesh used – try to keep below 5 µm
  - *inks can be high solids, UV curing, Hot air, IR etc.*
- Stencil – can accommodate large particle sizes
  - *inks can have high solids loading, UV curing, Hot air, IR etc.*
- Inkjet <100nm
  - *inks are low solids, UV curing, air, Hot air, IR etc.*

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# Particle size limitations

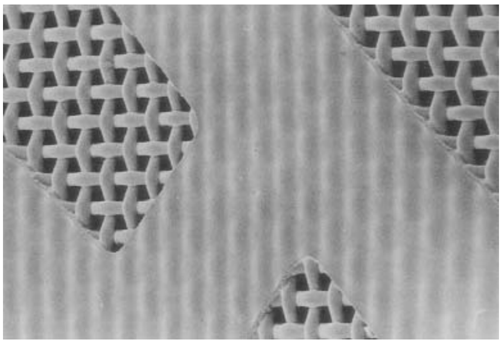
- Particles have to travel through or in and out of various constrictions
  - Blockage causes missing print area
- "Rule of thumb"

Pigment particle size should be less than 1/3 the size of:

- Gravure & flexo anilox cell size
- Screen mesh opening
- Inkjet nozzle



# Particle size



## Screen mesh

Open area dependent on thread thickness and number of threads per cm

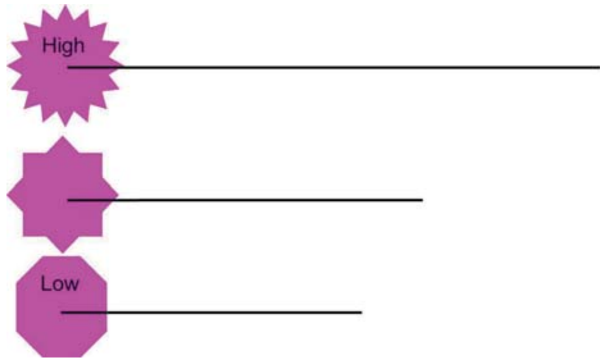
## Gravure cell

Capacity dependent on cell width length and depth

# Particle size and specific surface area

Specific surface area influences :

- Sedimentation
- Rheological properties
- Absorption rates
- Drying rate
- Gloss
- Rub resistance
- Dimensional stability (shrinkage of the ink film)




Titanium dioxide (white) 9 $m^2/g$

Graphite 10 $m^2/g$

Carbon black $<100$ $m^2/g$

Acrylamide red 48 $m^2/g$

Copper phthalocyanine 63 $m^2/g$

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# Solvent absorption

- Smaller particles absorb more solvent
  - More difficult to incorporate into resin
  - Higher ink viscosity
  - Might take longer to dry (locking in solvent)
- Example: Carbon ink
  - More carbon black less graphite
    - High viscosity
    - Thicker printed film
    - Prone to mesh marking
  - Carbon black is incorporated first

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## Particle sedimentation

- Stokes Law
- Big particles settle faster than small particles
- Denser materials sink faster
- The lower the viscosity, the faster the sedimentation

$$V_t = \frac{gd^2(\rho_p - \rho_m)}{18\mu}$$



## Viscosity and Rheology

- Study of flow and deformation
  - Resistance of an ink to flow
- Also known as
  - “runniness”, “thickness”, “thinness”, “consistency”, …
- Viscosity is often quoted as a single value for an ink
  - Pretty meaningless as viscosity changes during the shearing and recovery processes in printing
- Rheology encompasses elastic (solid) and viscous (liquid) properties of a material

# Viscosity and Rheology

- Critical to
  - Mixing, ink stability, printing properties, emulsification, drying, ink penetration, settling/slumping adhesion,…, etc
- Example: Line / Dot formation
  - If recovery of viscosity is not sufficiently fast or high, the features will slump

Ideal shape

slump shape

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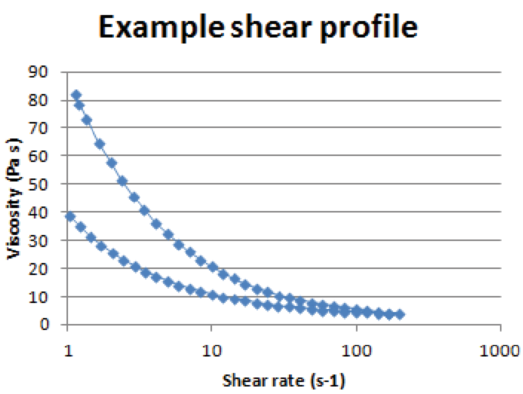
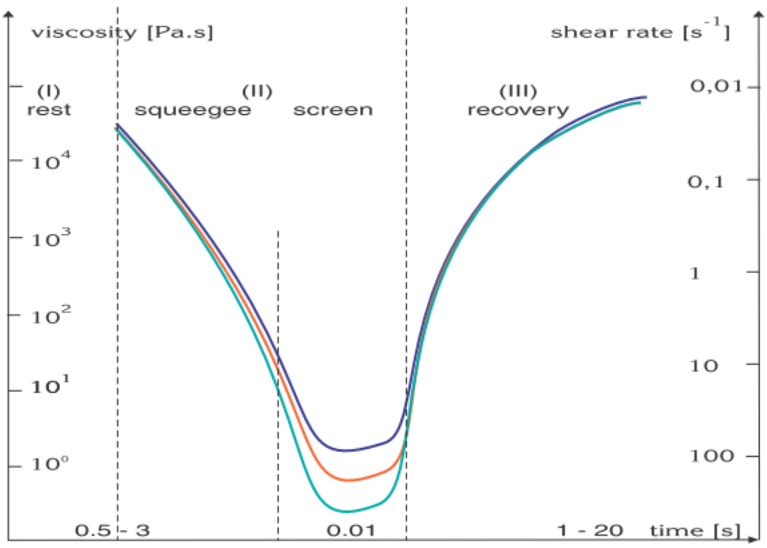
# Change in shear rate during printing

- *Example* - Screen printing – shear rate at maximum as ink is forced through screen
- Recovers after printing – dictates slumping

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# Ink components

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## Ink components

Most inks can be split in to the following components

### Active

- Pigments
  - Decorative
  - Functional
- Additives

### Polymer

- AKA
  - Base
  - Resin
  - Vehicle
  - Medium
  - Extender

### Liquid

- Solvent
- Diluent

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## Pigments

- Pigment – solid particles designed to impart colour and/or opacity
- Many materials with decorative applications also find use in electronics
  - Metal oxides
    - Titanium dioxide
  - Metals
    - Silver, aluminium, copper, nickel *etc*.
  - Carbon
    - Carbon blacks, graphite, carbon Nanotubes, graphene
  - Ceramics
    - Lead zirconate titanate
    - Barium titanate
      - Photorefractive Properties
      - Piezoelectric properties
      - Dielectric properties

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## Physical attributes of pigments

- Particle size
- Surface area
- Wetting and absorption of solvent

Example

- Carbon black
  - Very small particle size
  - Large specific area
  - Low settling potential
  - High solvent absorption

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# Polymer

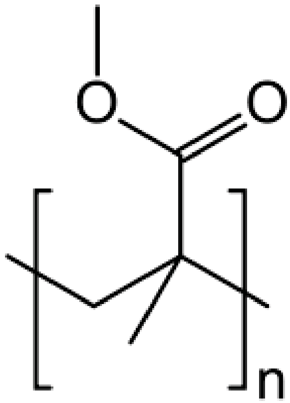
- Also known as: base, resin, medium, film former, binder, extender, vehicle
- Requirements:
  - Must provide transport for the pigment
  - Must bind the pigment together (cohesion)
  - Must provide adhesion to the substrate
  - Must suit the application process
  - Must not adversely affect appearance or functionality
    - **Polymer will hinder conductivity in a conductive ink but is needed to hold the ink together**



# Some polymer types

- Acrylates
- Alkyds
- Cellulose Acetates
- Nitrocellulose
- Epoxies
- Polyamides
- Rosin Modified phenolic
- Vinyl (chloride, alcohol, acetate co-polymers)
- Silicon
- Water soluble polymers
- UV curable (acrylates)
  - Some application in printed electronics
  - Inferior performance

# Acrylates



- Popular in many processes
- Chemically inert when cured
- Available in water-based suspensions
  - Emulsion
- Soluble in most popular solvents
- Screen, flexo & gravure, paint

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# Modified Rosin

- Rosin derived from pine trees and plants
  - Modified with phenolics
- Soluble in many solvents and oils
- Hard, high gloss & rub resistant film
- Widely used in offset ink

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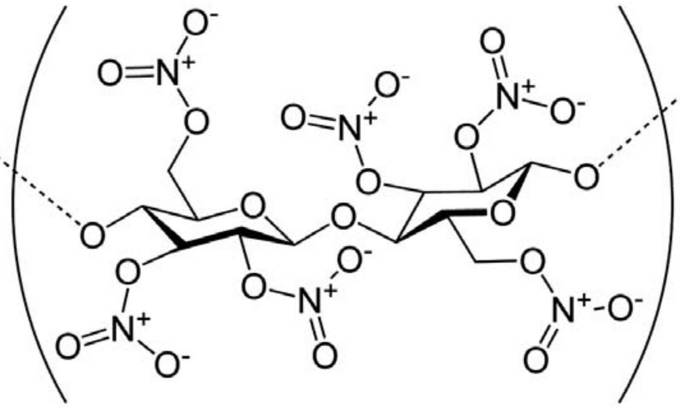
# Nitrocellulose

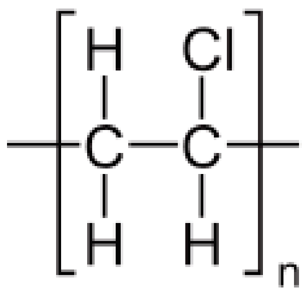
- Derived from cotton using nitric acid
- Soluble in polar solvents such as ketones, esters, ethers
- Good rub resistance, transparent
- High explosive in dry state (“gun cotton”) - damped in alcohol
- Flexo and gravure
    - Available in different viscosities
    - Different levels of nitration
        - Higher nitration – stronger solvent

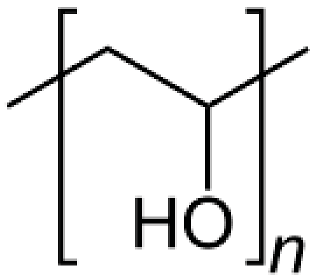




# Vinyls

- Simple straight-chain polymers primarily based on Poly (vinyl chloride)
    - Chloride, acetate, alcohol, carboxyl groups on same chain (co-polymer)
- Functional groups give complimentary properties
    - Aid solubility
    - Film forming
    - Flexibility
    - Adhesion
    - Cross-linking ability





## Water soluble polymers

- Poly(vinyl acetate), poly(vinyl alcohol), poly(ethylene glycol)
- Cellulose based polymers
  - Carboxy methyl cellulose
  - Hydroxypropyl cellulose
  - Popular in research applications
- Solubility in water is a processing advantage
  - But this makes the dry film vulnerable
- High surface tension
  - Surfactant or alcohol (if compatible)



## Liquid

Solvent

- Provides the medium through which all the other constituents can be dispersed
- Provides a means by which the rheological properties of the formulation can be altered to suit the application process
- Should dissolve base
- Should not dissolve the pigment

Diluent

- Does not need to dissolve the base
- Can be used to control rate of drying
  - “slow” or “fast” solvent
- Can be used to control rate of particle deposition
- Can be used to modify viscosity

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# Polar or non-polar

Polar

- Alcohols
- Ketones
- Water
- Ether
- Esters

Non-polar

- Alkanes
- Aromatics
- Chloroform



# Typical solvents

| Group | Examples |
|---|---|
| Aliphatic hydrocarbons | White spirit, petroleum |
| Aromatic hydrocarbons | Toluene, xylene |
| Alcohols | Industrial methylated spirits, Iso-propanol |
| Glycols & Glycol ethers | Ethylene glycol, Propylene glycol |
| Alkanones (Ketones) | Acetone, MEK |
| Esters | Ethyl acetate |

# Choice of solvent

- Choice largely governed by :
  - Ability to vaporise at appropriate rate depending on the process
  - Surface tension requirements of process
  - Solvent capabilities - what will it dissolve and what it will not
  - Negative effects on image carriers / substrate
- Often more than one solvent in an ink
  - Ratio varied according to ink/process requirements



# Solvent Speed

- Nominal “speed” scale
  - 1 is Butyl acetate, < 0.8 is slow, > 3 is very fast
  - Based on standard evaporation conditions
- Within a group of solvents
  - Higher molecular masses typically mean “slower” solvents
  - e.g. Propanol compared to methanol
- Co – solvents
  - More aggressive solvents to dissolve polymer
  - Slower solvents to dilute
    - Butyl acetate and propanol for nitrocellulose

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# Research to manufacture

- Many R&D applications use solvents which are not really suitable/desirable for volume printing
  - Chlorinated hydrocarbons - dichlorobenzene, chloroform
  - Aromatic hydrocarbons – toluene, xylene
    - Health and safety restrictions (use and emission)
    - Degradation of printing formes – flexo plate, screen etc.
  - N-methyl pyrrolidone
    - Toxic and slow to evaporate
- Might need to compromise quality of dispersion
  - Volume mixing processes tend to be open
    - Can't use magnetic stirring in a closed vessel



# A selection of common additives

- Typically small percentage of formula
- Dramatic effect on ink performance
- Additives tailored to each application

- Retarders
- Emulsion inhibitors
- Plasticisers
- Anti foaming agents
- Surfactants
- Bactericides
- Polymerisation catalysts
- Glossing / matting agents
- Wax
- Anti misting
- Conductivity promoter
- Adhesion promoter

## Additives in functional inks

- Additives can interfere with functionality of inks
  - Remain in dry film
- Alternatives
  - Use alcohol to reduce surface tension for water-based system
  - Change the process
  - Modify substrate or plate surface to make it more receptive to ink



# Manufacture

# Ink & Coating manufacture

- Manufacture may occur in two stages.
  - Mixing
  - Milling
- Mixing
  - Solubilizes  resin base
  - "Wets" the pigment
  - Disperses solids equally through the medium
- Milling
  - Breaks down aggregates of particles
  - Can shear particles into smaller pieces



# Mixing

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# What does mixing do?

- Polymer will usually be mixed prior to addition of pigment
- Pigment/functional ingredients can then be mixed
- Dispersion of ingredients evenly
- Removal of air from pigment surface

No wetting

Partial wetting

Complete wetting



# Mixer choice

- Selection based on:
  - Liquid viscosity
  - Vessel size
  - Mixing speed/shear rate
- Must transfer momentum to fluid
- Agitate all fluid in container
- More than one mixer may be required in a vessel
- A heating jacket may be required to disperse some polymers

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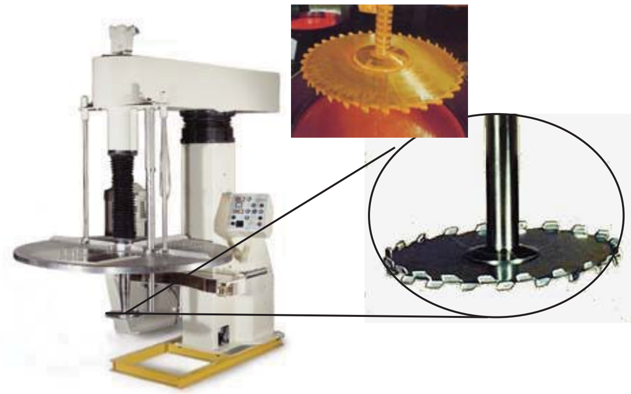
# Mixer Types

Folding / Butterfly mixer



High speed impeller mixer

Shear mixer

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# High speed impeller mixer

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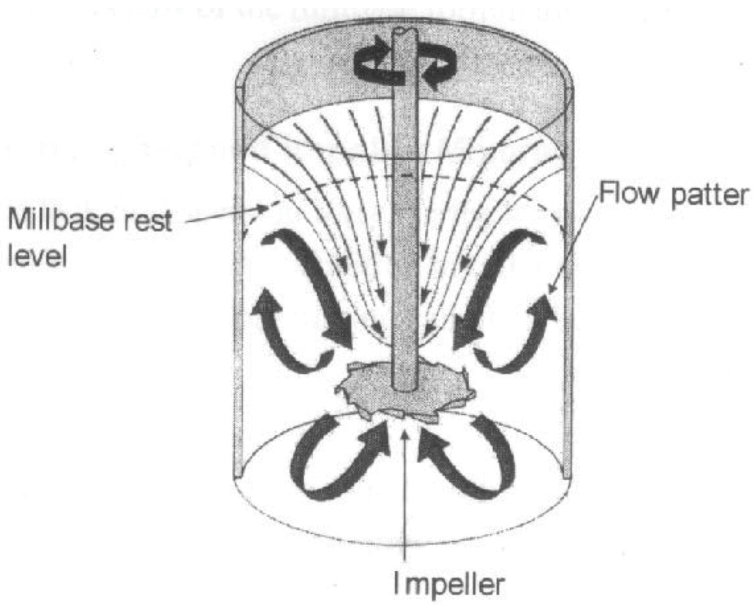
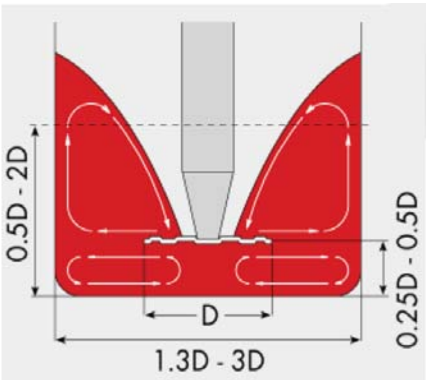
# High speed impeller mixer






# Matching viscosity, vessel, impeller and speed

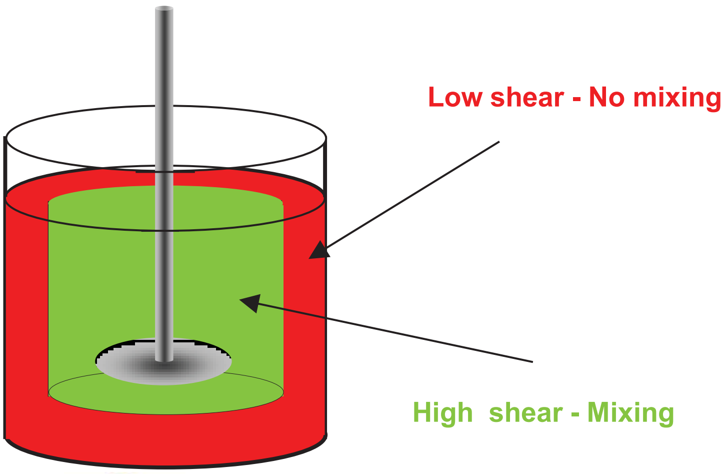
The Impeller must always be covered to avoid aeration




D = Diameter of impeller

The peripheral speed of the impeller should be ≥ 1200 m/min ideal 1500 m/min

Smaller impellers required greater speeds



# Milling

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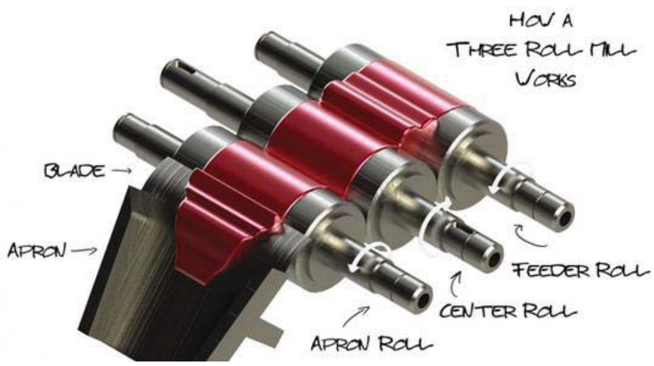
## Triple roll mill




TORREY HILLS TECHNOLOGIES, LLC

- Mill Modes
  - Gap
    - Distance between rollers
  - Force
    - Force between rollers
- Example speed ratios of rollers
  - Feeder 9
  - Centre 3
  - Apron 1
- Cooling can be used

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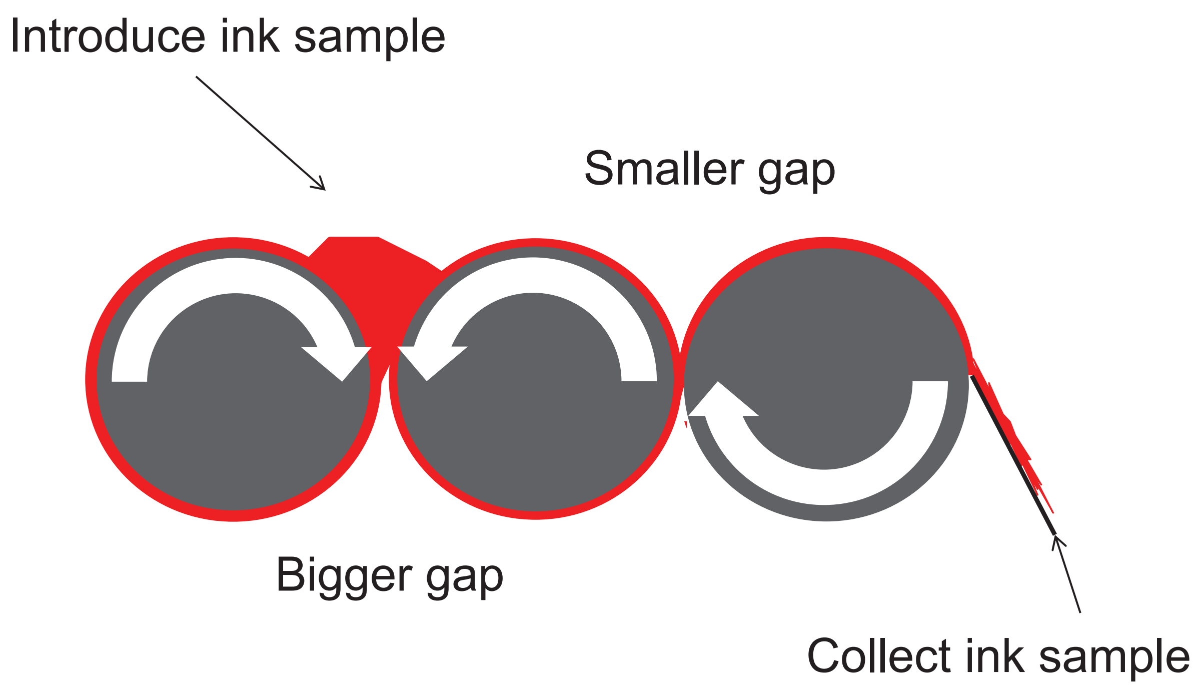
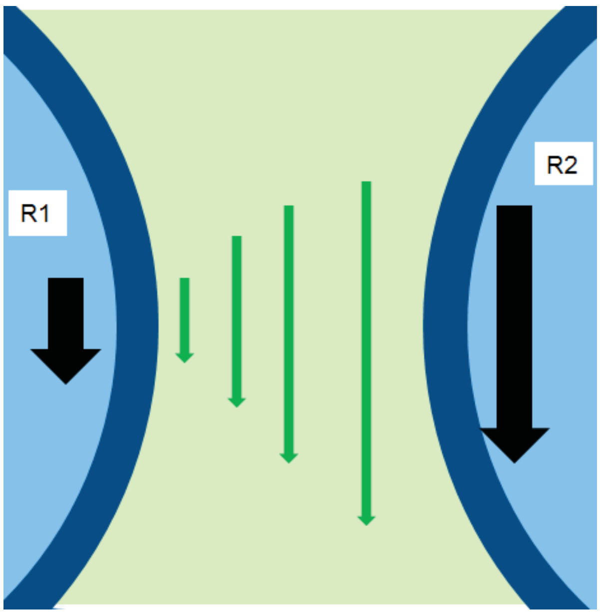
# Triple roll mill



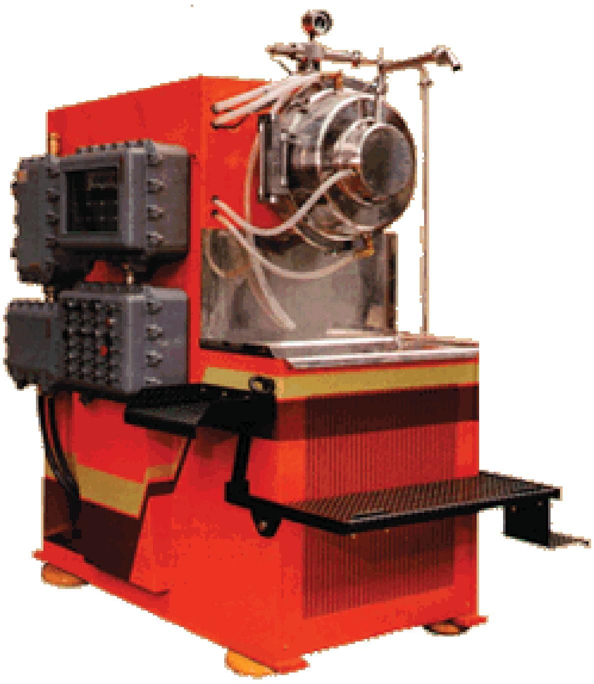



# Shear gradient

- Velocity gradient shears ink
  - 100s RPM
- Breaks up particles
- Fixed gap prevents over-sized particles getting through



# Bead milling



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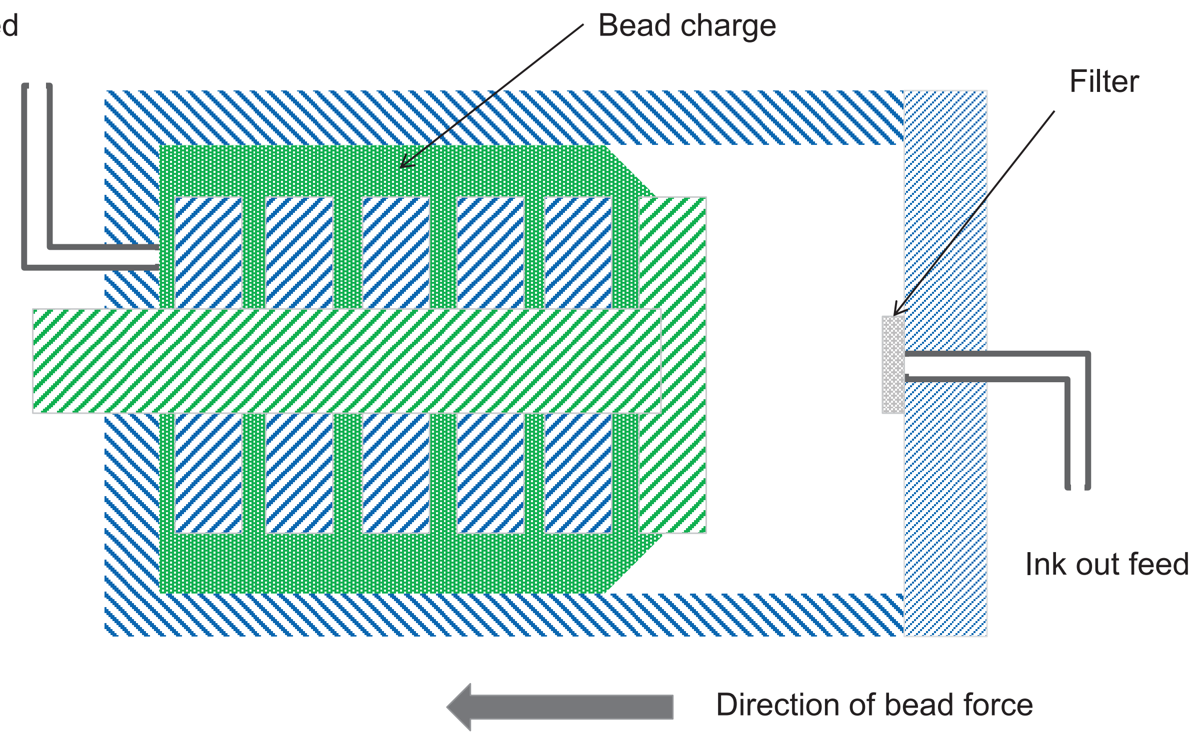
# Bead Mill

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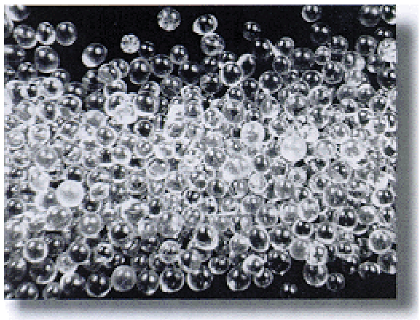
# Milling media

- Specific Gravity - 1.0 to 15.0.
- Diameters – 1 to 20 Microns (and smaller) to several cm
- Materials
  - Plastics
  - Glass
  - Ceramics
  - Metals
  - Tungsten carbide



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# Example protocol
# Screen Printing Paste ink

1. Heat solvent to mixing temperature
2. Add polymer and mix using impeller mixer until dissolved
3. Allow to cool
4. Place polymer suspension in folding mixer
5. Add conductive material gradually
6. Allow mixture to wet overnight
7. Stir again
8. Pass through triple roll mill with large gap settings
9. Repeat twice reducing gap settings each time
10. Clean mill and repeat previous pass

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# Closure

- Ink formulation depends primarily on application and type of printing process
  - Appropriate rheology and surface tension
- Formulation of functional inks for volume manufacture can be a compromise between function and practicality
  - What works in a lab might not be appropriate for large mixing equipment and printing presses


## Acknowledgements

Material provided by
Glyn Davies

## 18. Rheology

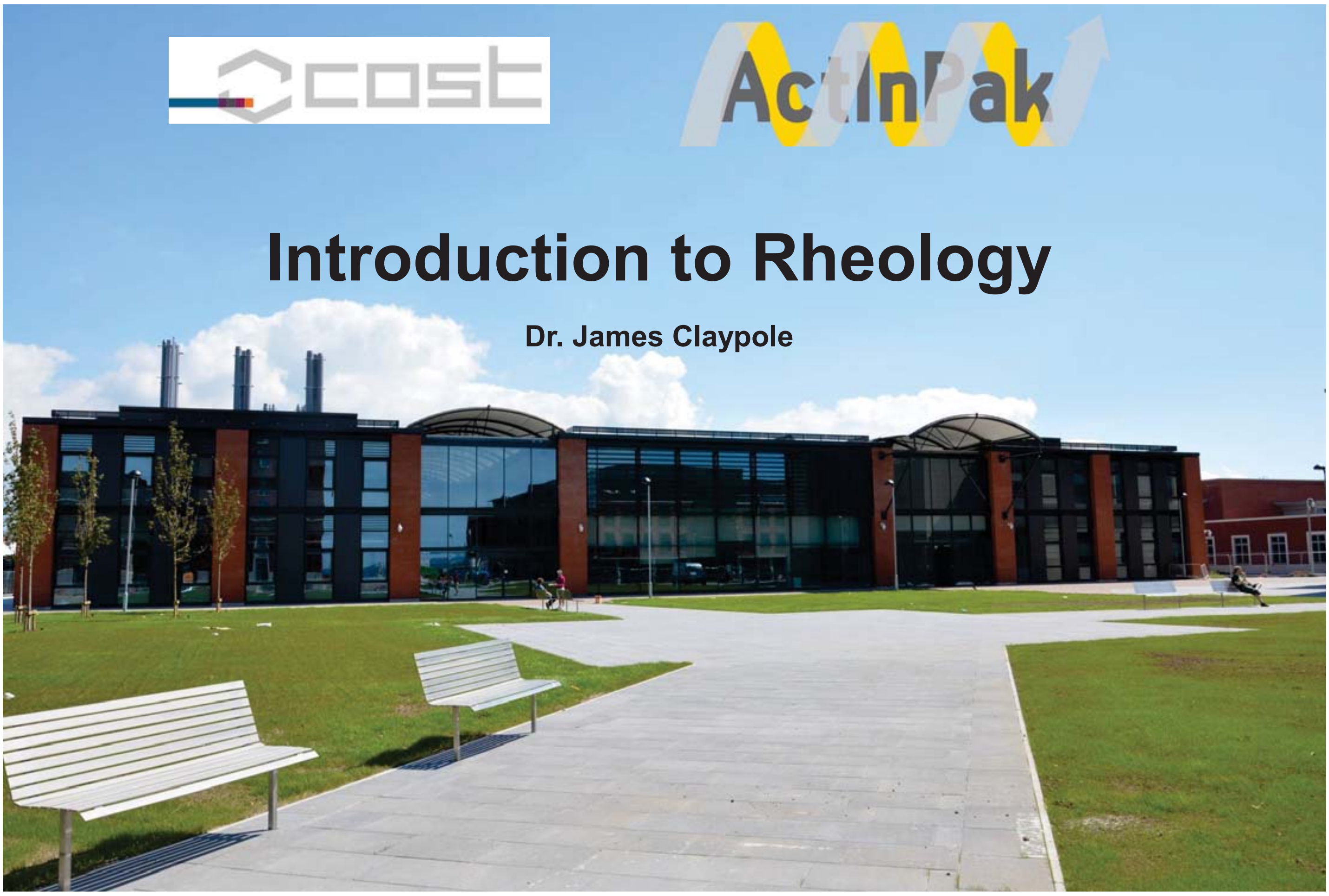
James Claypole, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a



# Introduction to Rheology

Dr. James Claypole



## Introduction

- What is Rheology
- Why is it important for the printing industry
- Basic principles
  - Viscosity
  - Gel point
  - Types of testing
- Rheometer set up
  - Parameter selection
  - Calibration
  - Sample loading
- Extensional rheology
  - CABER
  - Setting up and using extensional rheometer
- Advanced Rheological techniques

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## What is Rheology?

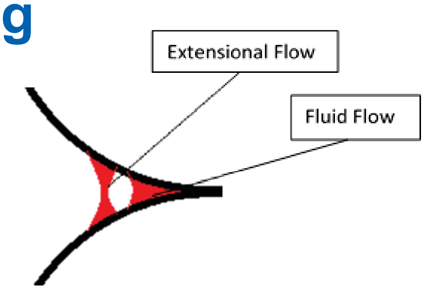
"the branch of physics that deals with the deformation and flow of matter, especially the non-Newtonian flow of liquids and the plastic flow of solids"

The study of fluids and how they behave under flow conditions

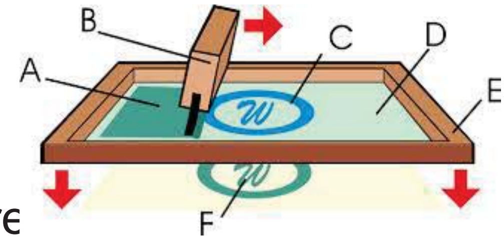
## Why is it Important in Printing?

- Printing process heavily influenced by the characteristics of the inks
- Changing formulas for the inks effects all its characteristics
- Understanding the best rheological characteristics improves the printing process
- Leads to high quality prints and better H&S for printers
- Repeatedly high quality prints are particularly important with functional materials
- Improve Quality Control in ink manufacturing

# Rheology in Printing




- Printing comprises of both extensional and shear flows
- Flexography/lithography – Extension in the nip and shear flow between the rollers
- Screen – High shear flow in the draw and extensional flow in the snap
- Inkjet – Extensional flow as droplets are produced






# Basic Principles

- Rheometry
- Newtonian/Non-Newtonian
- Viscosity
- Oscillatory
- Storage and Loss moduli
- Phase angle
- Viscoelasticity
- Gel points

# Rheometry

There are two main types of Rheometer that can be used to study fluids

Shear rheometer (stress and strain controlled)

Measures the response relative to a shear flow


Extensional rheometer

Measures the response of the fluid to and pulling/extensional flow



# Newtonian/non-Newtonian

Newtonian fluids are where the stress at each point in the flow is directly proportional to the strain rate

- Water
- Air
- Silicone oils

- Printing inks
- Cellulose
- Biopolymers – gelatine
- Silicone gels
- Plastics

Non-Newtonian fluids are anything that is not Newtonian.

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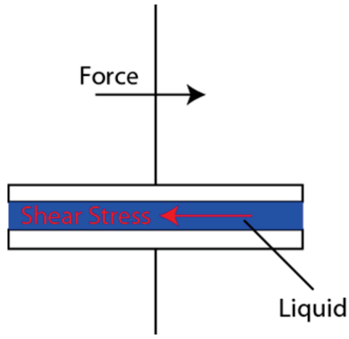
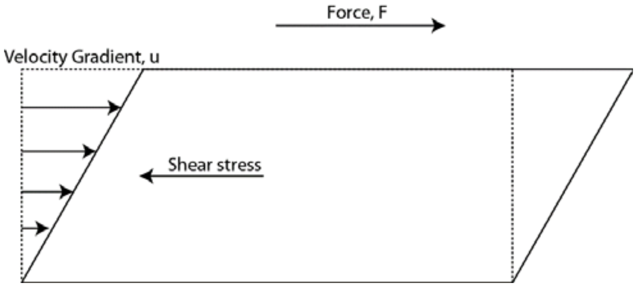
# Viscosity – Shear flow

- The force is applied to the top plate of the rheometer
- The rheometer measures the response of the fluid to this force




$$\tau = \frac{F}{A}$$ Shear stress

Shear rate $$\dot{\gamma} = \frac{dv}{dy}$$

Viscosity $$\eta = \tau\dot{\gamma}$$

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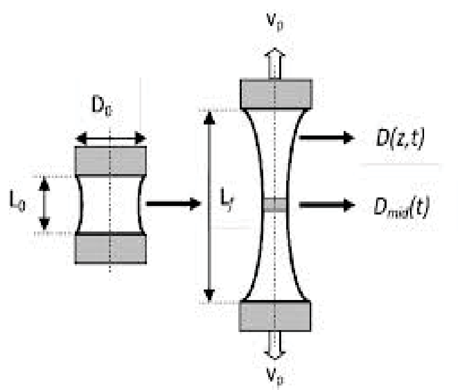
# Viscosity – Extensional flow

- Found using the Capillary break-up Extensional Rheometer (CABER) test
- Fluid is pulled apart between two parallel plates
- Rate of decay of the mid filament allows for the calculation of the extensional viscosity
- Trouton (1906) showed that of a pure Newtonian fluid:




$$\eta_e = 3.\mu$$

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# Oscillatory

- Fluid loaded between two parallel plates
- Force applied parallel to the plates
- The force is applied in a sinusoidal pattern
- The rheometer measures the response which will be a second sine wave
- Amplitude and Frequency of the sine wave are set as parameters
- Using Boltzmann's Superposition Principles to define the stress in terms of strain and angular frequency:

$$\sigma(t) = \gamma_0 \left[ \omega \int_0^\infty G(s) \sin(\omega s) ds \right] \sin(\omega t) + \gamma_0 \left[ \omega \int_0^\infty G(s) \cos(\omega s) ds \right] \cos(\omega t)$$



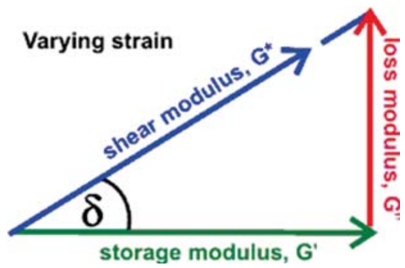
# Elastic and Viscous Moduli

Assuming the response waveform is sinusoidal the elastic (storage) and viscous (loss) moduli can be calculated

Storage Modulus

$$G'(\omega) = \omega \int_0^\infty G(s) \sin(\omega s) ds$$

$$G' = \frac{\sigma_0}{\gamma_0} \cos(\delta)$$




## Loss Modulus

$$G''(\omega) = \omega \int_0^\infty G(s) \cos(\omega s) ds$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin(\delta)$$

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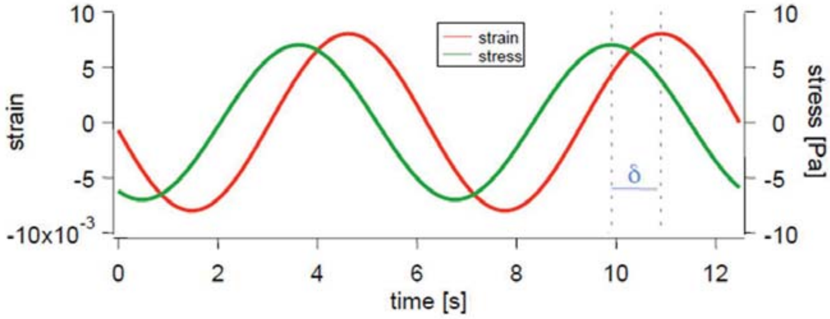
## Phase angle

The phase angle is the difference between the two sinusoidal waveforms that are used in oscillatory rheology

*The phase angle can be expressed in terms of the storage and loss moduli:*

$$\delta = \tan^{-1}\left(\frac{G''}{G'}\right)$$

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## Phase angle

The phase angle is a number measured between 0 and 90 degrees

For a Newtonian fluid:

$$\sigma = \eta\dot{\gamma}$$

$$G'(\omega) = 0 \qquad G''(\omega) = \eta\omega$$

$$\delta = \tan^{-1}\left(\frac{G''}{G'}\right) = \frac{\pi}{2} = 90$$

For a Hookean solid:

$$\sigma = G\gamma$$

$$G'(\omega) = G \qquad G''(\omega) = 0$$

$$\delta = \tan^{-1}\left(\frac{G''}{G'}\right) = 0$$

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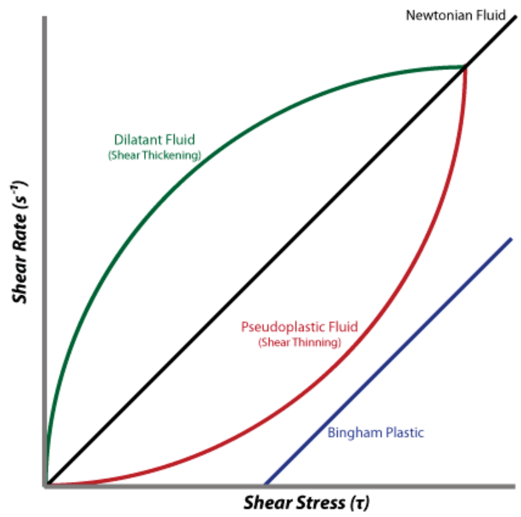
## Shear thinning/thickening

Shear thinning and thickening are both time independent non-Newtonian effects

- Shear thinning – the material viscosity decreases with increasing shear stress
- Printing ink, silicone coating, paint etc
- Shear thickening – the material viscosity increases with increasing shear stress
- Corn starch, some suspensions

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## Thixotropic/Rheopexy

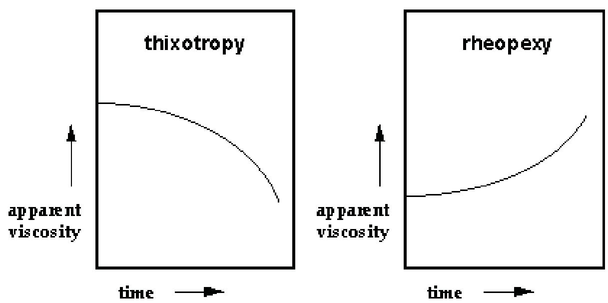
Time dependant viscoelastic effects

Thixotropic

- Viscosity decrease over time
- Clays, paints, suspensions, yogu

Rheopexy

- Increase in viscosity over time
- Very rare occurrence
- Gypsum paste

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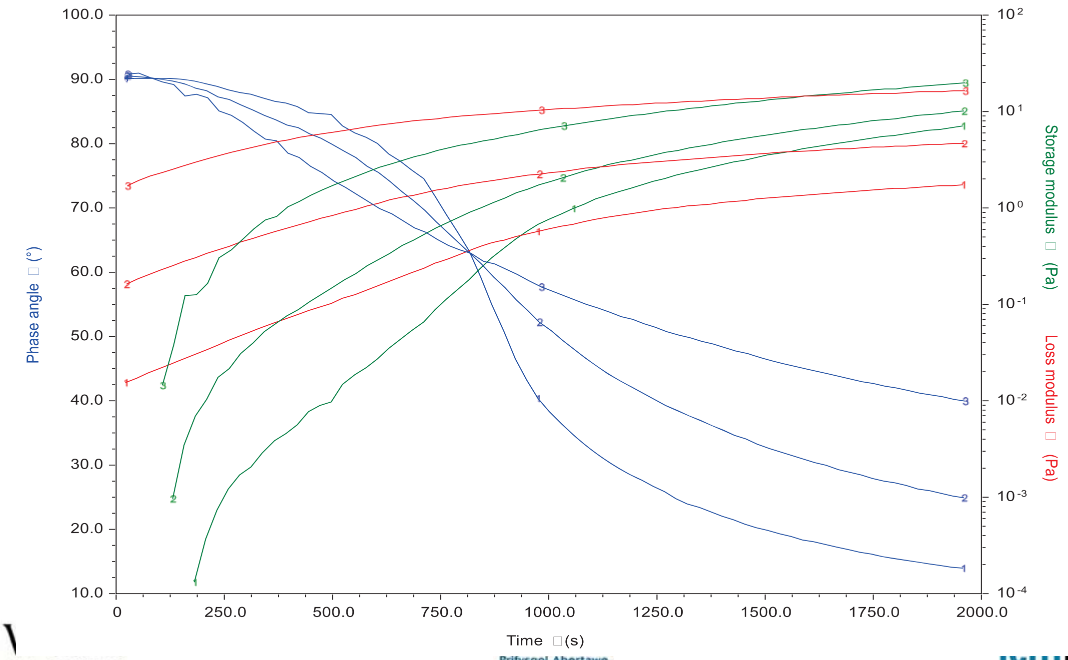
# Gel points

The gel point is the point at which the material goes from being a liquid to a solid

The original theory was the point where the G' and G'' curves intersect at a phase angle of 45 degrees

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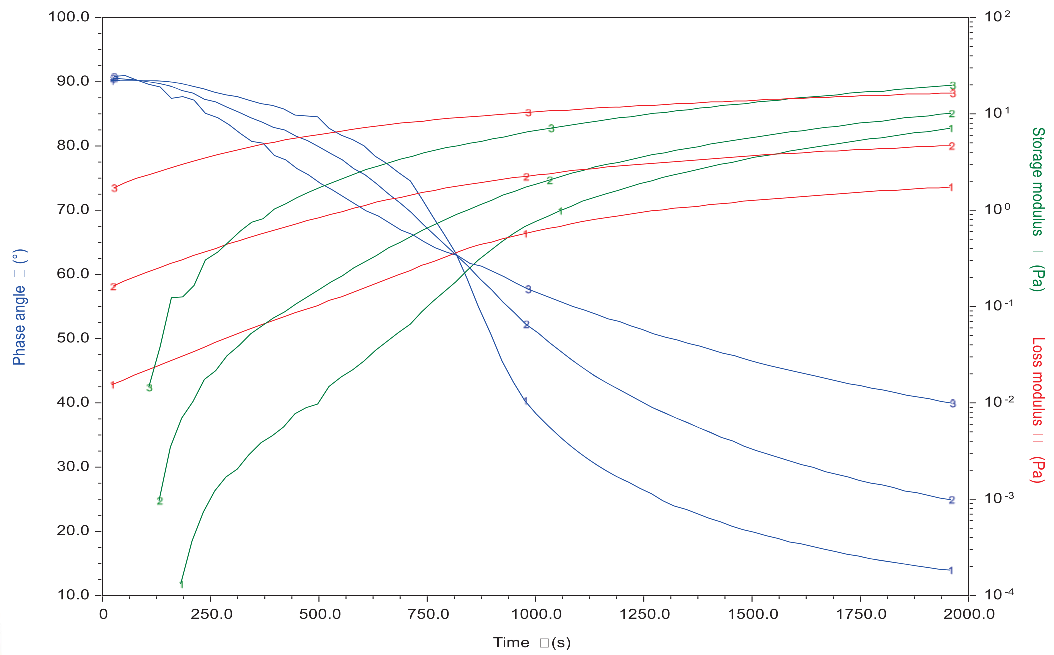
# Gel points

The new method is the point where the phase angle curves at a number of different frequencies intersect

This was proposed by Winters and Mours (1997) and is the accepted method for finding the gel point

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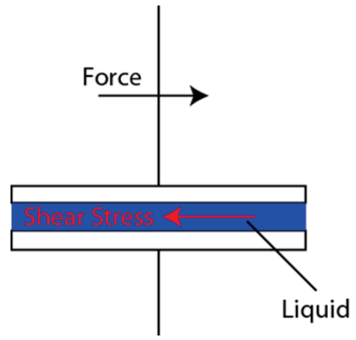
# Types of Testing - Viscometry

The viscometry test is the most common test used to give a basic characterisation of the material




- Stress/Strain ramped
  - Force is varied between two points
  - Used to find viscosity
  - And viscoelastic effects such as shear thinning
- Constant stress/strain
  - Used to find time dependant effects
- Temperature ramp
  - Change in viscosity with temperature

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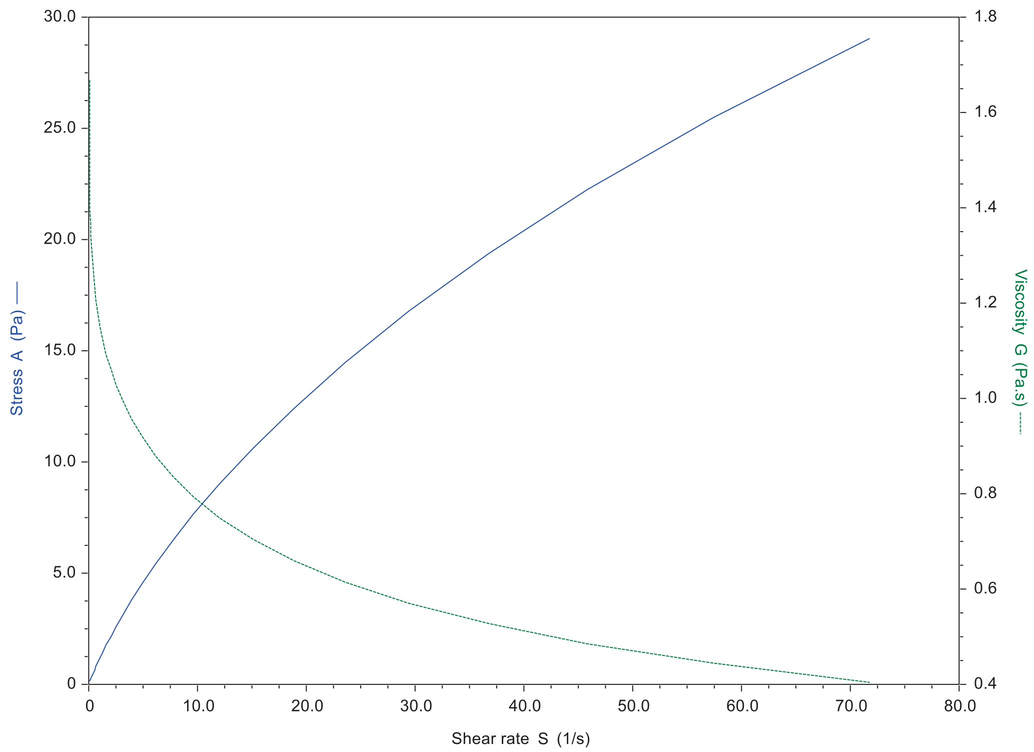
# Stress ramped viscosity test

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# Types of Testing - Oscillatory

There are a number of different oscillatory test used to identify different viscoelastic properties

- Small angle oscillatory shear (SAOS)
- Linearity testing
- Multi-wave SAOS testing
- Fourier Transform Mechanic Spectroscopy (FTMS)

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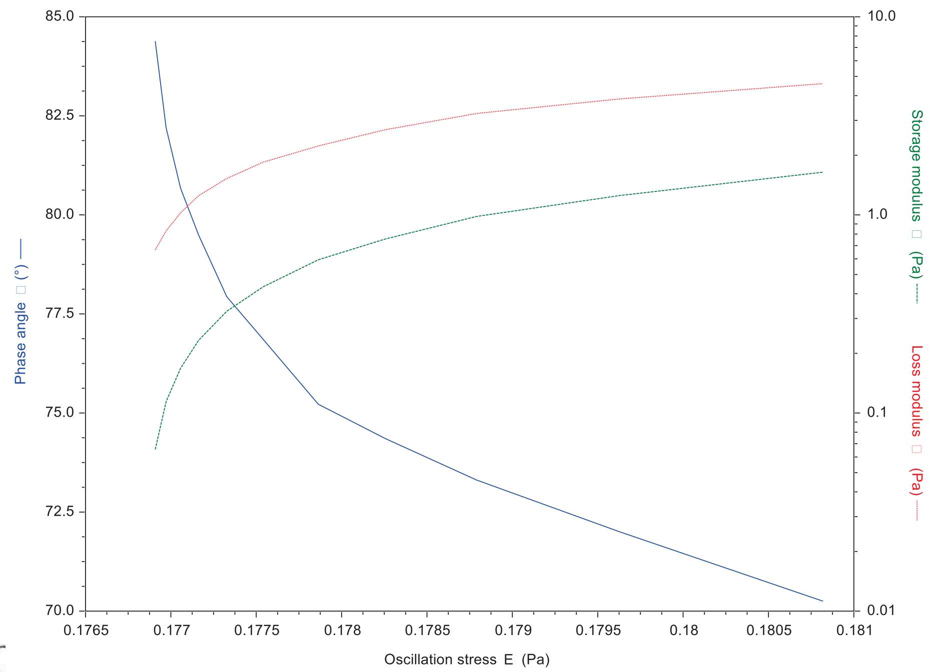
# Oscillatory - SAOS

Used to find the storage/loss moduli and the phase angle of a viscoelastic fluid

Varying oscillatory stress or frequency with time

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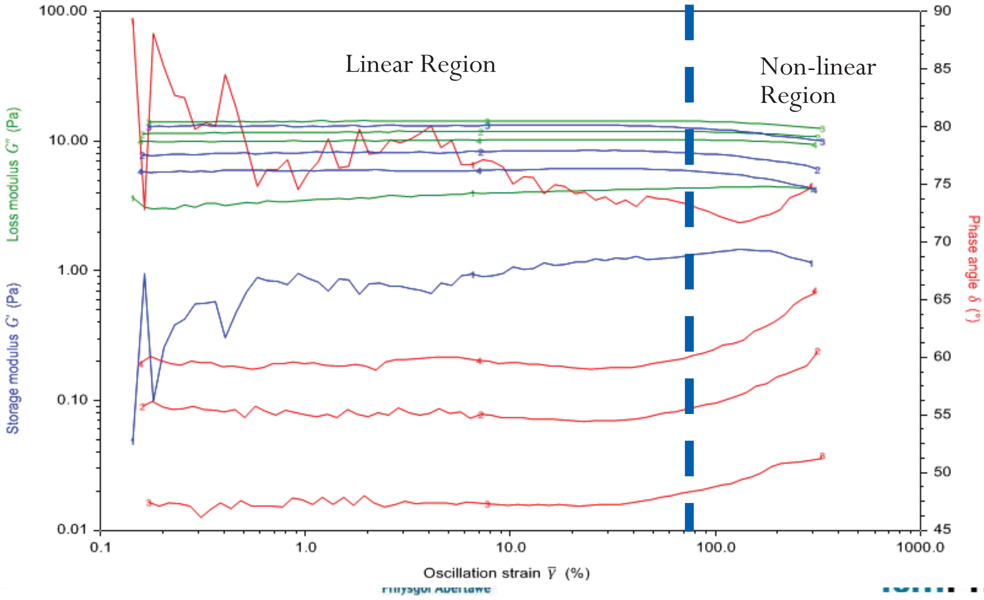
# Linearity testing

The material is said to be in the linear region where the values of G’ and G’’ are independent of the stress being applied.

The oscillatory test, in the linear region, is only a measurement of the material and not affecting the materials properties

To test this the stress is ramped until the G’ and G’’ values begin to deviate

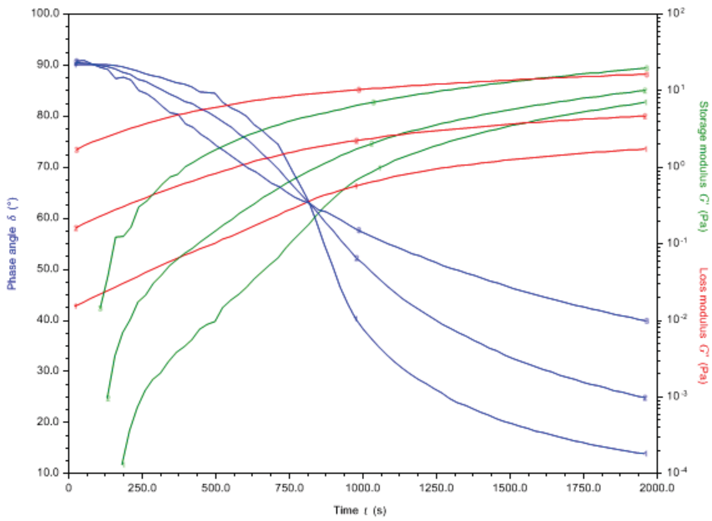


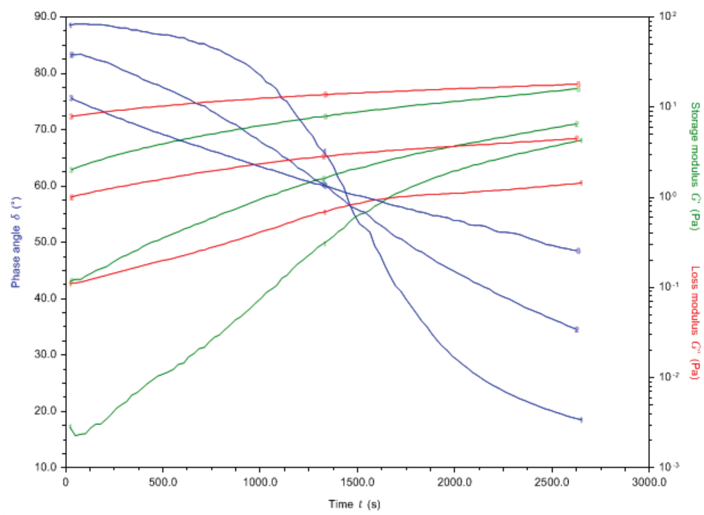

# Multi-wave SAOS

Used to find the gel point of materials with long gel times

Normally about 3-5 different frequencies

1 complete sine wave is completed at each frequency



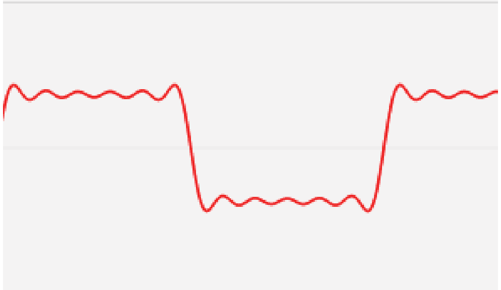



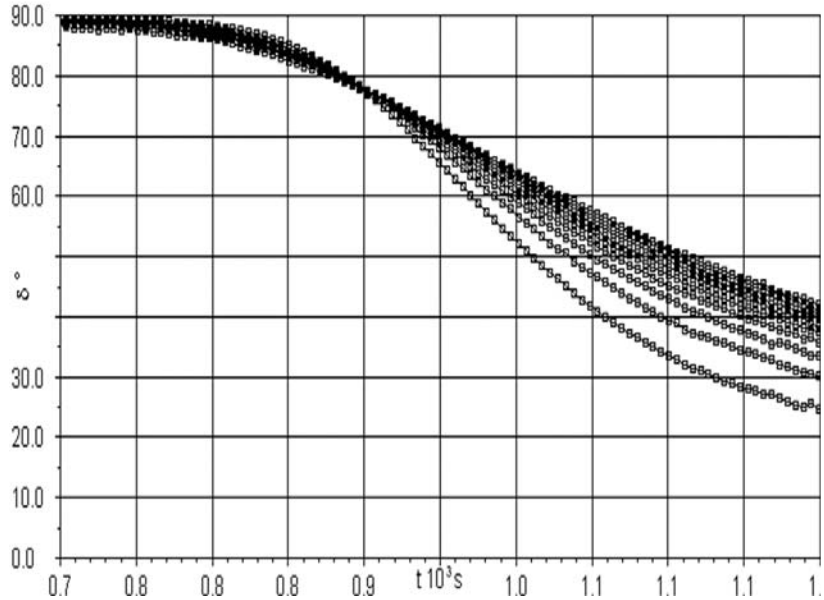
## Oscillatory FTMS

One complex waveform comprised of a carrier frequency and smaller child frequencies

Allows for all the frequencies to be measured in a single time step

Allows for faster measurement and removes the mutation problem seen with multi-wave measurements



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## Rheometer Setup - Shear

This is a guide to setting up the rheometer

All rheometer are different but they have very similar setup procedures to ensure the accuracy of the tests

- Parameter selection for different materials
- Geometry selection
- Calibration
- Sample loading

## Parameter Selection

Selection of parameters for the experiment is important

There are a range of different parameter you can control, this is done in most cases by changing the value on the software running the rheometer

- Gap
- Stress/strain controlled
- Shear rate/stress
- Temperature
- Frequency (Oscillatory only)

## Setting the Gap

The Gap refers to the distance between the top plate/cone on the rheometer and the peltier plate

It should be at least 10x the size of the large particles present in the sample

If the Gap size is too large it will present difficulties in appropriately loading the material

Typical sizes:

- 75-150 Microns for cone and plate
- 150-250 Microns for flat plate geometries

## Stress/Strain Controlled

Most Rheometers are either stress or strain controlled

Allows to either set a stress or strain when performing a test, one is always controlled and the other is measured

**Stress Controlled**

Advantage: Does not damage structure of gelling materials

Disadvantage: Is harder to relate between materials

**Strain Controlled**

Advantage: Easy to relate between different materials

Disadvantage: Can damage the structure of gels by ramping the stress

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## Other Parameters

These are some rough guidelines for suitable parameters, the material being used will define more exactly what is best

Stress

- 0.01 and 100 Pa
- Normally over 2 decades

Strain

- 0.01 and 100
- Normally over 2 decades

Frequency

- 0.1 and 10Hz
- Oscillatory stress tests use 1Hz
- Normally over 1 decade if frequency sweep

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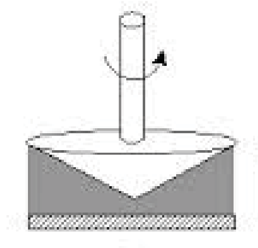
# Geometry selection

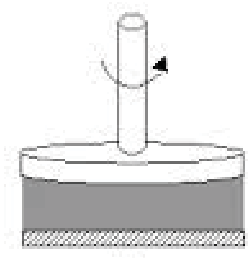
The geometry refers to the measuring top plate of the rheometer. This is normally one of two shapes:

**Cone**

Gives a uniform distribution of stress across the whole of the sample

requires a small gap size to be effective





**Flat Plate**

Can be used with a larger gap size than the cone

Does give an uneven stress distribution

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# Calibration

To keep the accuracy of the measurement the rheometers will need to be properly calibrated

## When and what to calibrate

**Temperature** – machine checked when it is serviced. Also should be checked if performing high temperature tests

**Rotational** – when the geometry is changed so the machine can calculate the inertia effects to remove

**Zero the gap** – This is done before the sample is loaded

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# Sample Loading

The rheometer is loaded by placing an amount of material onto the lower plate and moving the top plate down

The sample is then added of removed till the plates are filled properly

Once the sample is properly filled the solvent traps/silicon oil are used to encapsulate the sample to stop drying out effects when measuring



# Overfill and Under fill

The sample should be loaded so that the sample is flat with the edge of the plate

Overfill

- Material around the edge not subjected to any stress
- Can distort the results

Under fill

- Less material than the edge of the plate
- Machine is applying a stress higher to the remain fluid than accounted for

# Extensional Rheometer

So far dealt with only shear rheometry

Extensional rheometry can be used to find more information about how materials behave when subjected to extension

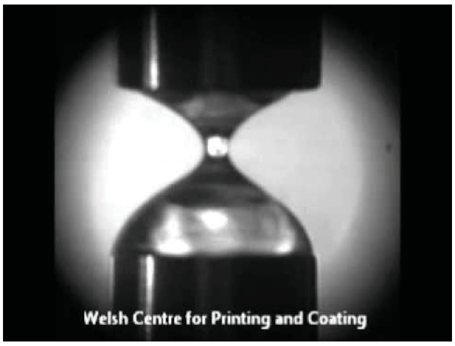
The most common test is the CABER test

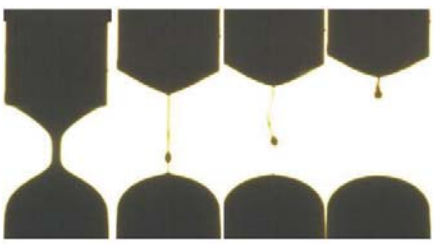


# CABER

Capillary break up extensional rheometer

- Pair of parallel plates are loaded with a sample
- The sample is then rapidly extended
- A liquid Bridge is formed



- The sample is allowed to break under its own forces
- The measurements of the mid filament diameter are taken using a high speed camera

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## CABER Results

The CABER test is analyses using the equation derived by Anna & Mckinley:

$$\bar{\eta}_{app}(\varepsilon) = \frac{\frac{2\sigma}{D_{mid}(t)}}{\left(-\frac{2}{D_{mid}}\frac{dD_{mid}}{dt}\right)} = \frac{\sigma}{\frac{dD_{mid}}{dt}}$$

Where the apparent extensional viscosity is calculated using the surface tension and the change in mid filament diameter with time



## Sample Loading

The sample is loaded on the rheometer in a similar way to the shear rheometer

The biggest different is that the plates are already at the correct separation distance before the sample is loaded

It should be flat with the sides of the plate for the results to be valid and can have similar overfill and underfill problems like in shear rheology

## Extensional Results

- The results taken and measured using image analysis software to produce

- The problem with the CABER test is that the results can be subjective
  - Difference in the image analysis measurements
  - Difference in the step strain characteristics affecting the end result



## Ink Misting

The extensional rheometer can be used to mimic some of the problems seen in the printing process

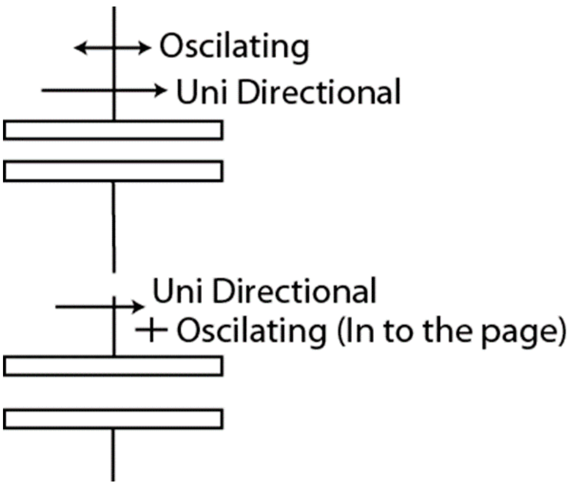
This includes ink misting

By rapid extension on the ink filament, it can be made to break up in multiple places and produce satellite droplets

# Advanced rheological tests

There are a number of new advances in rheological techniques

One of these is Controlled Stress Parallel Superposition (CSPS)




A unidirectional shear stress is applied to the sample in addition to a SAOS measurement

Allows for the study of how the materials behave under shear flow

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## 19. Electrical Characterisation

Tatyana Korochkina, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a

## 20. Surface Characterisation (WLI, AFM & SEM)

Chris Phillips, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a


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# 3D Surface Characterisation

## White light interferometry, Scanning Electron and Atomic Force Microscopy for Imaging 3D Structures

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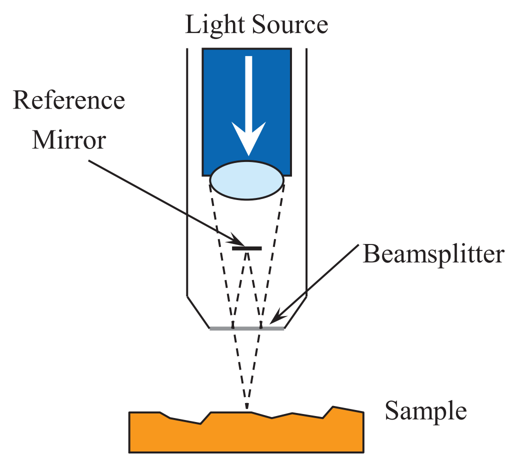
# Content

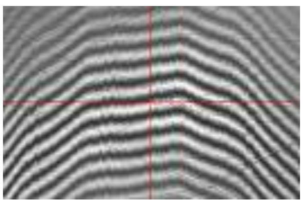
- White light interferometry
- Scanning Electron Microscopy
- Atomic Force Microscopy
- Operating principles
- Considerations
  - Sample preparation
  - Resolution
  - Measurement time

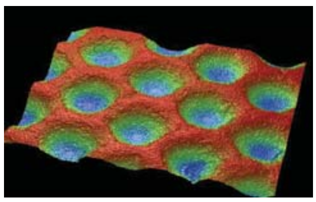


# White Light Interferometry

- Non-contact method of measurement.
- 3D topographic image of surface
- Utilises white light.
- Scans through set depth.
- Interference fringes at best focus.





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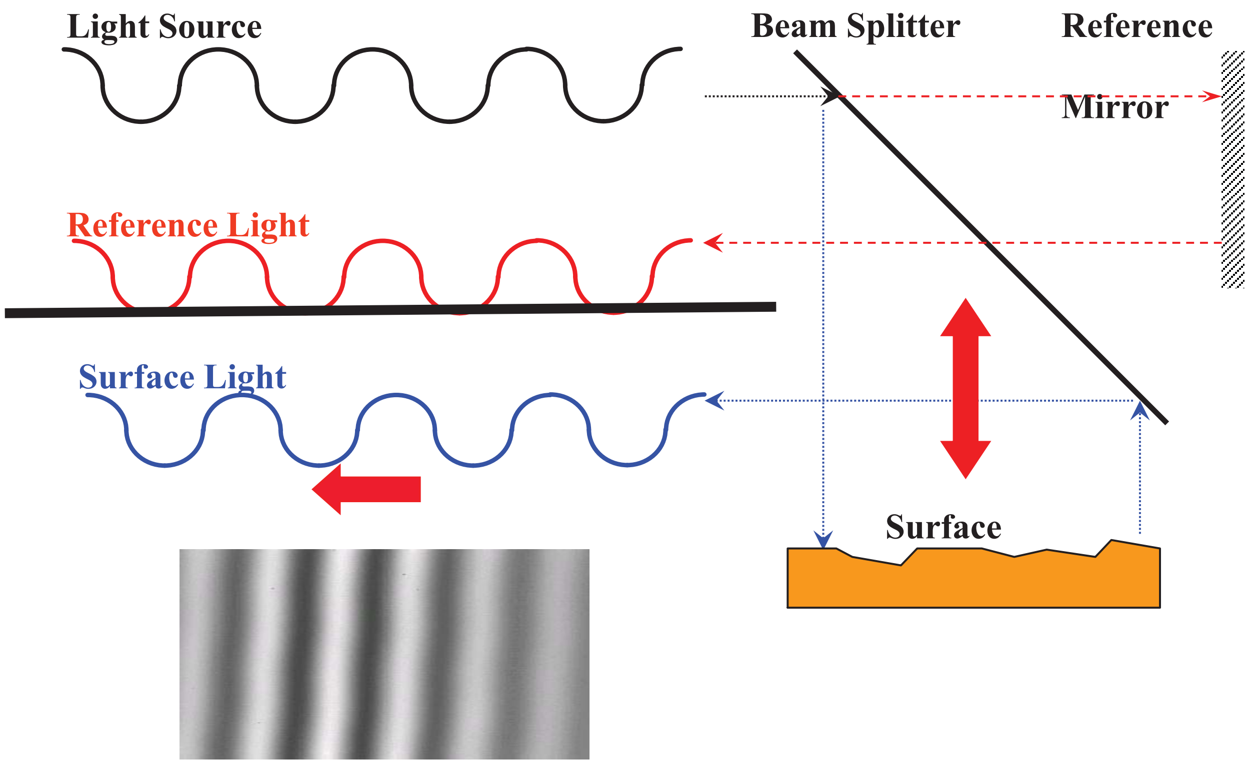
# Principle of Interferometry

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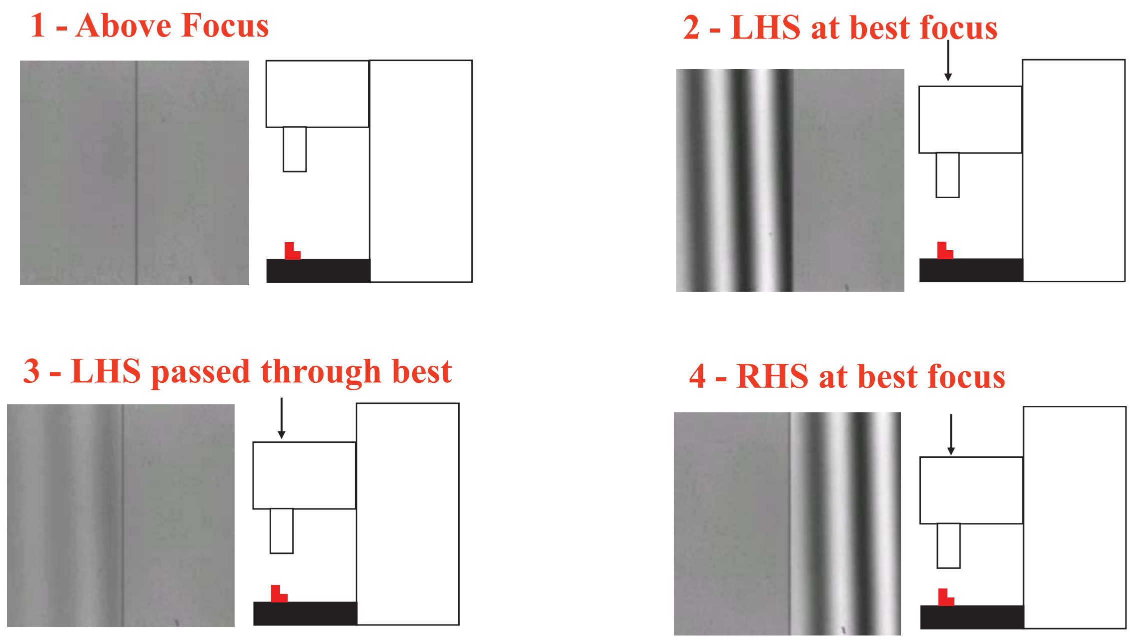
# Vertical Scanning Interferometry

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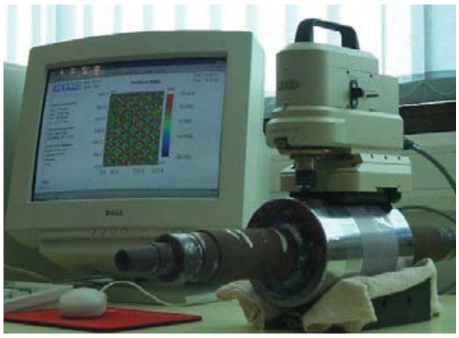
## Interferometers at WCPC

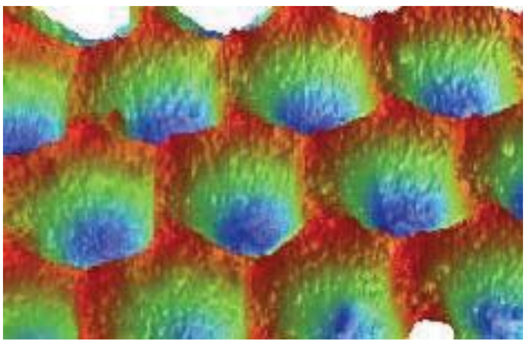
- 2 Workstations
  - Prints
  - Substrates
  - Plates
- 2 Rollscopes
  - Gravure cylinders
  - Portable
  - Less accurate



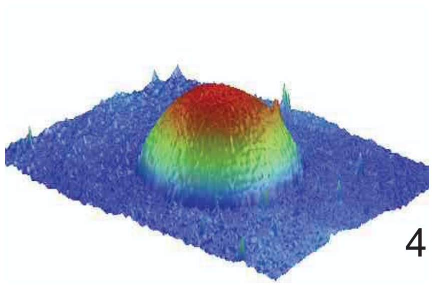


## 3D Measurements

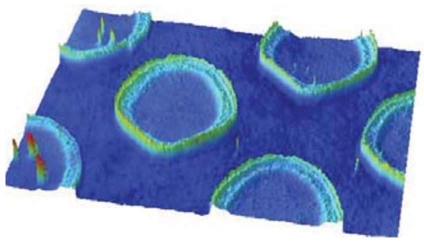
- WCPC : Pioneers in 3D surface characterisation of anilox and gravure rolls and printed dots
  - Several WLI interferometers



Anilox surface



Flexo dot
4 μm height



Gravure dot

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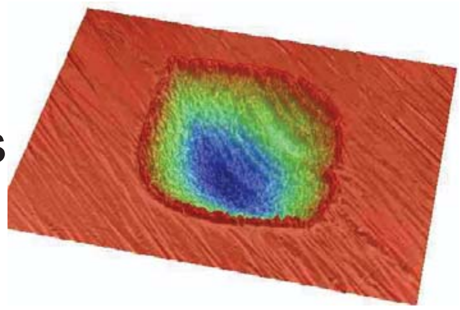
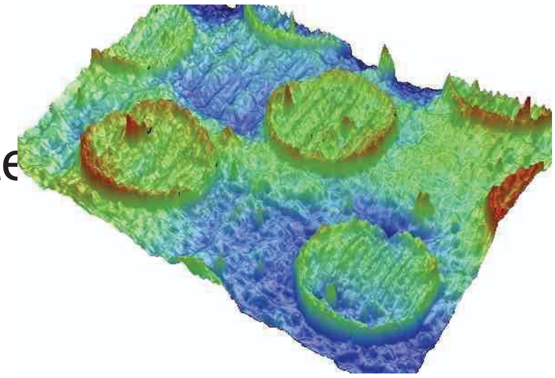
# Volume Studies:

- Cell Volumes:
  - Cells engraved in cylinders
  - Rollscope



- Printed Dots Volumes:
  - Printed dots on substrate
  - Workstation



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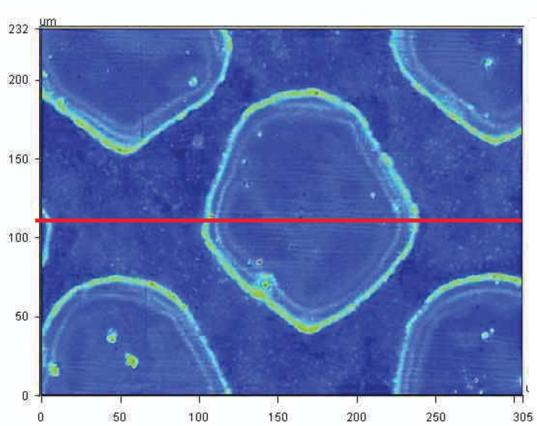
# Printed dots volume: gravure

- The dots printed by rotogravure are very thin (100nm) and have a ring shape



45-60-130 50% Magenta



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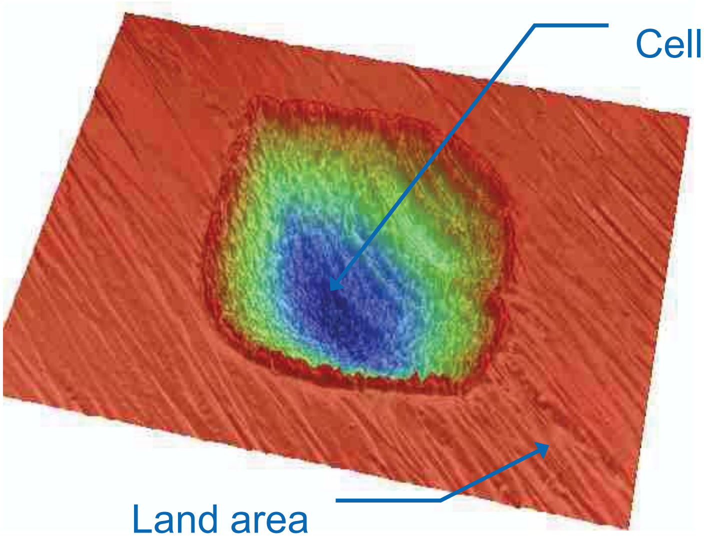
# Geometrical cell parameters

For a quantitative analysis measurable parameters have to be extracted

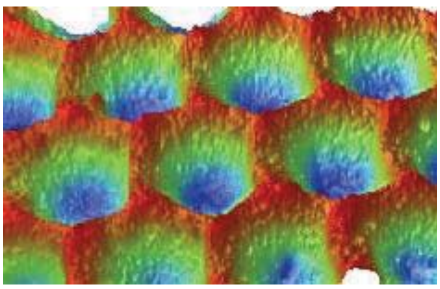



- Common Parameters:
  - Width, depth, length
  - Open area
  - Cell Volume
  - Land area roughness
  - Screen angle

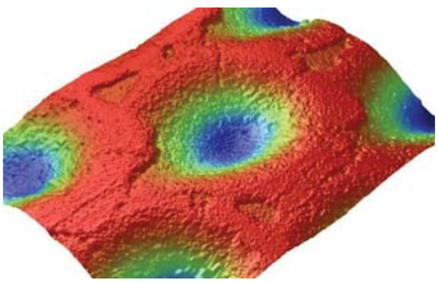


# Cell measurement

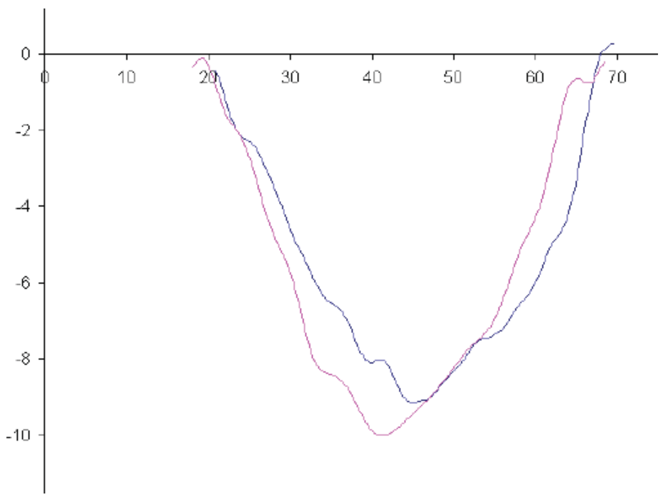
- Measurement 3D: not only volume but quality



Anilox surface



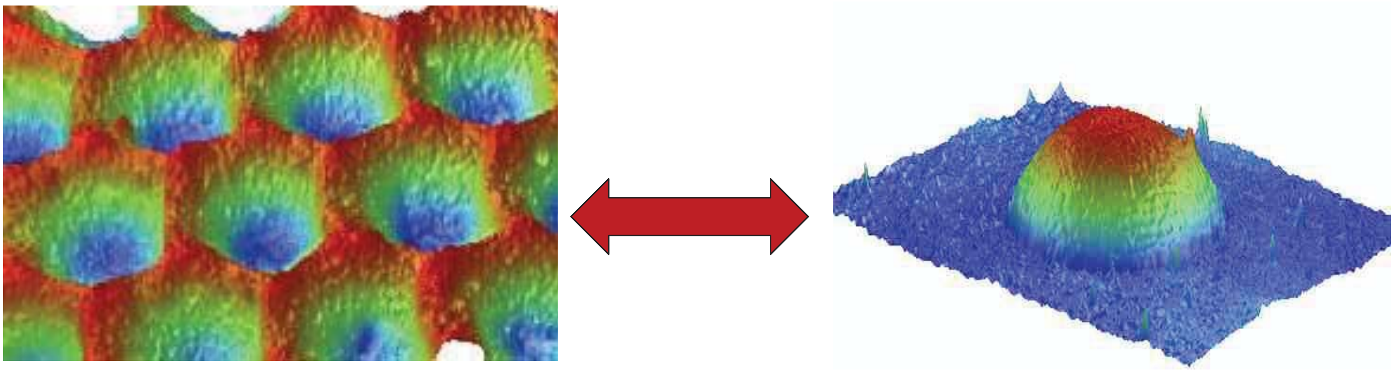
Engraving issue




YAG cell (violet) vs CO2 (blue)

## 3D Measurements

- Analysis of ink release from anilox cell
  - Depth-to-Open ratio effect
  - Half-tone effect: variable dot size on plate



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## Advantages/disadvantages

- Very quick to measure
  - Couple of minutes
- No sample preparation
  - Samples can be measured directly
  - Can measure large objects
- Direct 3D measurement and quantification
- Lower resolution than SEM and AFM
- Low detail on rougher surfaces

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# Scanning Electron Microscopy

- Produces images of a sample by scanning it with a focused beam of electrons - raster
- Electrons interact with atoms in the sample, producing signals that can be detected with information about surface topography and composition
- A Tungsten filament cathode is used in a thermionic electron gun


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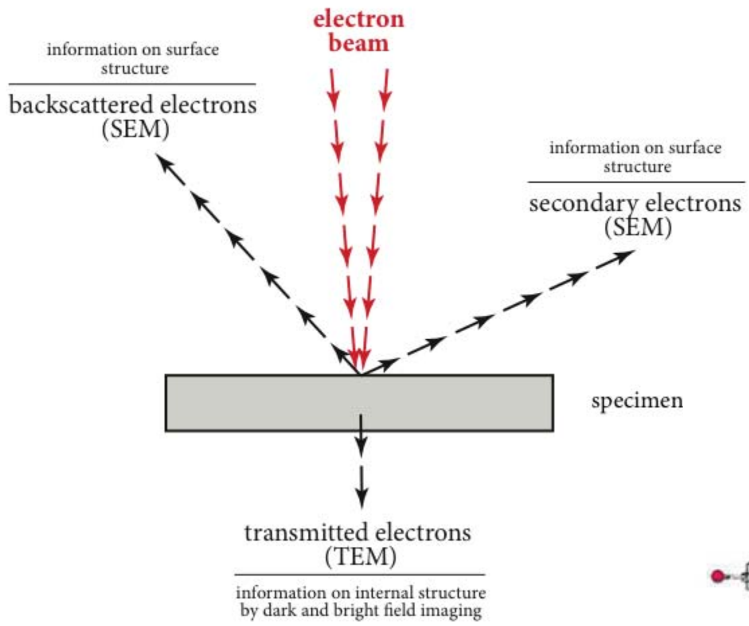
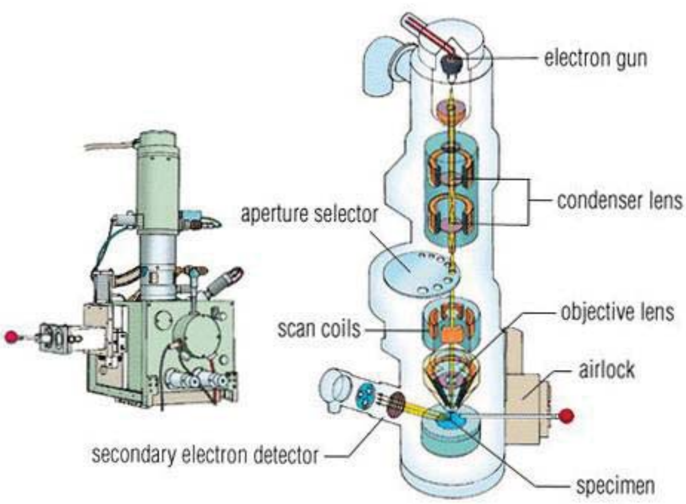
# How an electron beam works

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# Scanning Electron Microscopy

- The electron beam, which typically has an energy ranging from 0.2 to 40keV, which is focused by one or two condenser lenses to a spot about 0.4 to 5nm in diameter.
- The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the *x* and *y* axes so that it scans in a over an area of the sample surface.
- Chemical characterisation can be performed using energy dispersive X-ray analysis (EDX). The electron beam stimulate the atoms and they send out X-rays of specific energies for each element, the so called characteristic X-rays.

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# The Principle

•When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering known as the interaction volume, which extends from less than 100nm to approximately 5μm into the surface.

•The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen (density). The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering.

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# Magnification

- Magnification in a SEM is controlled over a range 10 to 500,000 times
    - 100s times higher than optical methods
- Image magnification is not a function of the power of the objective lens
- SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen

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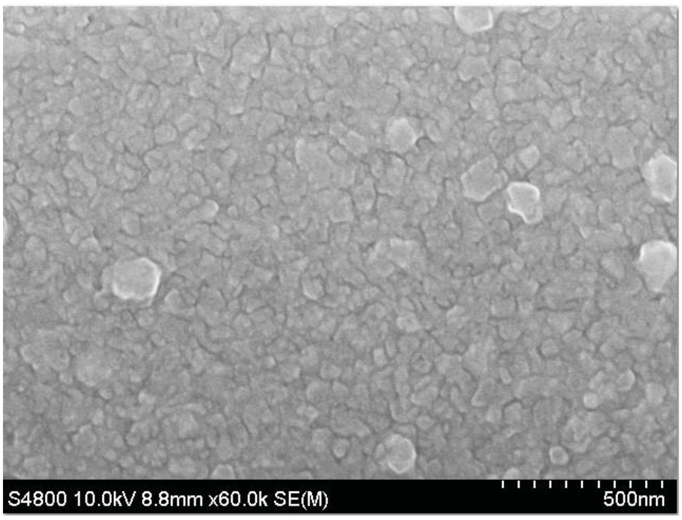
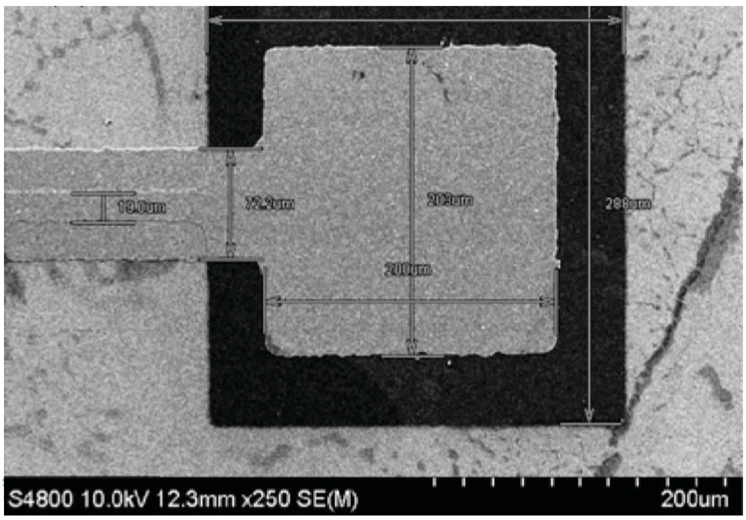
# Scanning Electron Microscopy

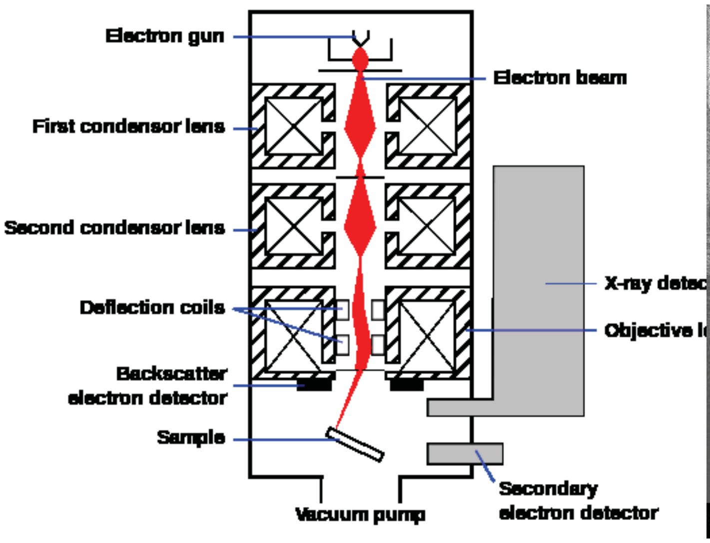
•The most common mode of detection is by secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons is a function of the angle between the surface and the beam.

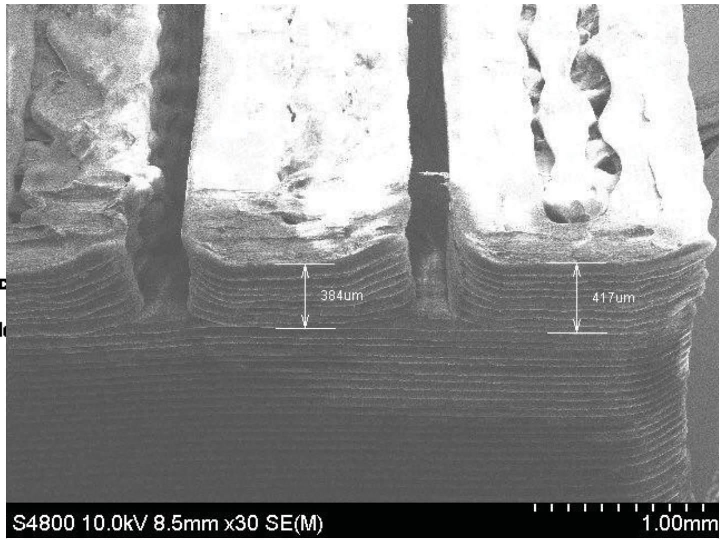


# Tilt Scanning

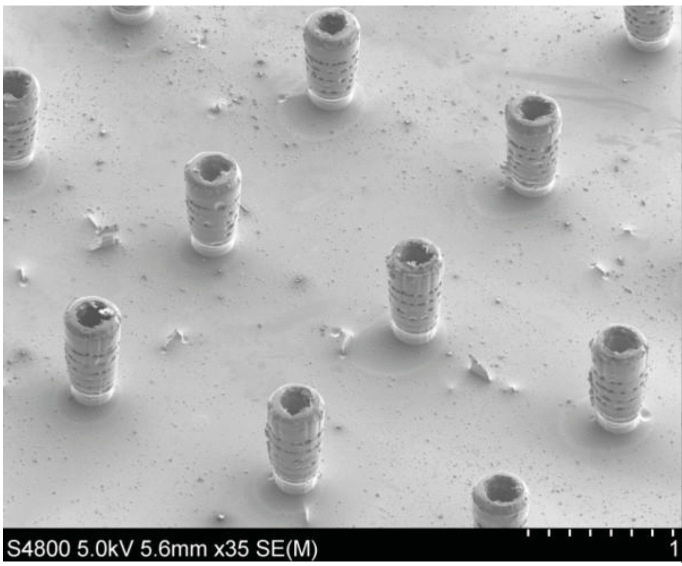
- On a flat surface, the plume of secondary electrons is mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the tilt of the surface is created.

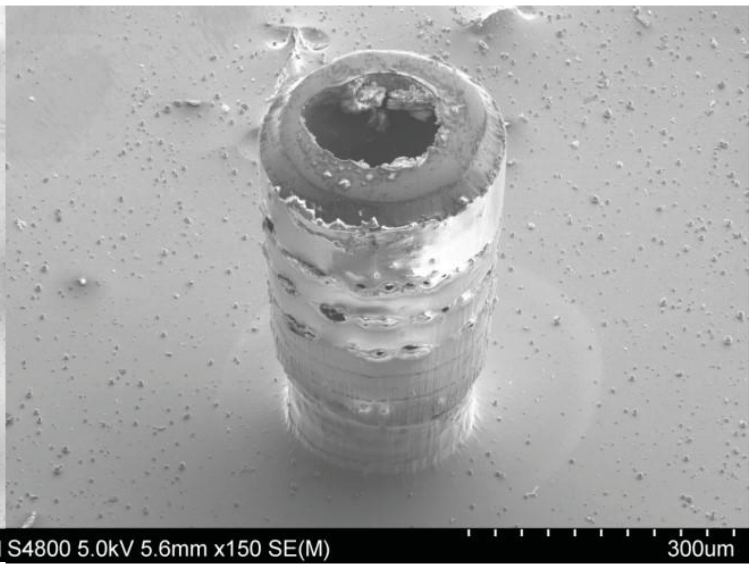



# Imaging Ultra Deep Objects

- Tilt images provide a perspective of depth.
- This is especially useful when dealing with ultra deep objects such as these cylinders.



# 3D Image generation

- SEMs do not naturally provide 3D images. However 3D data can be obtained using two main methods, such as:
- Photogrammetry taken from two or three images from a tilted specimen.
- Vertical stacks of SEM micrographs plus image-processing software
- Possible applications for this include roughness measurement or measurement of internal structures for modelling applications.



# Advantages/disadvantages

- High resolution
- Provides data on topography and composition
- Slow measurement compared with optical techniques
- No direct 3D measurement
- Samples must be cut to fit in SEM
- Normally requires samples to be electrically conductive and grounded
    - Coating of non-conductives

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# Atomic Force Microscopy

- Atomic force microscopy (AFM) is a very high-resolution non optical-based microscopy, with resolution on the order of fractions of a nanometer
- The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale
- Information is gathered by “feeling” the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on electronic command enable very precise scanning.

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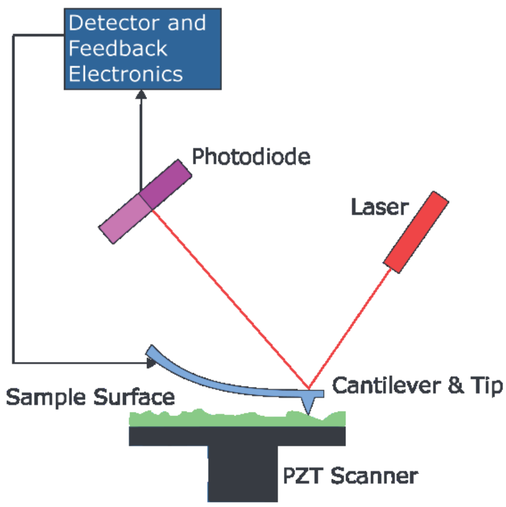
# Atomic Force Microscopy

- Tip interacts with surface
- Photodiode measures deflection

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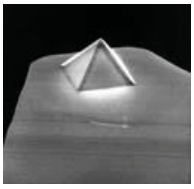
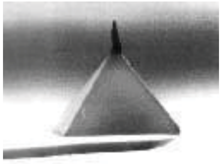
# Types of Tip

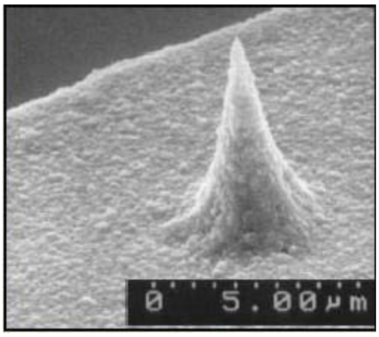


Normal Si Tip

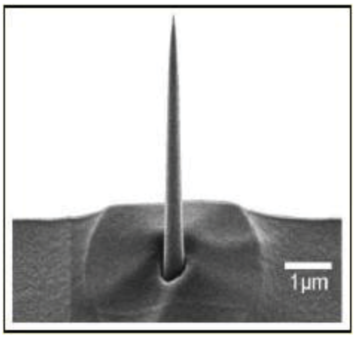


Si Supertip

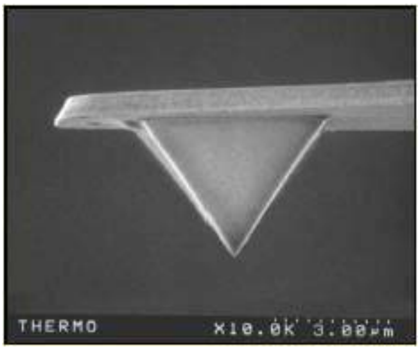
Si Ultralever




Diamond-coated tip




Sharpened tip




Gold-coated Si3N4 tip

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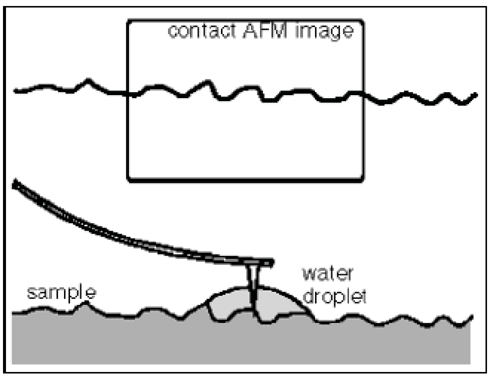
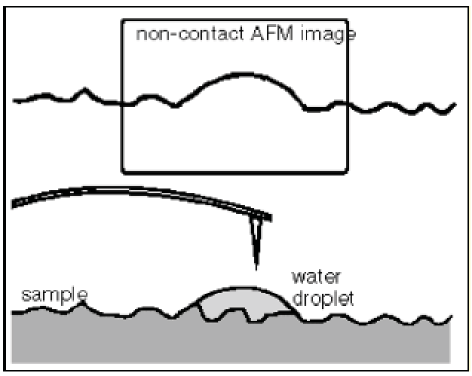
# Scanning modes

- **Contact mode imaging – "dragging"**
  - Influenced by frictional and adhesive forces, and can damage samples and distort image data.
- **Non-contact imaging – oscillaitng probe affected by van der Waal interactions with surface**
  - Provides lower resolution and can also be hampered by a contaminant such as liquid interfering with oscillation.




**Contact**




**Non-Contact**

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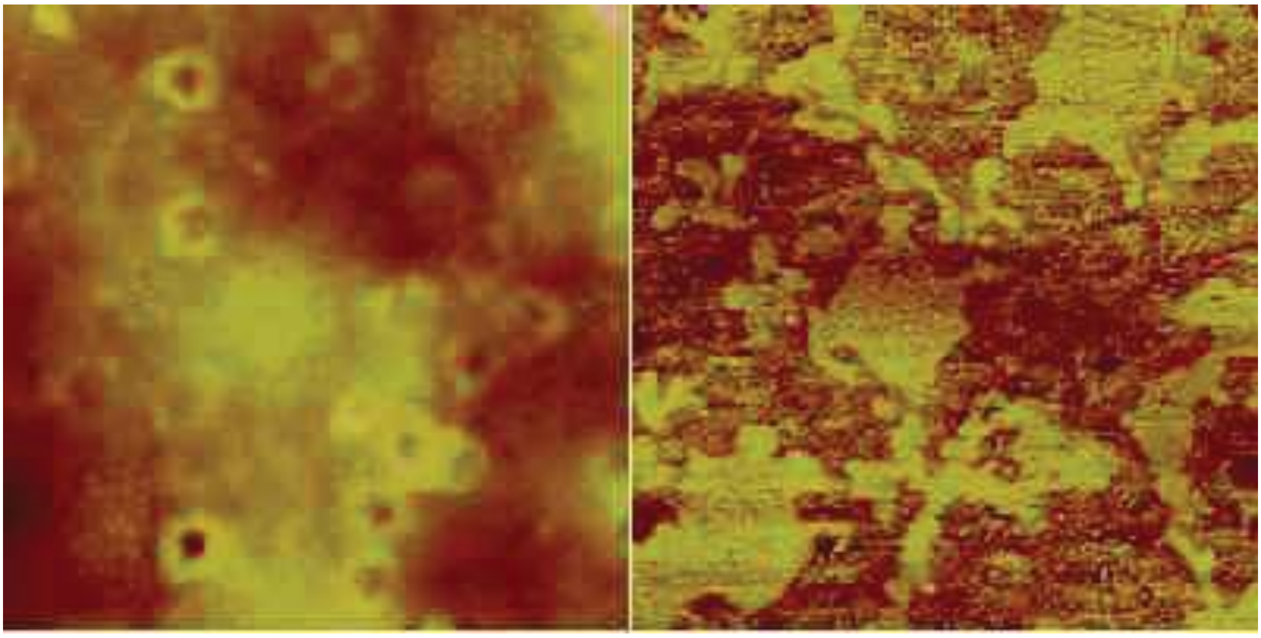
# Scanning modes



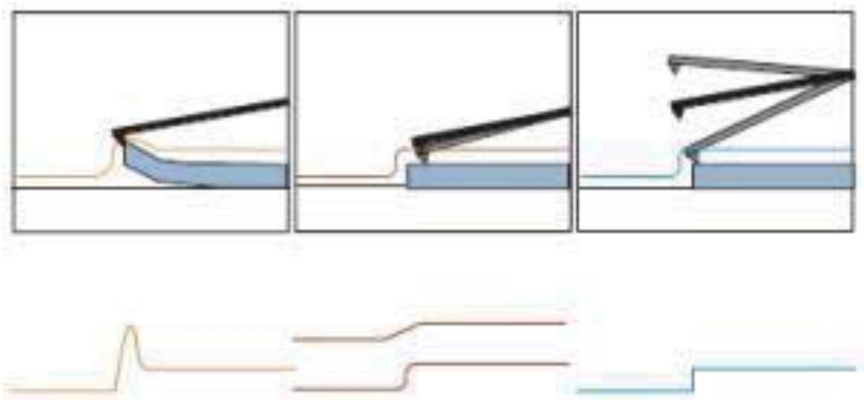
Non Contact Scan

Contact Scan



# Tapping Mode

- **Tapping Mode imaging** takes advantages of the two modes. It eliminates frictional forces by intermittently contacting the surface and oscillating with sufficient amplitude to prevent the tip from being trapped by adhesive meniscus forces from a contaminant layer.



Contact Non-Contact Tapping

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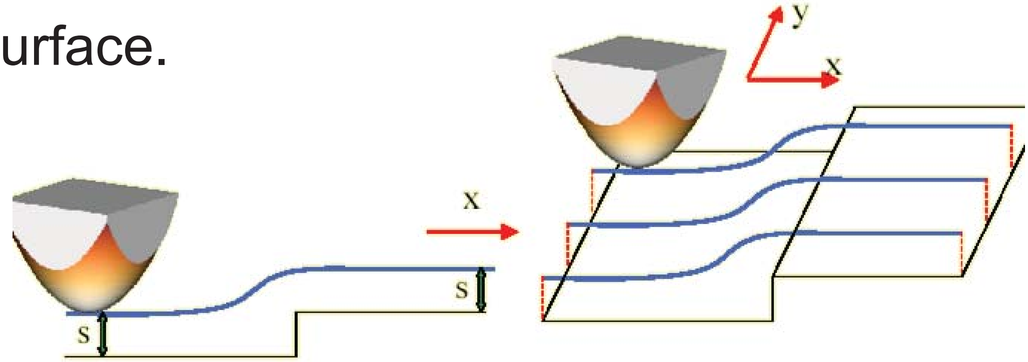
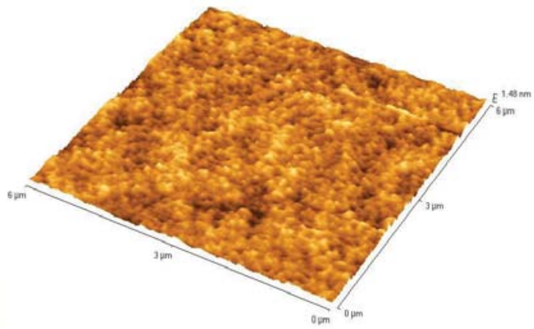
# Generating a Surface 3D Profile

- By scanning multiple paths then we can generate a three dimensional profile of the surface.




Parameters such as surface roughness extracted.





# Advantages/disadvantages

- High resolution
- No sample preparation
- Provides 3D data
- Very slow measurement compared with optical techniques
- Scan areas a couple of centimetres at most
  - 2 hours
- Samples must normally be cut to fit
- Height range limited to 10-20 microns
  - Cannot cope with steep transitions

## Closure

- Choice of technique depends on
  - Resolution range required
  - Sample
    - Size and aspect ratios
    - 2D or 3D
    - Conductivity
    - Destructive or non-destructive
  - Throughput
- Printing is a tens of micron scale process
  - Feature assessment can be carried out using optical methods (interferometry)
  - SEM good for morphology of nano-particles in print
  - AFM good for ultra thin coatings

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cost ActInPak


## Acknowledgements

Material provided by
Davide Deganello
and Daniel Thomas


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## 21. Drying Characterisation and Measurement

David Beynon, Welsh Centre for Printing and Coating

### Biography

n/a

### Abstract

n/a


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# Drying Characterisation and Measurement

Dr David Beynon

## Overview

- Ink Drying Processes
  - Absorption
  - Reaction
  - Evaporation
- Drying Effect
  - Viscous Fingering
  - Capillary Flow
- Drying Measurement
  - FTIR
  - ASII

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## Drying

- What do I mean by drying?

- The transformation from liquid ink to solid film following the final transfer of ink to the substrate

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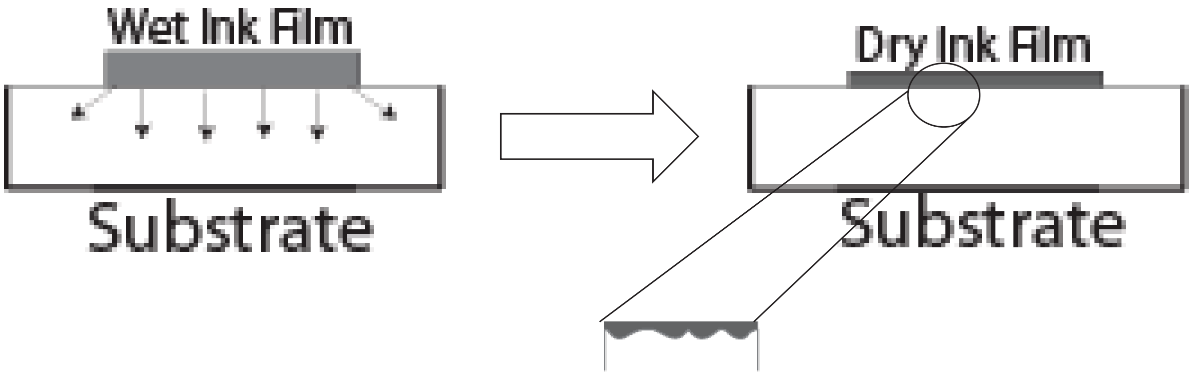
# Drying Processes

- Absorption
- Reaction
  - “2 pot inks”
  - UV/EB
  - Decomposition
- Evaporation



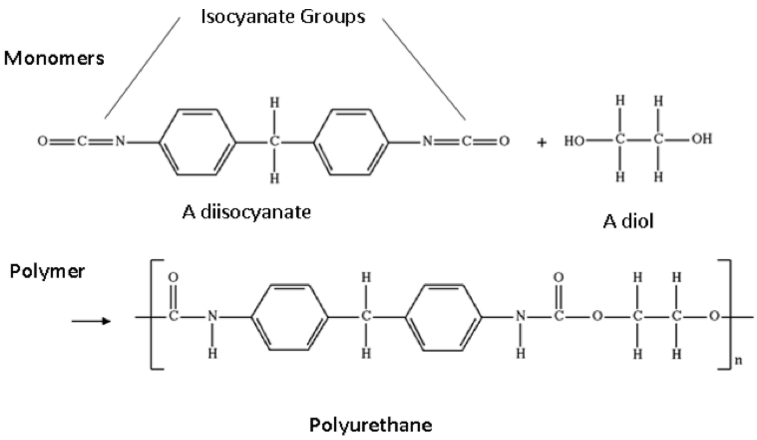
# Absorption

- Physical Process
  - Liquid components of ink absorbed by porous substrate



# Reaction

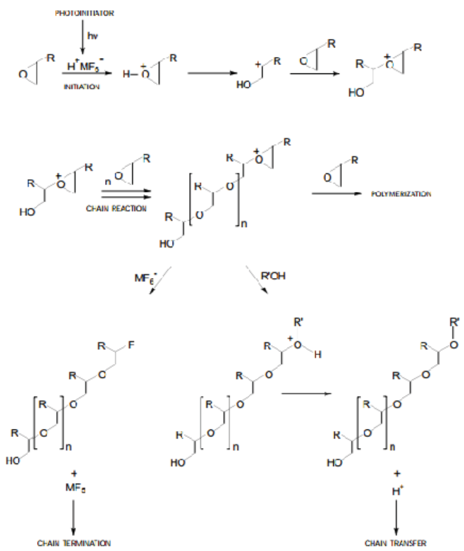
- Chemical Process
  - "2 pot" systems
    - Ink combined with catalyst before printing
    - Reaction begins immediately
    - Heat after printing accelerates reaction

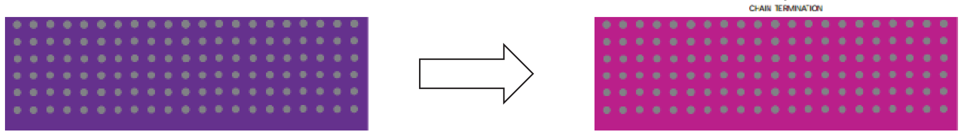





# Chemical Processes

- UV Curing
  - Reactive chemicals in the ink
  - Photoinitiator
    - Accepts UV light
    - Initiates reaction
      - Free radical
      - Cationic



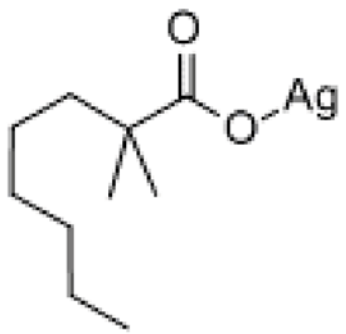



WET INK

DRY INK

# Chemical Process

- Decomposition
  - Metallic atom bound in chemical
    - E.g. silver neodecanoate
    - Heat or UV decomposes chemical
    - Metallic film remains



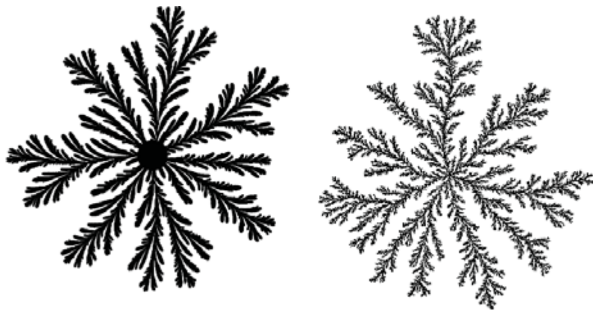



# Evaporation

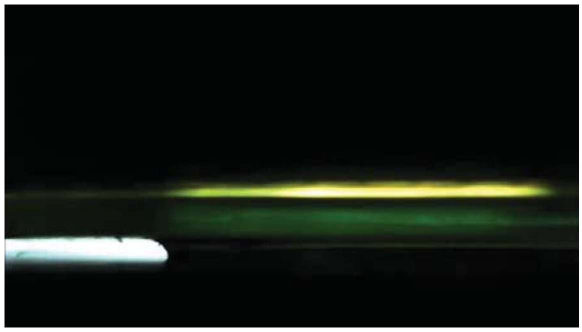
- Solvent loss from wet ink
  - Solids remain
- Stages in Drying process
  - Evaporation
  - Viscosity increase
  - Particle packing
  - Particle deformation
  - Film formation

# Drying Phenomena

- Viscous Fingering
  - Saffman-Taylor instability
- Not true viscous fingering
  - Spreading of liquids of different viscosities
- Gravure/Flexo
  - Hydrodynamic forces
  - Moving contact lines in nip



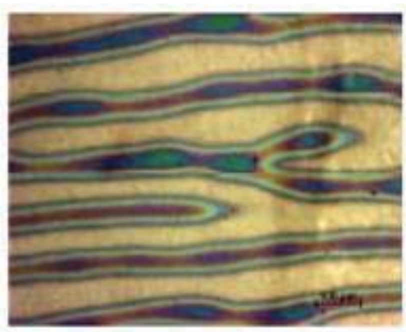
The universality classof diffusion-limited aggregation and viscous fingering. Mathiesen, Procaccia, Swinney, Thrasher. Europhys. Lett. 72 (2006)





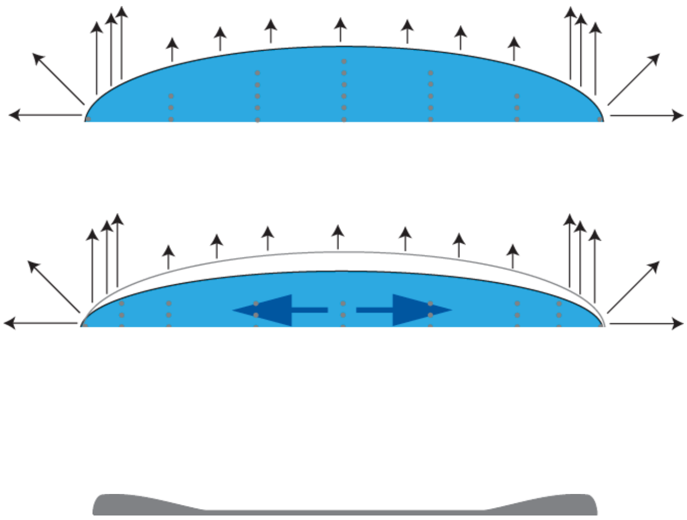
# Viscous Fingering

- Pattern of non-homogenous thickness
  - Orientated in print direction
    - Reduced conductivity
    - Reduced activity
    - Show through of next layer
- Levelling of ink reduces effect
  - Low viscosity
  - Drying time
  - Surface tension
  - Film thickness
- Drying time must be longer than levelling time



# Capillary Flows

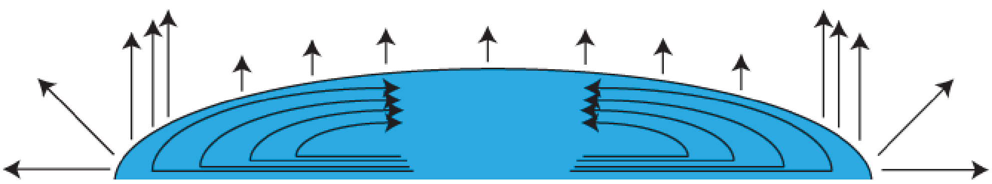
- Evaporation driven flow
- Solvent evaporates at edge
  - Surface tension increases
  - Flow induced
  - Solids carried to edge
- Coffee stain effect





# Coffee Stain Effect

- Reduction
  - Marangoni flows
  - Mixed volatility solvents
    - Solvent blends



- Particle shapes
  - Reduced effect for ellipses

# Measurement of Drying

- Mechanical Testing
- FTIR
- ASII

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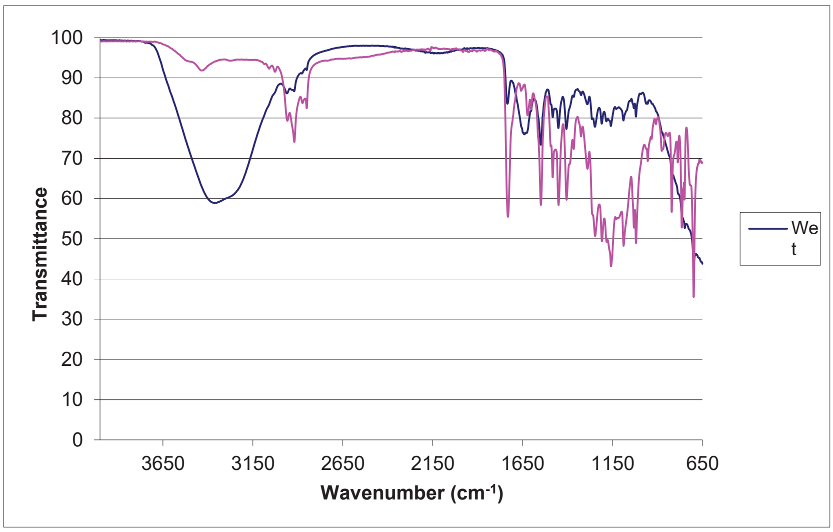
# FTIR

- Infra Red spectroscopy
- Absorption by specific chemical bonds
  - Characteristic spectrum
- Selected absorption band
  - Reduces through drying





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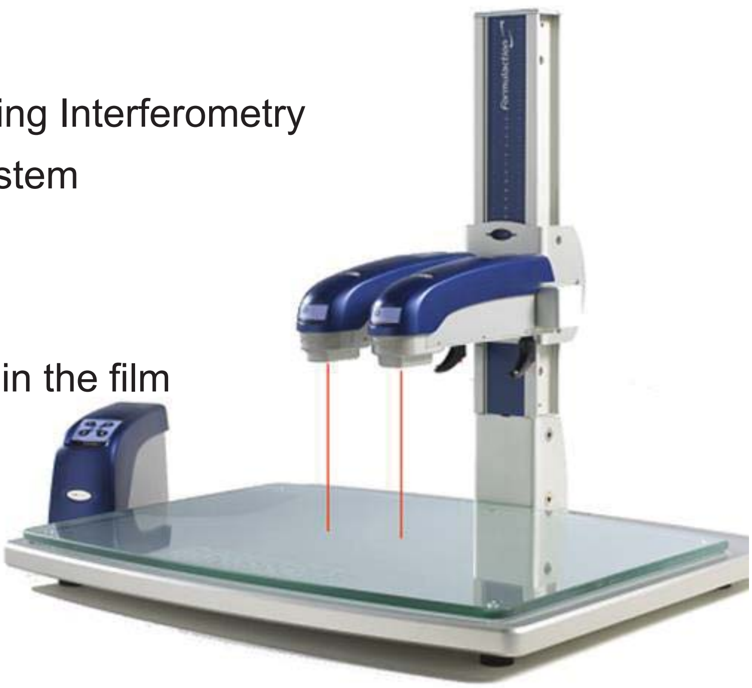
# ASII

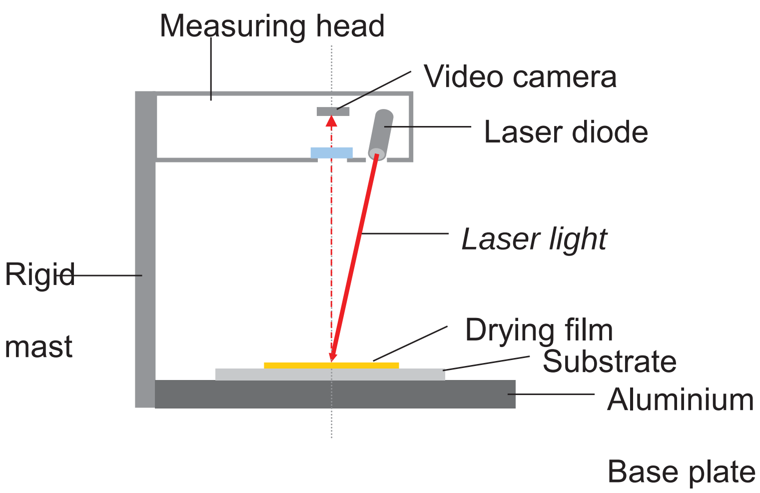
- A system for analysing drying and film formation
- ASII
  - Adaptive Speckle Imaging Interferometry
  - Forumlaction Horus System
- Optical measurement
  - Monochrome laser
  - Detects movement within the film





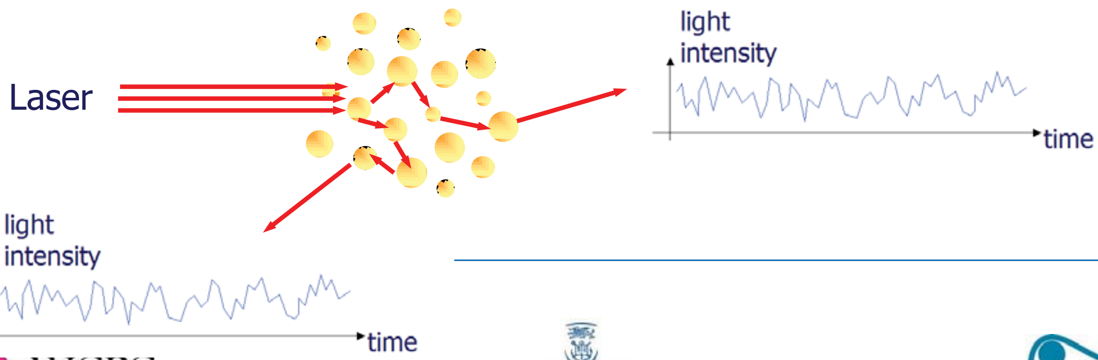

# Measurement Principle

- Sample coated onto substrate
- Reflected laser captured by video camera



# Diffusing Wave Spectroscopy

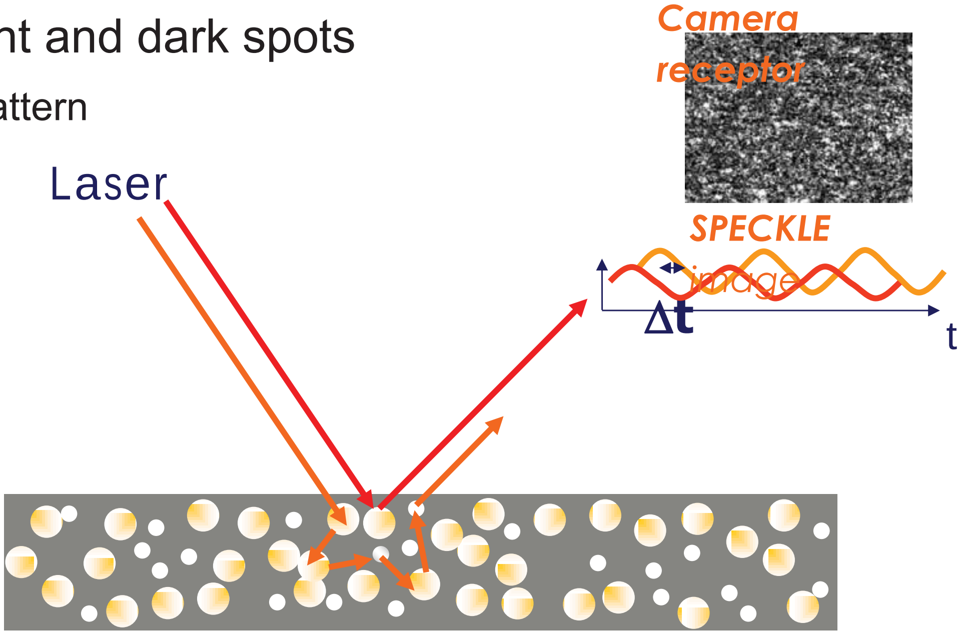
- DWS
  - Laser enters ink film
  - Distance travelled depends on path light takes through ink film
  - Depending on path light intensity reflected varies with time






# Multi- Speckle DWS

- Interference captured by camera
- Pattern of light and dark spots
  - Speckle pattern




*Scatterers = particles, droplets, fibers ...*

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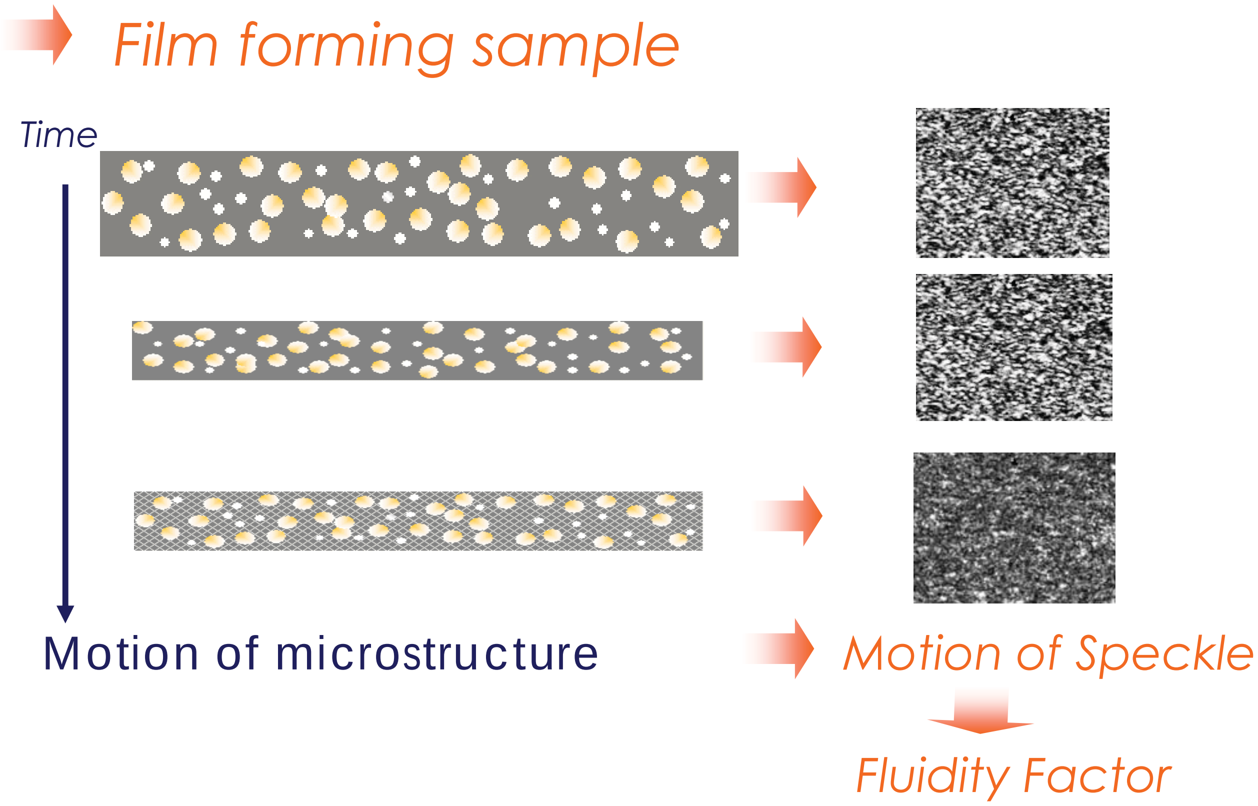
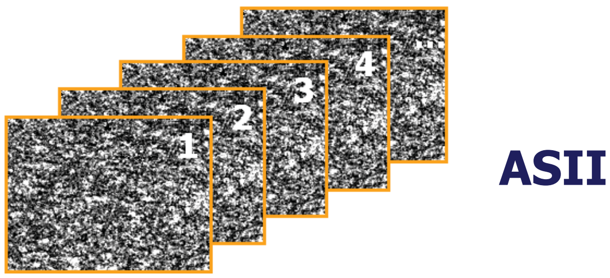
# Measurement Principle






# Measurement Principle

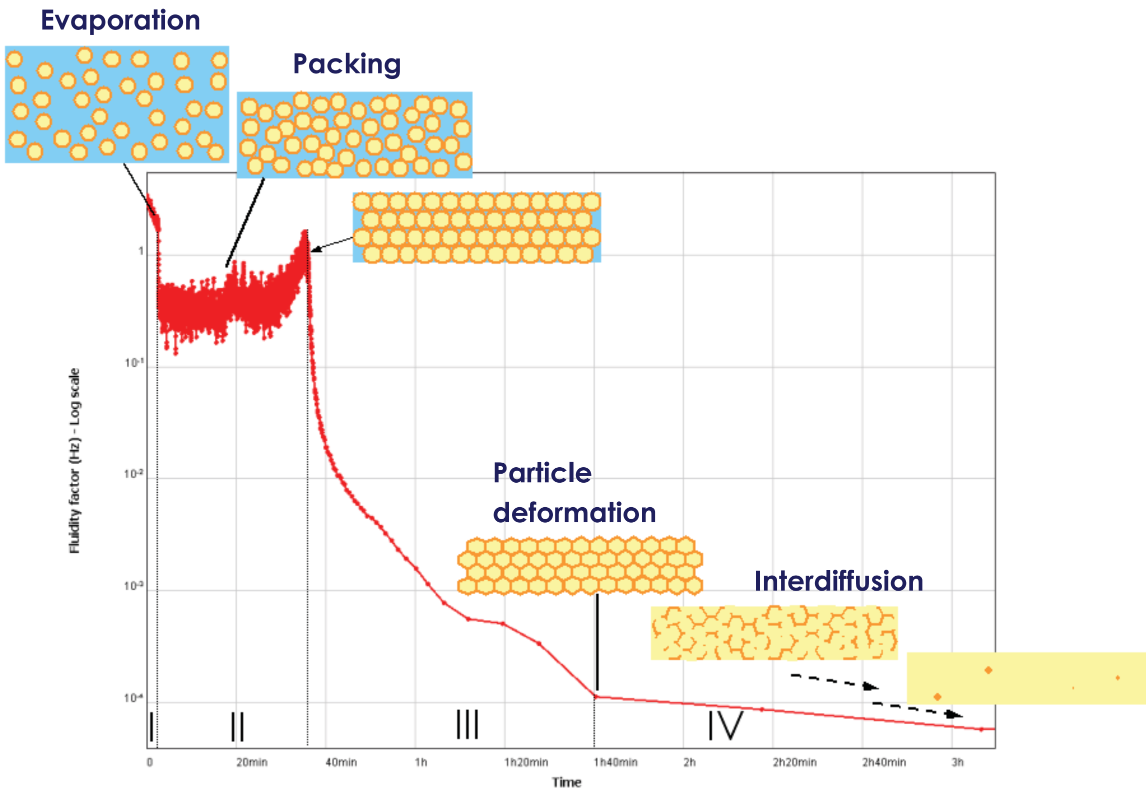
- Determination of Fluidity Factor
  -Set of speckle images captured
  - Time for significant change of speckle image recorded




Fluidity factor = 1/T

WCPC Swansea University Prifysgol Abertawe icmPrint

# Drying Characteristics – ASII Stages

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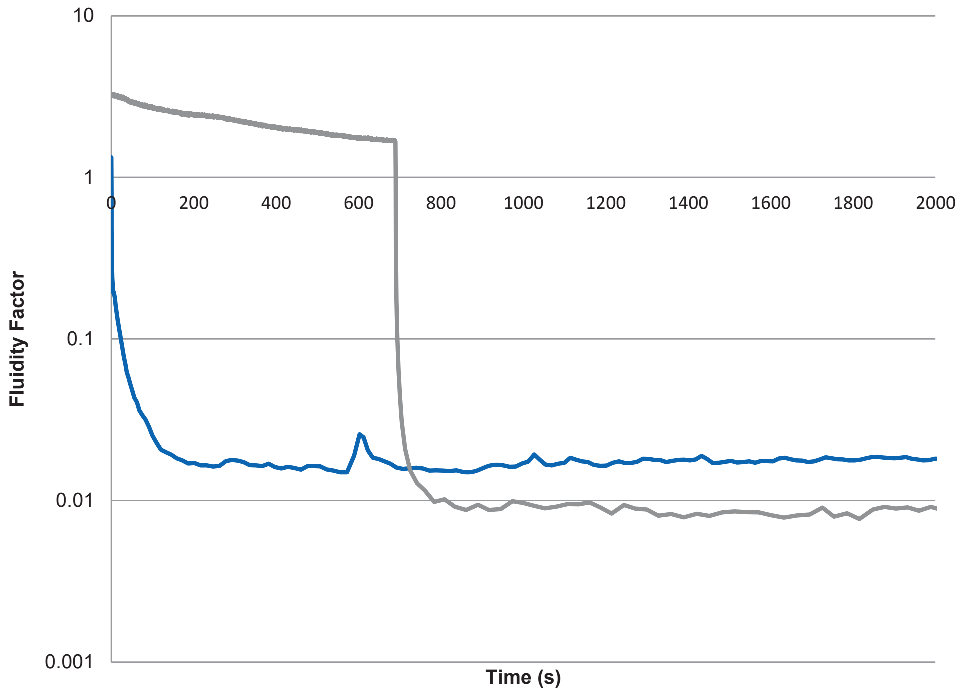
# Examples – Ink Drying in

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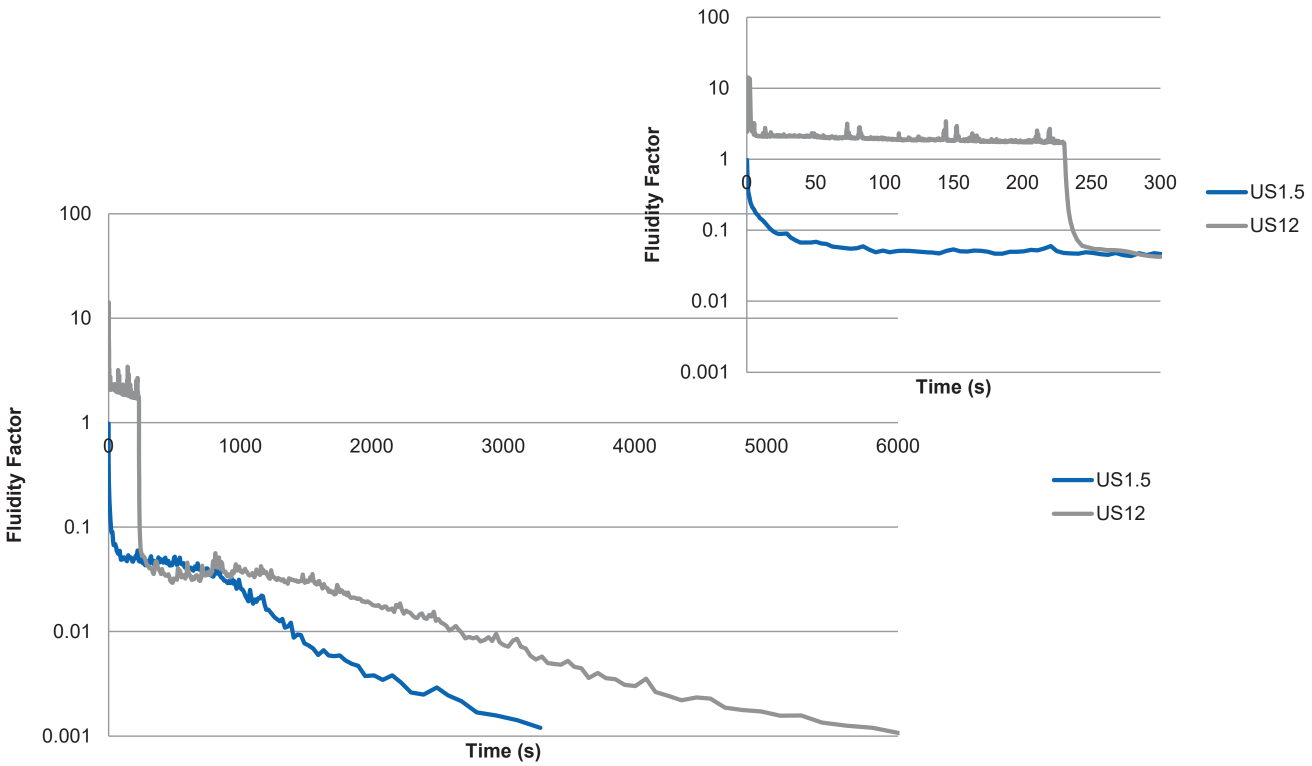
# Ink Film Thickness

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# Thank you for Listening

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Prifysgol Abertawe

icmPrint

## 22. Chemical Measurements


### Marta Klanjšek Gunde, National Institute of Chemistry, Ljubljana


### Biography

Marta Klanjšek Gunde is senior researcher at National Institute of Chemistry, Ljubljana, Slovenia and associate professor of information and graphics technology at University of Ljubljana, Faculty of Natural Sciences and Engineering. She has been working in materials science since her diploma in 1982. She made her PhD in physics on infrared spectroscopy of thin solid films. Her research is concentrated on various homogeneous and heterogeneous materials in bulk and layered forms and their properties in the ultraviolet, visible, and infrared spectral regions. She has been working on materials used for microelectronic applications, coatings for various purposes and for printed functionalities (printable electronics and thermochromics).


### Abstract

Printable electronics should benefit on involvement of materials science and engineering which may help to realize and optimize all necessary features. The more-or-less new materials and application processes have to be controlled also on a very small scale to get the desired functionality. Lot of efforts is required to reach stable technologies, to optimize functional printing inks, and to address the environmental and safety issues. Most of these goals include also analysing of materials in all forms, such as liquid, solidified, cured, stabilized. Proper function of each material in a final device is subject to materials science, which uses several analytical methods to get the corresponding chemical structure and physical properties. A short overview of some frequently used analytical methods will be given in the presentation. Some examples from the area of printable electronics will be discussed with tight focus on the analytical methods that may give important information.

Summer School 2016
at WCPC Swansea University

# Chemical measurements
## in science and engineering of printable electronics

**Marta Klanjšek Gunde**
National Institute of Chemistry
Ljubljana, Slovenia

# Overview

- Introduction
- Analytical methods
  - Vibrational spectroscopy (FTIR, Raman)
  - UV-VIS-NIR spectroscopy
  - Sampling methods
- Selected examples
  - Homogeneous materials
  - Composites (heterogeneous materials)
  - Multilayered functionalities
- Conclusions

# Printable functionalities

- **Printable functionalites** are diverse and have different complexity.
- Many products are on the market already, great many in industrial pipelines or in the research labs; some possibilities are extensively researched.

**HOWEVER**:

- Lot of efforts are required even for existing products
  - to reach stable working technologies,
  - to optimise printing inks, substrates
  - to optimise printing process
  - to recognise the needs for new products or to create such needs (define/find customers),
  - to address environmental and safety issues.





# Chemical analyses

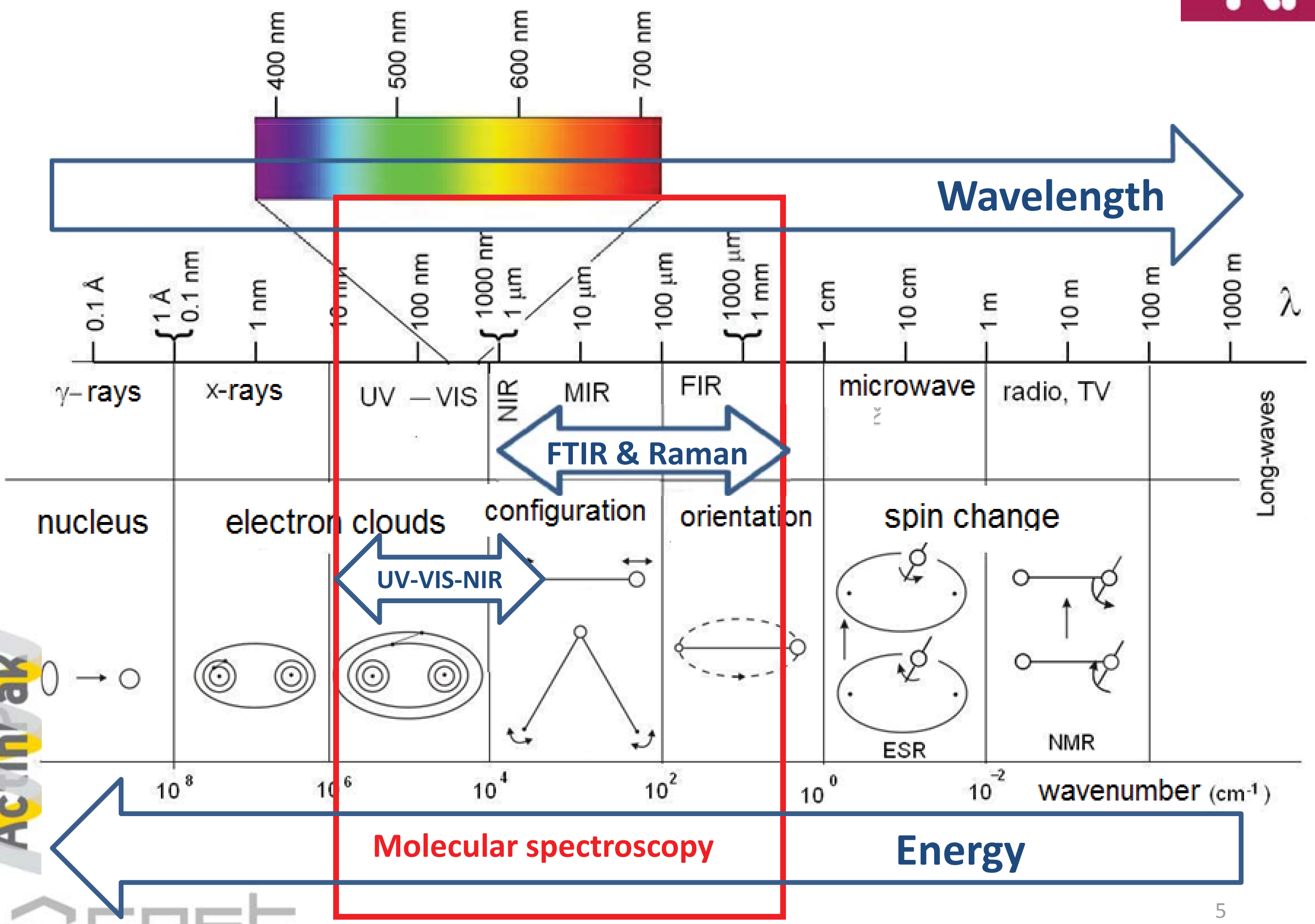
**Why?**

- Proper function of each material in a final device is subject to chemical analyses (materials science).
- Excellent structuring and stabilizing of material inside layers give a well operating device.
- Special structures and materials are required for each device, therefore continuous need for chemical analyses.

**<u>The aim of this lecture</u>**

- **Which methods are suitable for chemical analysis of functional materials in liquid and in solid (layered) forms?**
- **Benefits of analysing the chemical structure**

# Electromagnetic spectrum








# Vibrational spectroscopy

- Infrared (IR) spectroscopy is an old technique
  - first IR spectra were measured in 1881
  - 1905-1908 published first catalogue of IR spectra (Coblentz Society)
  - these spectra were measured in dispersive mode
- FTIR (Fourier-transform IR) technique
  - Michelson interferometer (1887)
  - fast Fourier transform algorithm (1964)
  - computers and excellent detectors
- Raman spectroscopy
  - Invented 1928 by Indian scientist Sir C. V. Raman
  - detection of vibrational, rotational, and other low-frequency modes

## Vibrational spectroscopy (configuration & orientation)

| Infrared | Raman |
|---|---|
| elastic scattering<br>transmission-reflection based<br>special preparation or sampling<br>carefull interpretation for optical effects | inelastic scattering<br>scattering-based<br>no need for a fancy sample<br>so special pre-interpretation methods |
| excitation by globar source<br>continuous illumination by all $\lambda$<br>FT makes small intensities measureable | excitation by lasers<br>- $\lambda_0$=785 nm: Fluorescence less probable; lower Raman signal<br>- $\lambda_0$=532 nm: Fluorescence more probable; stronger signal |
| 2D imaging with resolution up to $\mu$m | 2D imaging resolution below 50 nm |
| 3D imaging rarely possible | 3D imaging (confocal features) |
| Several experimental possibilities<br>(measuring cells: T, R, dR, ATR, NGIA) | several types of Raman<br>Raman, confocal Raman imaging, SERS |
| **Selection rules** dictate which molecular vibrations are probed<br>Some vibrational modes are both IR and Raman active | |
| molecular groups with dipole transition moments (asymetric modes) | molecular groups with quadrupole moments (symetric modes) |

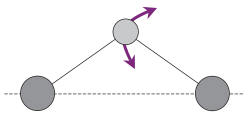


# Molecular vibrations

- All atoms in excited molecular group vibrate with the same frequency (group frequency)
- **Group frequency** depends on:
  - masses of vibrating atoms (reduced mass of the system)
  - force constants (binding energy)
  - geometry of the atoms in the group
- The set of group frequencies respresents **the vibrational fingerprint of the sample**
- The intensity (peak area) is proportional to **the amount of corresponding vibrational units**

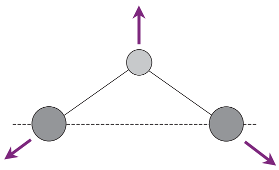
# Vibrations of symmetrical triatomic molecule

$SiO_2$



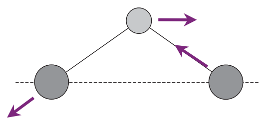
Rocking — $450\ cm^{-1}$

(medium IR activity)



Symmetrical stretching — $800\ cm^{-1}$

(low IR activity)



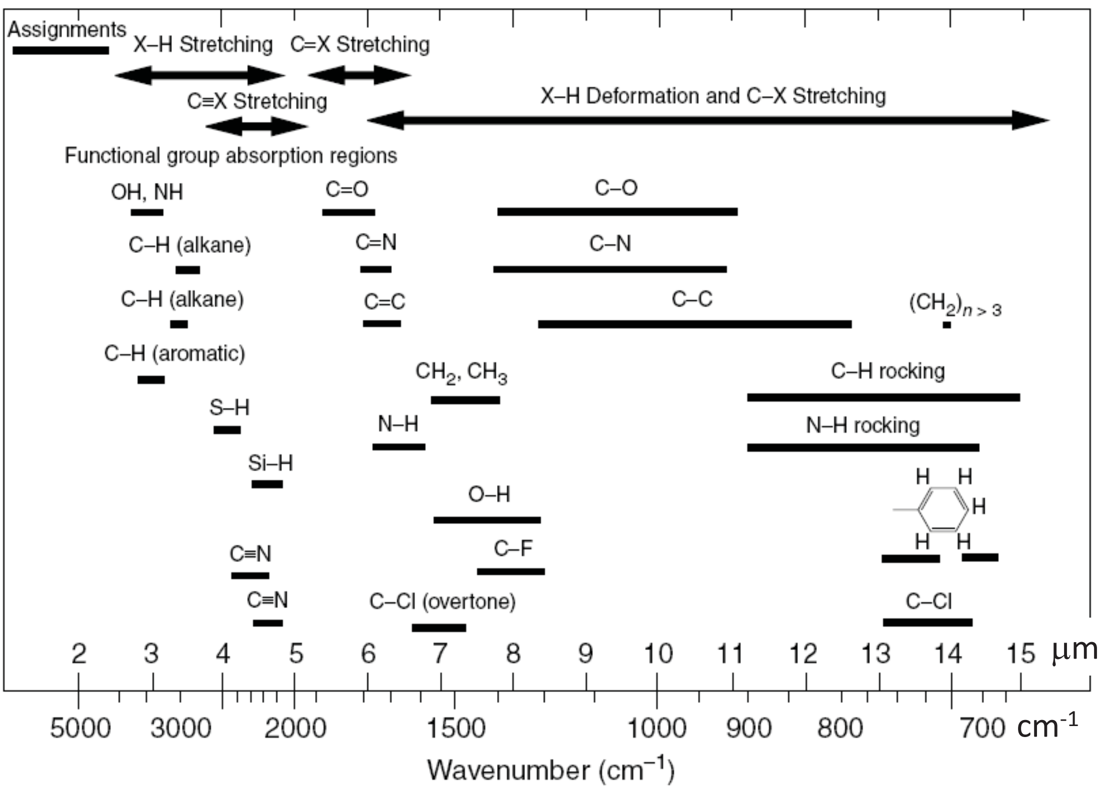
Asymmetrical stretching — $1050\ cm^{-1}$

(high IR activity → strong IR absorption band)



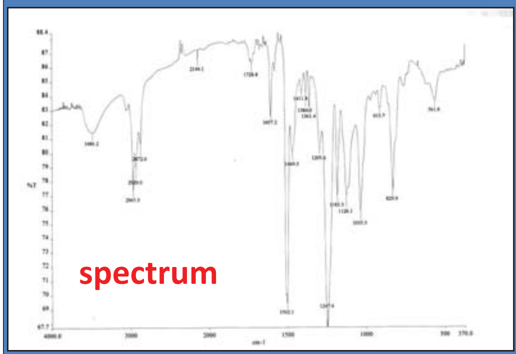
# Spectral analysis

Correlation table for polymers



# Analysis of unknown substance

- Correlation table
- <u>Databases</u>




**Search results**

KBR-EP~1.SP / SPECTRUM.LST   Euclidean Search Hit List

0.867 PA0461 PA0465.DX SHELL EPON 1009
0.840 HA0267 0267.SP BISPHENOL A-EPICHLOROHYDRIN CONDENSATION PRODUCT BISPHENOL A-E
0.840 HA0907 0910.SP EPOXY RESIN WITH 30% GLASS FIBER, ETHYLACETATE EXTRACT EPOXY R
0.835 PA0353 PA0356.DX EPON 1004
0.822 HA0901 0904.SP EPOXY RESIN BASED ON BISPHENOL A AND EPICHLOROHYDRIN; EPOXIDE E
0.822 HA0902 0905.SP EPOXY RESIN BASED ON BISPHENOL A EPOXY RESIN BASED ON BISPHENO
0.813 HA0266 0266.SP BISPHENOL A-EPICHLOROHYDRIN CONDENSATION PRODUCT BISPHENOL A-E
0.807 HA0268 0268.SP EPOXY RESIN BASED ON BISPHENOL A AND EPICHLOROHYDRIN EPOXY RES
0.805 HA0909 0912.SP MODIFIED EPOXY RESIN MODIFIED EPOXY RESIN DOBECKOT 505 146
796 HA0906 0909.SP EPOXY RESIN WITH INORGANIC FILLER, CH2CL2 EXTRACT EPOXY RESIN
794 HA1881 1887.SP EPOXY RESIN BASED ON BISPHENOL A AND EPICHLOROHYDRIN EPOXY RES
89 HA1403 1406.SP MODIFIED DICYANODIAMIDE (SIMPLIFIED STRUCTURAL FORMULA) MODIFI
8 HA0019 0019.SP REACTION PRODUCT OF BISPHENOL A DIGLYCIDYLETHER WITH M-PHENYLEN
74 HA1395 1398.SP ALIPHATIC-AROMATIC AMINE ALIPHATIC-AROMATIC AMINE LEKUTHERM L
73 HA1305 1308.SP EPOXY RESIN BASED ON BISPHENOL A WITH FURTHER COMPONENTS EPOXY
.762 HA1848 1854.SP EPOXY RESIN BASED ON BISPHENOL A AND EPICHLOROHYDRIN EPOXY RES
0.753 HA0094 0094.SP NA LIGNIN OF CORN STALKS NA LIGNIN OF CORN STALKS 1439 NR
0.739 HA0269 0269.SP EPOXY RESIN BASED ON BISPHENOL A AND EPICHLOROHYDRIN EPOXY RES
0.713 HA0096 0096.SP NA LIGNIN FROM RICE STRAW NA LIGNIN FROM RICE STRAW 1439
0.711 HA0097 0097.SP THIOLIGNIN FROM RICE STRAW THIOLIGNIN FROM RICE STRAW 1439
0.709 HB0115 0115.SP BISPHENOL F DIGLYCIDYLETHER BISPHENOL F DIGLYCIDYLETHER RUETA
0.704 HA0785 0788.SP GLYCEROL ESTER OF VINSOL RESIN GLYCEROL ESTER OF VINSOL RESIN
0.702 HB0100 0100.SP OXY-BIS(4-BISPHENOL A-OXYETHYLENE) OXY-BIS(4-BISPHENOL A-OXYET
0.700 HA0898 0901.SP BISPHENOL F BIS(GLYCIDYL ETHER); 50% 4,4';40% 4,2;10% 2,2'-ISOM
0.692 PA0328 PA0331.DX ISOPROPOXYDIPHENYLAMINE
0.687 SF0161 SF0161.DX OCTYLPHENOXYETHOXYETHYLDIMETHYLBENZL NCL
0.685 HB0397 0397.SP ALIPHATIC-AROMATIC EPOXYETHER ALIPHATIC-AROMATIC EPOXYETHER
0.682 HA0900 0903.SP EPOXY RESIN BASED ON BISPHENOL A EPOXY RESIN BASED ON BISPHENO

FDM ATR Spectra of Drugs, (c) 2002-2003, Fiveash Data Management, Inc.

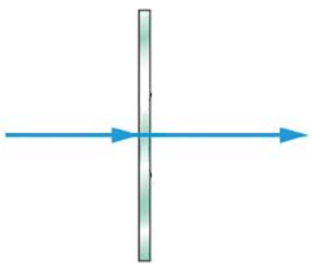


# Sampling methods

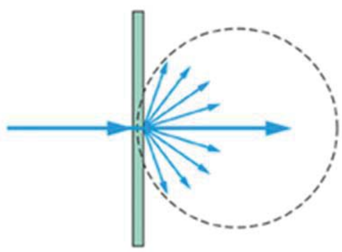
(all spectroscopies)

Perfectly smooth and homogeneous samples

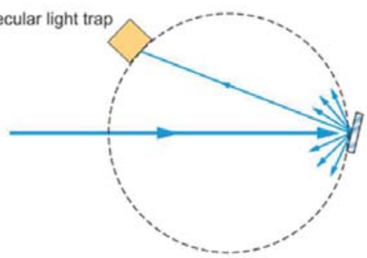
Irregularly diffuse samples



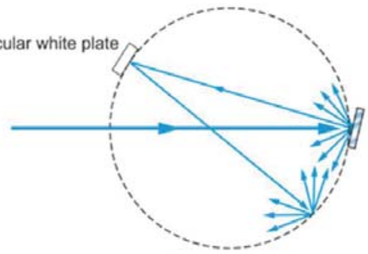
Normal Transmittance



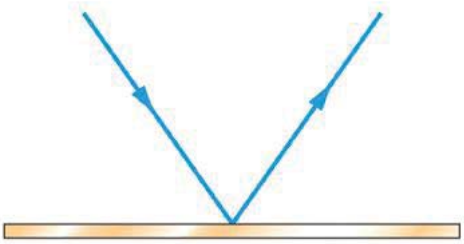
Diffuse Transmittance



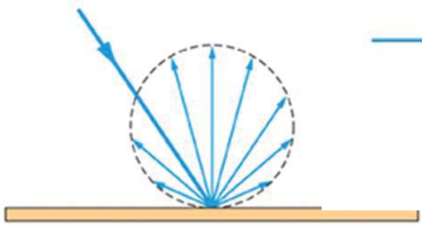

Diffuse Reflectance




Total Reflectance



Specular Reflectance (Polished surface)



Diffuse Reflectance (Matte surface)

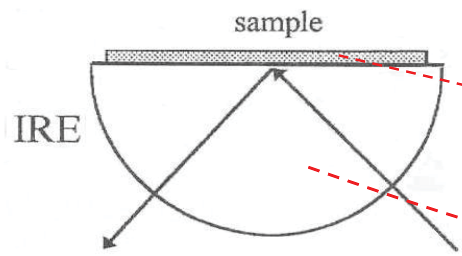
Integrating sphere

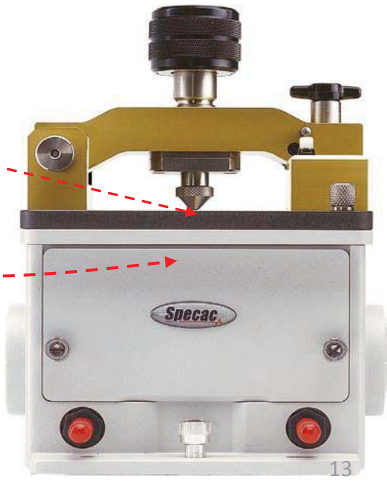
# Sampling methods
(only in FTIR)

Attenuated total reflectance (ATR)

ideal technique for liquid samples

Surface spectroscopy (penetration depth: several μm)




"Golden gate"



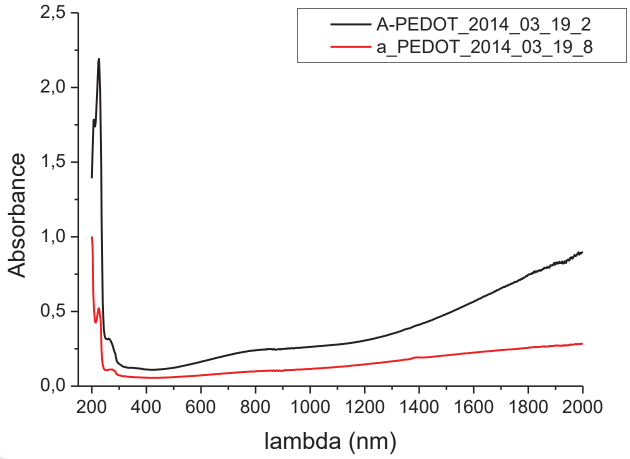
# (semi)Conductive polymers

EXAMPLES

- PEDOT:PSS
  - (reference) vs. (Syrovy, Kubac)
- Sample preparation:
  - UV-VIS : layers on quartz discs, transmission
  - FTIR: layers on ZnSe discs, transmission
  - Raman: spin-coated layers on glass

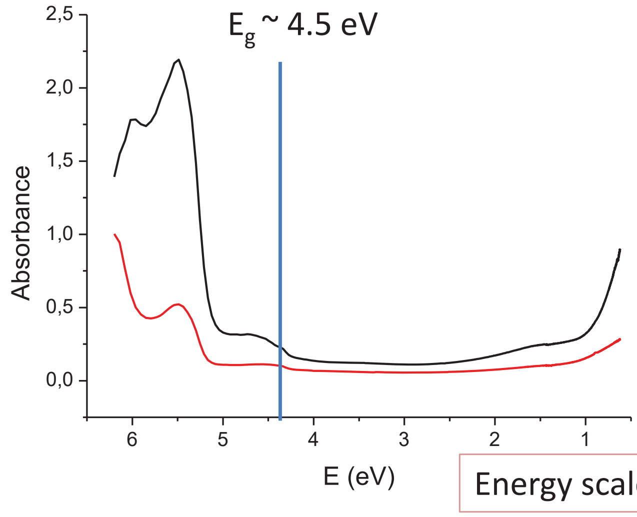
# PEDOT:PSS (UV-VIS-NIR region)

EXAMPLES




Wavelength scale

Si: $E_g$ ~ 1.1 eV




Energy scale

**PEDOT:PSS sample is a broad-band semiconductor**



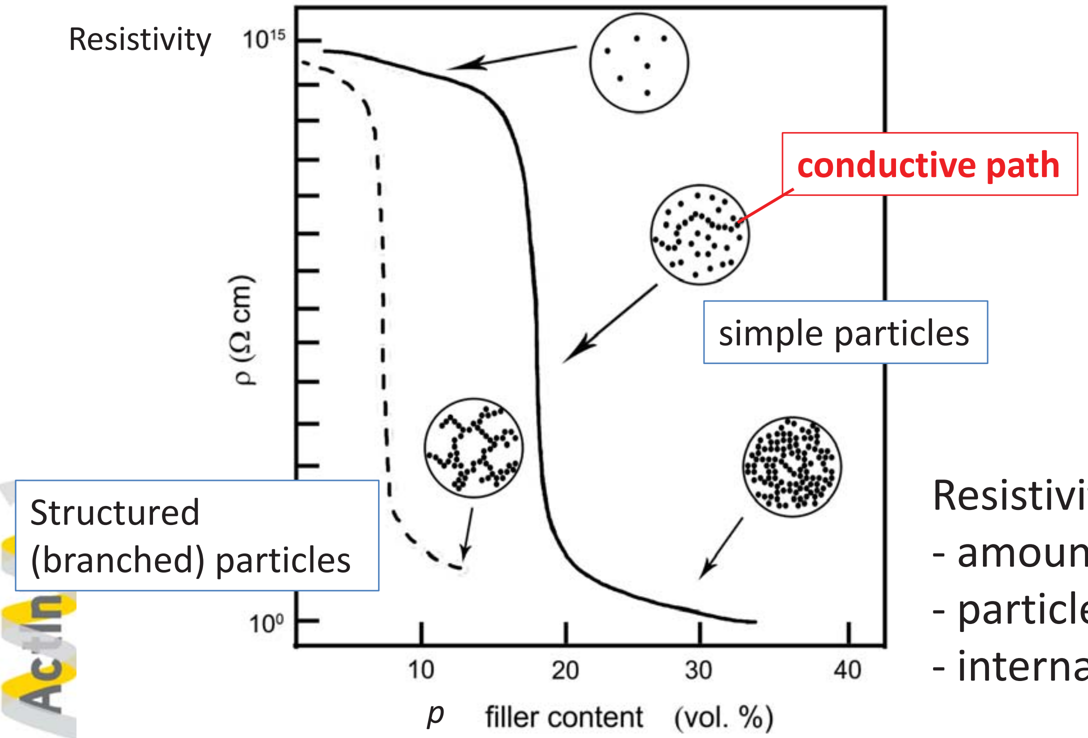
# Conductive polymer composite

EXAMPLES

- Mixture of polmer (insulator) and conductive particles.
- Conductivity is described by the **percolation theory**.
  - statistical theory, describes the conditions in which a disordered system becomes opened for something to flow through (fluid, heat, electric current, moving objects, …)

# Resistivity at percolation

EXAMPLES




Resistivity depends on:
- amount of particles
- particle distribution
- internal structure

R. Strümpler and J. Glatz-Reichenbach, Journal of Electroceramics 3 (1999) 329-346



# Conductivity of **functional printing inks**

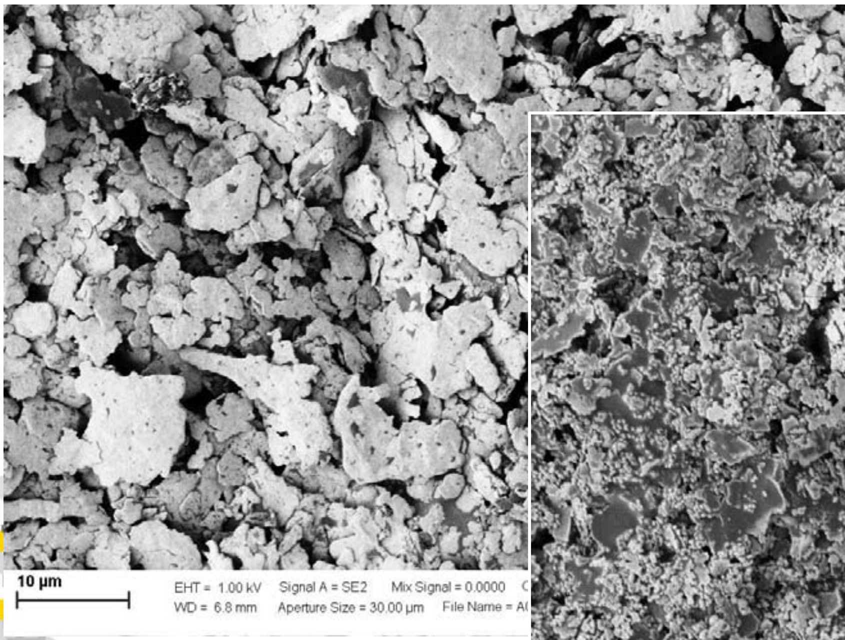
EXAMPLES

Depends on:

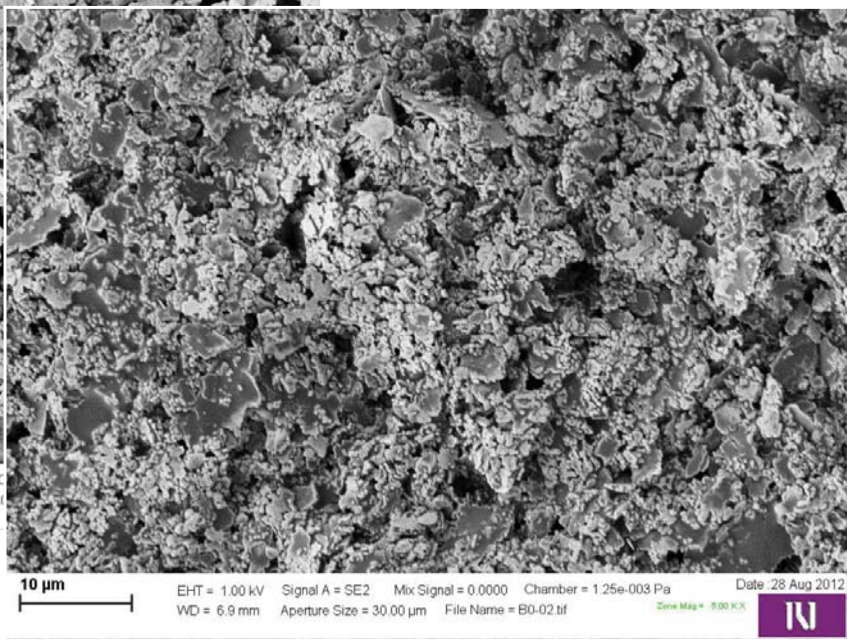
- Conductive particles (percolation theory)
  - Concentration
  - Distribution
  - Internal structure (branching)
- Polymer (alternating double bonds, crosslinking)
- Particle/polymer interlayer (contact resistivity)

# Different inks with Ag particles

EXAMPLES



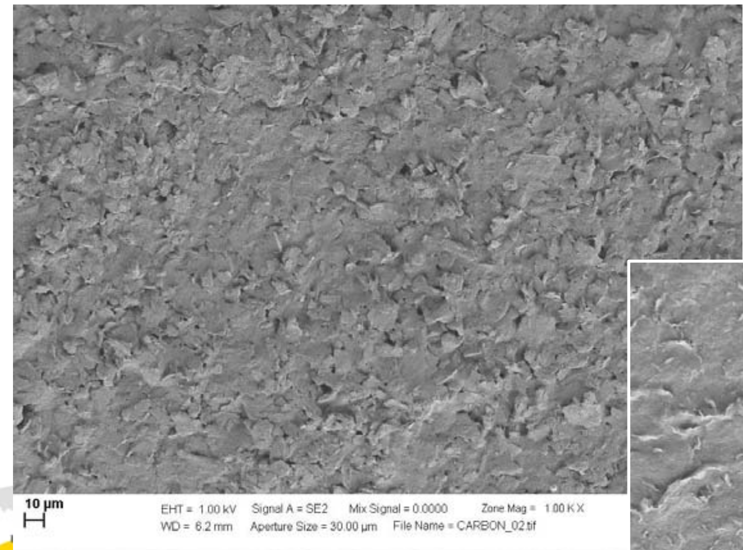

SEM pictures Ag-filled composite





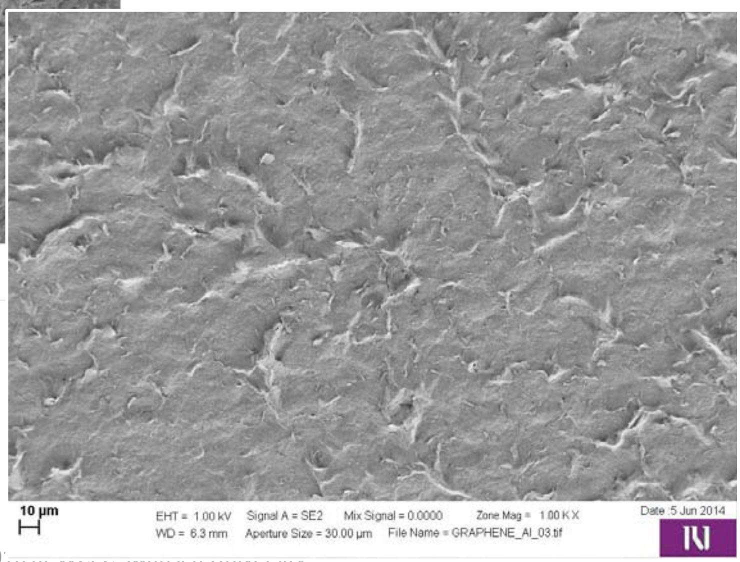

# Carbon-based conductive inks

EXAMPLES



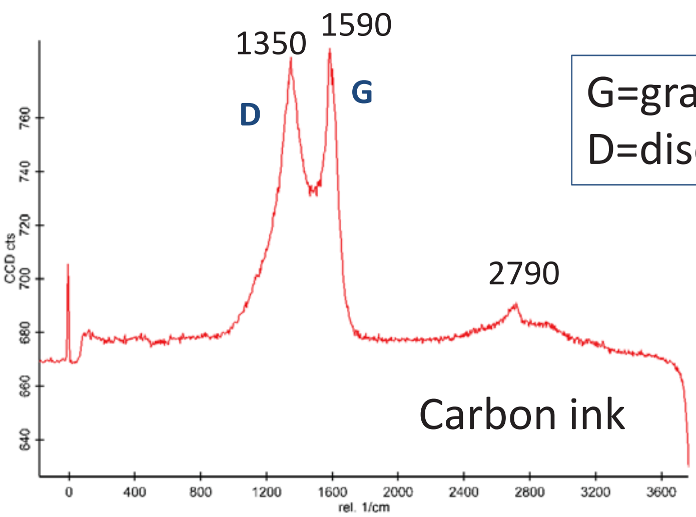

Carbon ink (carbon black)

Graphene ink

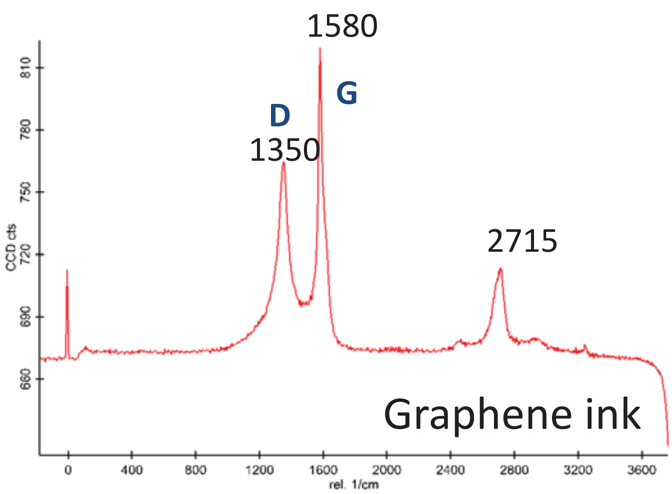


# Carbon-based inks (Raman)

EXAMPLES




G=graphitic
D=disordered






# Insulators / dielectrics

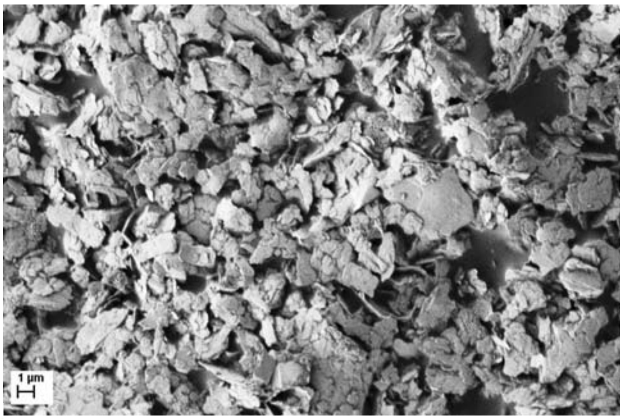
EXAMPLES

- large dielectric strength (good insulators)
  - direct current voltage between two electrodes of a capacitor at which dielectric breakdown occurs
  - most polymers: 100 - 300 kV/cm.
- able to polarize (separate internal charges)
- large dielectric constant $\varepsilon$
  - non-polar polymers: $\varepsilon < 3$
  - polar polymers: $\varepsilon > 3$

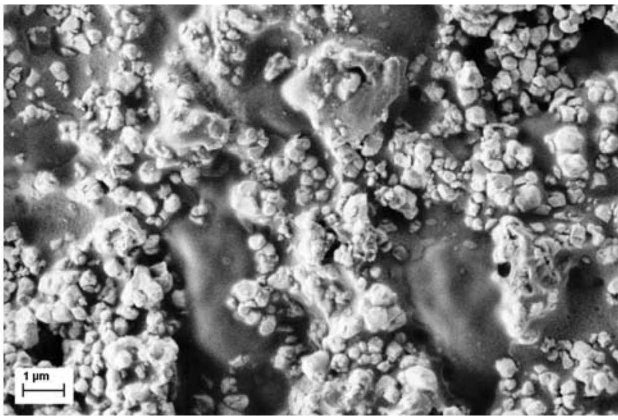
# Dielectric inks

EXAMPLES

high concentration of particles with large ε




magnesium silicate particles ($\varepsilon_p$ ~ 6)
urethane acrylate binder ($\varepsilon_M$ ~ 3)
$\varepsilon_{eff}$ = 5.09




Aluminum oxide particles ($\varepsilon_p$ ~ 9)
fluorinated acrylate binder ($\varepsilon_M$ ~ 5)
$\varepsilon_{eff}$ ~ 6



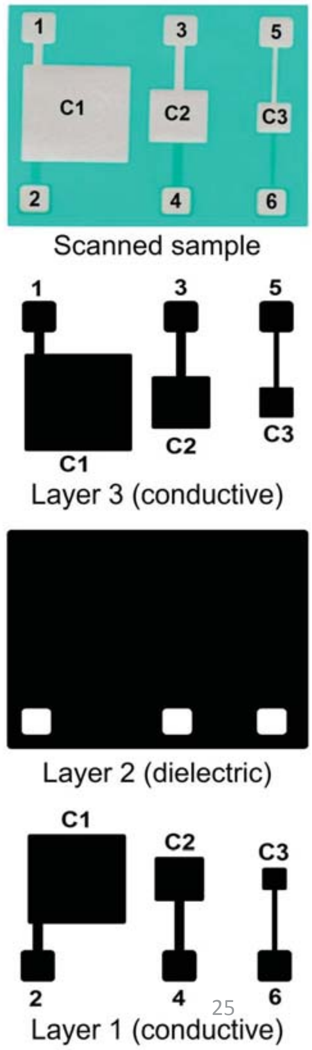
# Multilayered functionalities

EXAMPLES

Inevitable components of printed electronics
- capacitors, transistors, sensors, OLED, …..
- several layers are printed one over another
  - Interlayers ?
  - Influences of top layer (liquid) and its drying on the underneath layers

Example: Flat-plate capacitor
- to store electric charge
  - resonant RCL circuits (e.g. in RFID tags)
- to create homogeneous electric field
  - electrochromic effect in displays

# Flat-plate capacitors




Conductor ink

- silver-based ink
  (Ag particles in a thermoplastic resin, solvent-based, thermal drying)

Dielectric ink

- magnesium silicate (talc)
  in urethane acrylate binder, $\varepsilon = 5.09$
  UV curable (400–700 mJ/cm$^2$)

Screen printing on paper

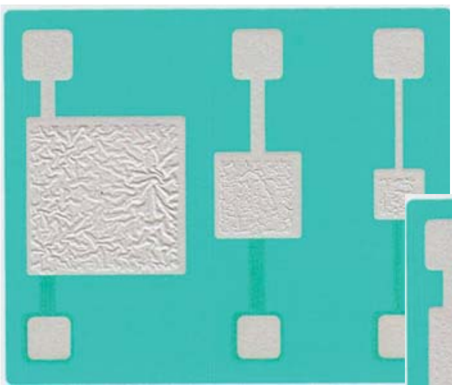
Double printed dielectric layer (wet-to-dry)
(normal procedure to prevent electrical shorts)



EXAMPLES

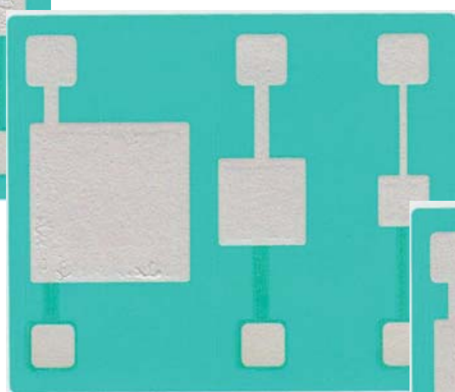
# Flat-plate capacitors

What happens if dielectric layer is single-printed ?

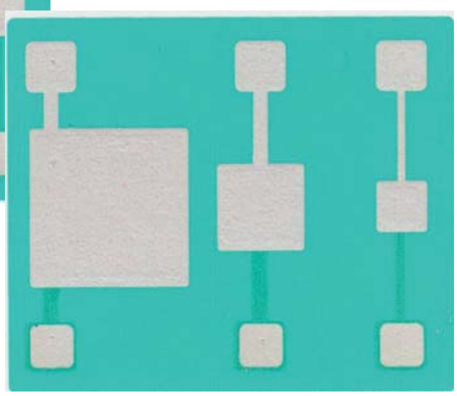


450 mJ/cm$^2$

Surface wrinkels of the top conductive layer
→too low curing energy for dielectric layer



900 mJ/cm$^2$



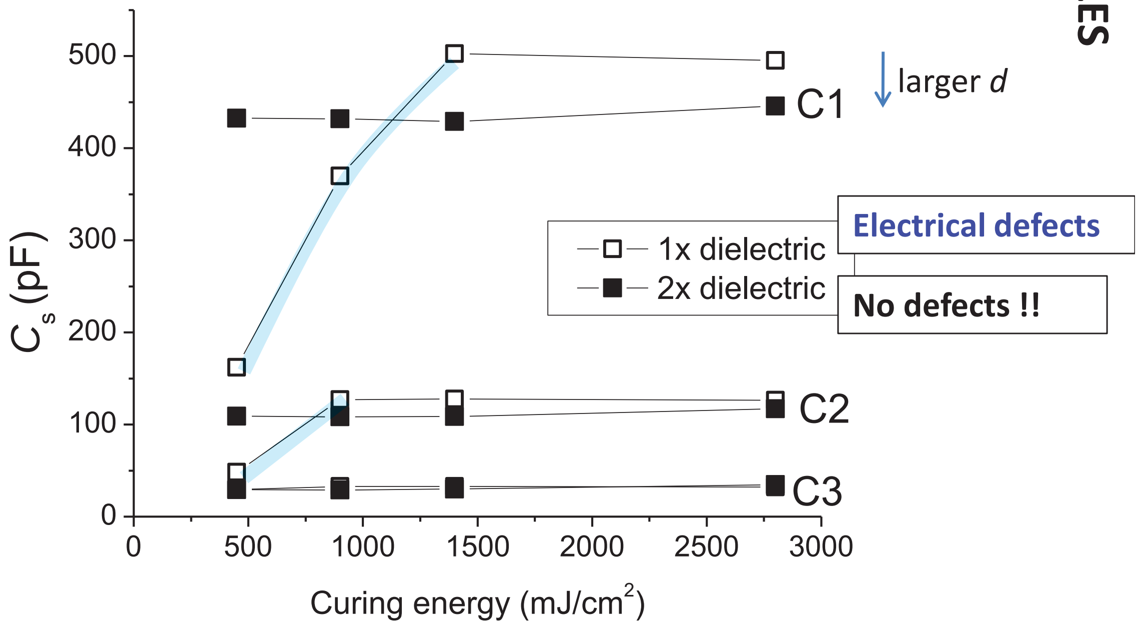
1380 mJ/cm$^2$

Surface efects dissapears
at curing energy $\geq$ 1000 mJ/cm$^2$

M.Horvat, T.Vidmar, M.Maček, M.K.Gunde, J Electron. Mater. 2015

# Capacity of samples

EXAMPLES




$C_s$ depends on curing energy ➔ $\varepsilon$ depends on curing (?)

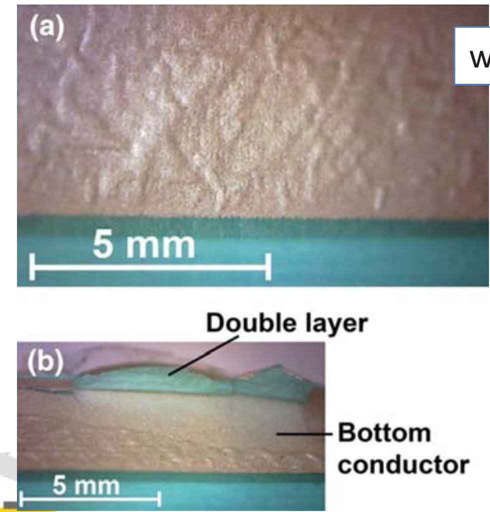
Capacitors with double-printed dielectric layer do not show this effect



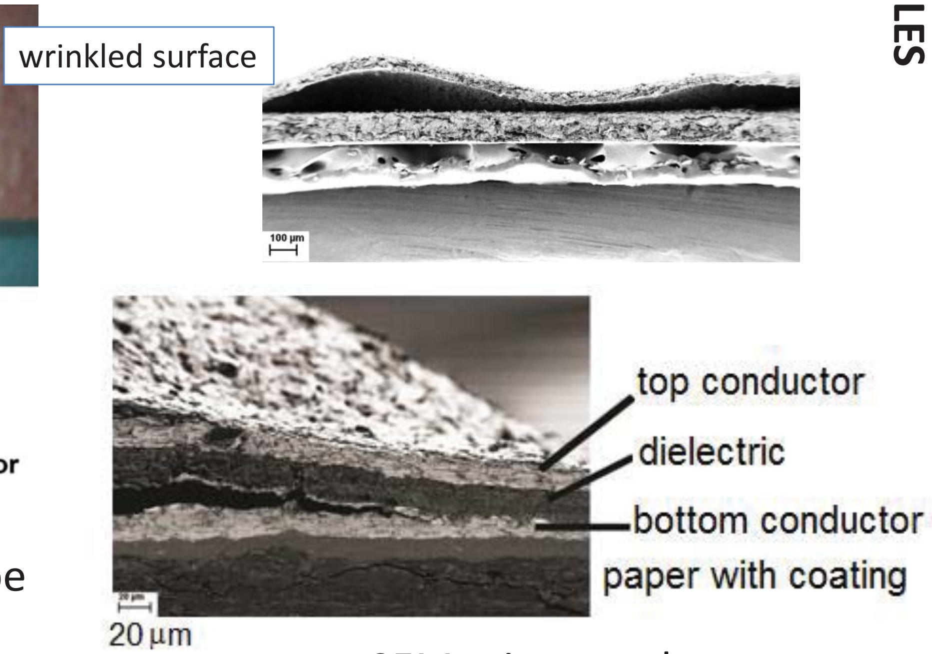
# Surface defects

EXAMPLES

samples with single-printed dielectric layer




Optical microscope



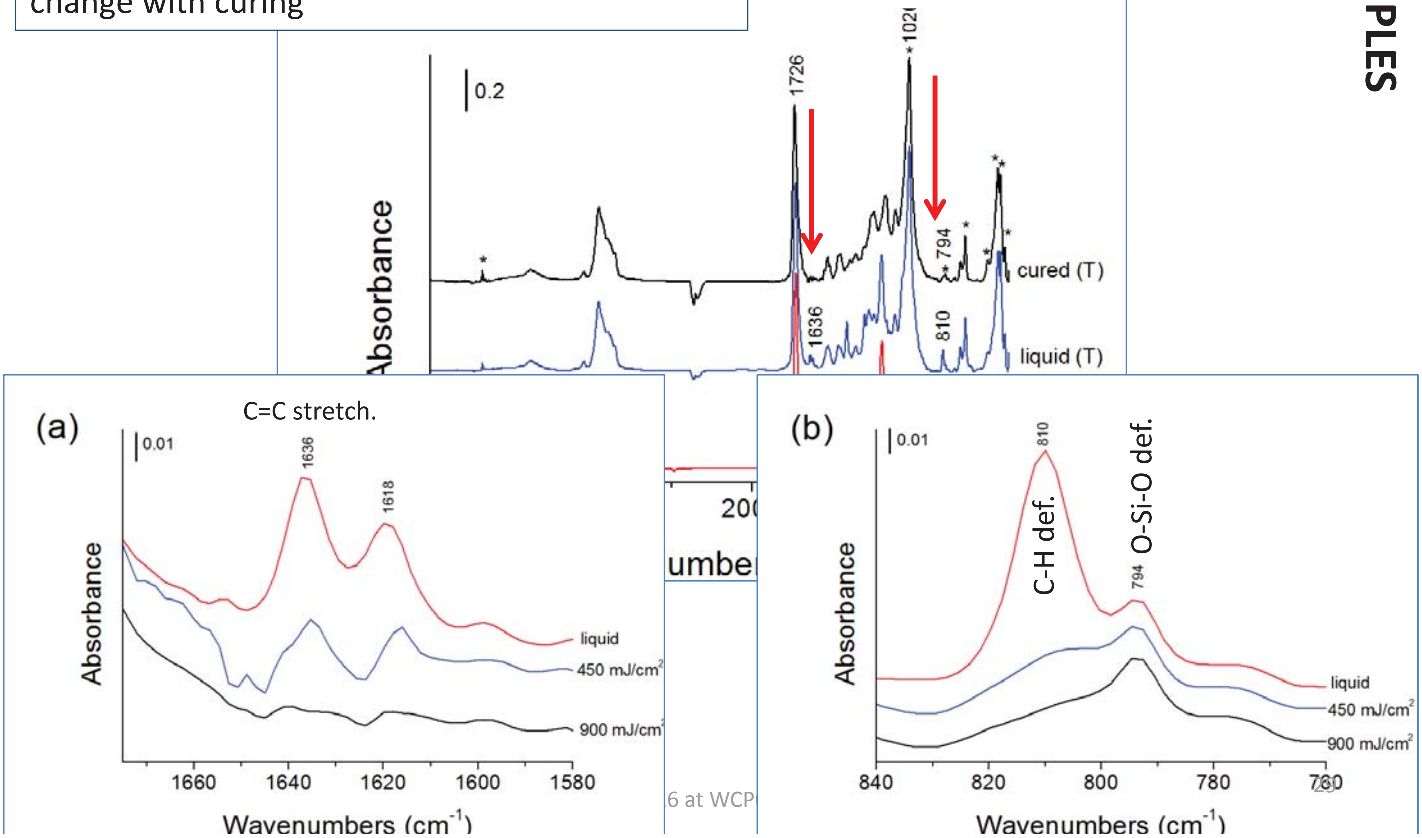

SEM micrographs

M. Horvat, T. Vidmar, M. Maček, M.K. Gunde, J. Electron. Mater. 2015

# FTIR analysis of dielectric layer

EXAMPLES

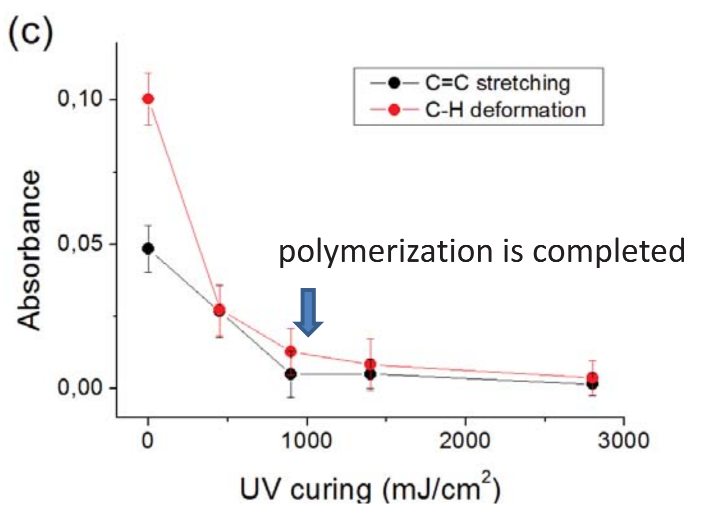
Vibrations due to polyurethane acrylate binder change with curing




# FTIR analysis of dielectric layer

EXAMPLES

- The presence of reactive acrylate groups in polyurethane backbone is evidenced by the two acrylate vibrations.
- The two bands diminish with curing energy and completely disappear when the process is finished.

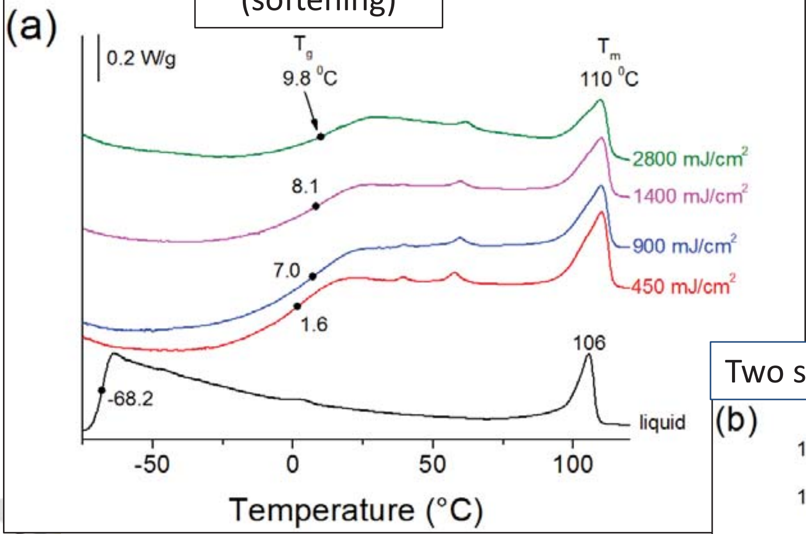



M.Horvat, T.Vidmar, M.Maček, M.K.Gunde, J Electron. Mater. 2015

# Thermal analysis of dielectric layer

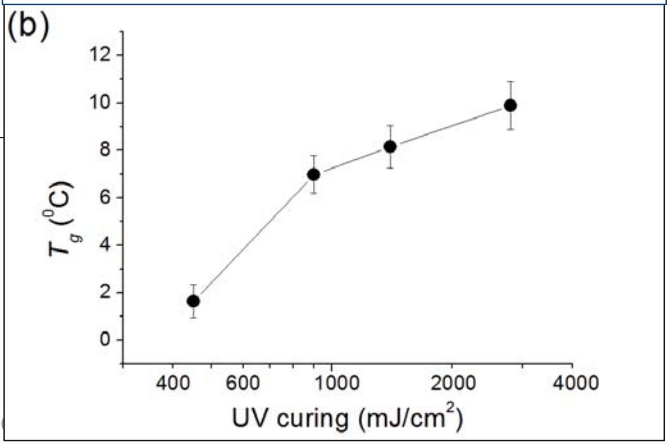
EXAMPLES

glass transition (softening)




DSC = differential scanning calorimetry

Two slopes gives evidence of two processes




M. Horvat, T. Vidmar, M. Maček, M.K. Gunde, J Electron. Mater. 2015

# Multilayered functionalities

EXAMPLES

- Dry but non-completely polymerized layer may allow permeation of the solvent from the overprinted layer → surface wrinkles.
- A fully polymerized layer is a good barrier for solvents.
- Electrical shorts might be connected with incomplete polymerization of the dielectric layer.
  - Double bonds are still present (acrylate double bonds), which could support conductive paths across the layer
- This is the evidence of a connection between the structure of polymerized layer and its electrical properties.

M. Horvat, T. Vidmar, M. Maček, M.K. Gunde, J. Electron. Mater. 2015

# Conclusions

- Chemical analyses could help to optimize/enable printable electronic applications
- Combination of many methods can provide useful results
- Each problem is unique
- No routine procedures are used
- What is urgently required now?
  - Materials control?
  - Process monitoring?
- Could we benefit from:
  - Materials control like in microelectronics?
  - Analyses used for polymers?
  - Some new approaches?



# Acknowledgements

**Special thanks to**

**Tomáš Syrový**

Katedra polygrafie a fotofyziky, Univerzita Pardubice, Czech Republic

**Maša Horvat, Metka Hajzeri**

National Institute of Chemistry, Ljubljana, Slovenia

## 23. An overview about (nano) cellulose based active packaging materials

Carmen Freire, University of Aveiro

### Biography

Carmen Freire studied Chemistry in the University of Aveiro (UA) (degree in Chemistry in 1998). Then, in 2003 she has got a PhD degree in Chemistry, also by the UA. In the period of 2003-2005 she had a post-doc fellow position in the Department of Chemistry of UA and in the École Française de Papeterie et des Industries Graphiques (presently Pagora) (Institute Polytechnique de Greboble). In 2006 she became a staff member of CICECO-Aveiro Institute of Materials (UA) as Auxiliary Researcher and since 2013 as Principal Researcher (Biorefineries and Bio-based Materials). Her research interests are centered on the chemistry and applications of natural polymers (cellulose, starch, chitosan and proteins); new biocomposites and paper materials; nanostructured bio-based materials for biomedical applications (wound healing and drug delivery) and packaging; and isolation, characterization and chemical transformations of bioactive natural compounds. Carmen Freire is author/co-author of more than 130 scientific papers in international peer-reviewed journals, 4 patents, 9 book chapters and several communications in International and National Conferences.

http://orcid.org/0000-0002-6320-4663

http://www.ciceco.ua.pt/CarmenFreire

### Abstract

Active packaging systems, aiming to extend products shelf life or to improve safety, while preserving quality, have emerged in response to the increasing demands of the modern society. Nowadays, one of the main challenges for active packaging is to develop more sustainable materials, for example by using active compounds derived from natural resources and biodegradable polymeric matrices.

In this scenario, nanocellulose forms, as nanofibrillated cellulose, bacterial cellulose and cellulose nanocrystals, because of their renewable character and singular properties, are gaining particular relevance on the design of nanostructured active packaging systems. Thus, the aim of this talk is to provide an overview of the research and innovation trends on nanocellulose based active packaging materials.

## Summer School 2016 at WCPC- Swansea University

# Active Packaging: nanocellulose based materials


Carmen S.R. Freire
CICECO- Aveiro Institute of Materials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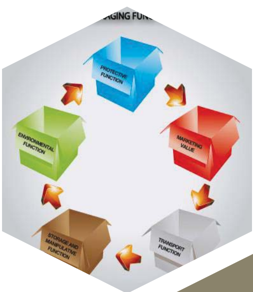
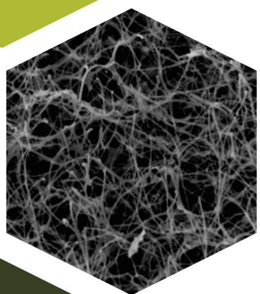
Lecture Outline



Introduction

Nanocellulose based packaging materials



Research@UA

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UNIVERSITY of AVEIRO

- ✓ **young (1973) Institution, innovative – education, research, cooperation, tech transfer**
- ✓ **binary system – about** 15 000 students, 900 teaching staff, 120 researchers, 300 pos-docs
    - University (16 Departments)
    - Polytechnic schools (since 1997, 4 schools)
- ✓ **Public foundation with private law**
- ✓ **Yearly budget** ~ 130 M€

https://www.ua.pt/

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## CICECO-Aveiro Institute of Materials

**CICECO is the largest Portuguese institute in the field of materials science and engineering,**

- 48 academic staff,  32 full-time researchers and,
- In December 2013, 91 post-doctoral associates, 119 PhD students, and ca. 77 other students.

**CICECO is one of the most productive research institutes in the country in all scientific areas.** Between 2002-13 we have produced:

- an average publication of 4.5 SCI papers per year per academic staff or full-time researcher;
- almost 3808 SCI papers (many in top journals);
- 99 patents;
- 204 PhD theses.
- In 2011 we published more than 450 SCI papers.

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# CICECO  main lines of expertise are:

**L1- Information and Communication Technology**

**L2- Energy and Industrial Applications**

**L3- Sustainability and Health**

**Biorefineries, Biobased Materials and Recycling**

**L4-Computind and Modelling**

macromolecular and lignocellulosic materials
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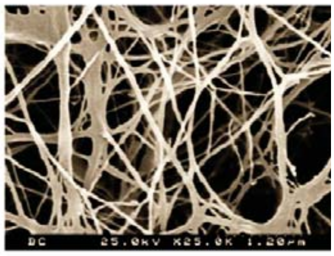
CICECO

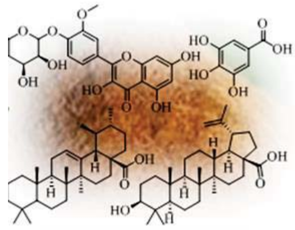
# Main activities




macromolecular and lignocellulosic materials
CICECO-UAveiro

- **New materials from (nano)cellulose fibers and other biopolymers** (PulpBleach FP6; Sustainpack FP6; Sunpap FP7)

- **High value low molecular weight compounds from agro-forest residues**
  (WaCheUp FP6, ERA-NOEL FP6, Afore FP7)



- **New Polymeric materials from renewable resources (e.g. polyesters, polyurethanes, etc.)**

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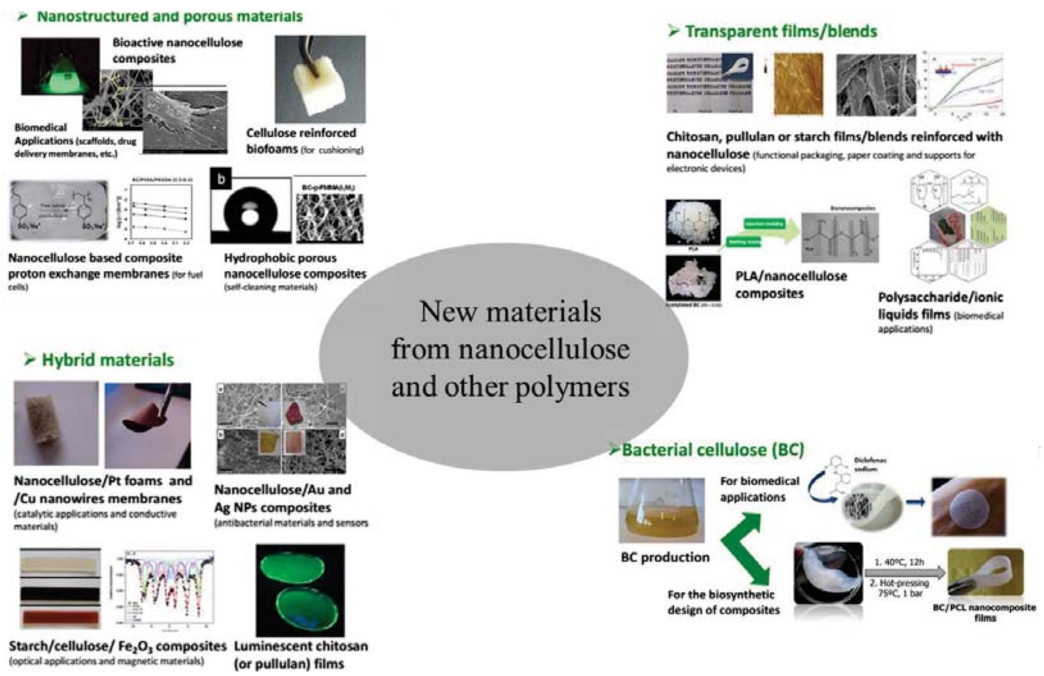
CICECO
Introduction

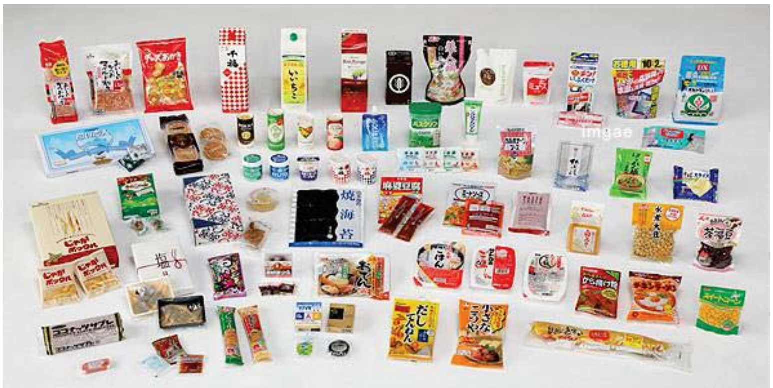

macromolecular and lignocellulosic materials
CICECO-UAveiro





## Packaging functions

Food Packaging has been developed to contain food products, maintain food quality and inform consumers about the properties of the products

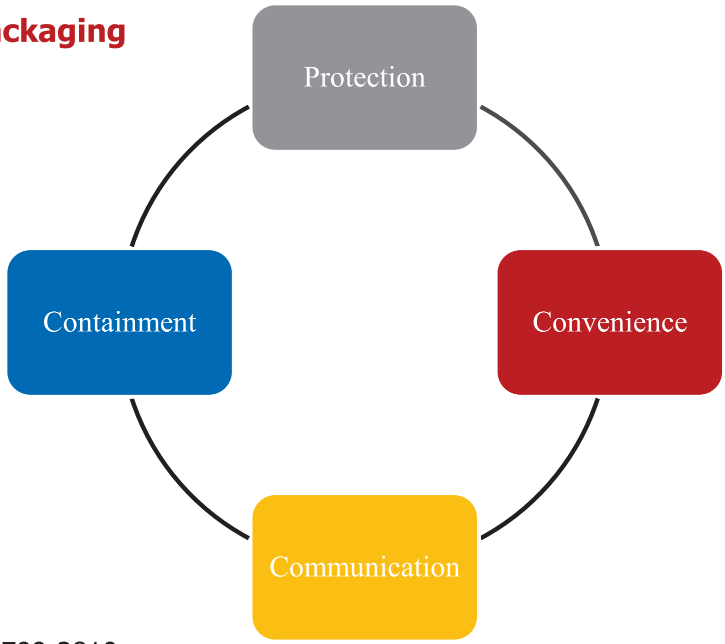


J. Sci. Food Agr. 2015, 95 2799-2810
Comprehensive Reviews in Food Sci. and Food Safety, 2016, 15, 3-15

Introduction- Packaging Functions

## Packaging functions

**Primary Functions of Packaging**




J. Sci. Food Agr. 2015, 95 2799-2810
Comprehensive Reviews in Food Sci. and Food Safety, 2016, 15, 3-15



## Packaging functions

Innovations in the food packaging industries leads to a variety of terminologies, some of them used to describe similar concepts

### SMART and INTELLIGENT PACKAGING

http://www.foodonline.com/doc/the-active-and-smart-packaging-market-will-see-steady-growth-this-year-0001

J. Sci. Food Agr. 2015, 95 2799-2810
Comprehensive Reviews in Food Sci. and Food Safety, 2016, 15, 3-15

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Introduction- Packaging Functions

## Packaging functions

Smart Packaging is any type of packaging that provides specific functionality beyond the role of physic barrier between the food product and the surrounding environment

Smart packaging can be viewed as an ehancement of the primary packaging functions

Intelligent packaging is described as a system that conveys information to the consumer about the enclosed product

Comprehensive Reviews in Food Sci. and Food Safety, 2016, 15, 3-15

## Packaging functions

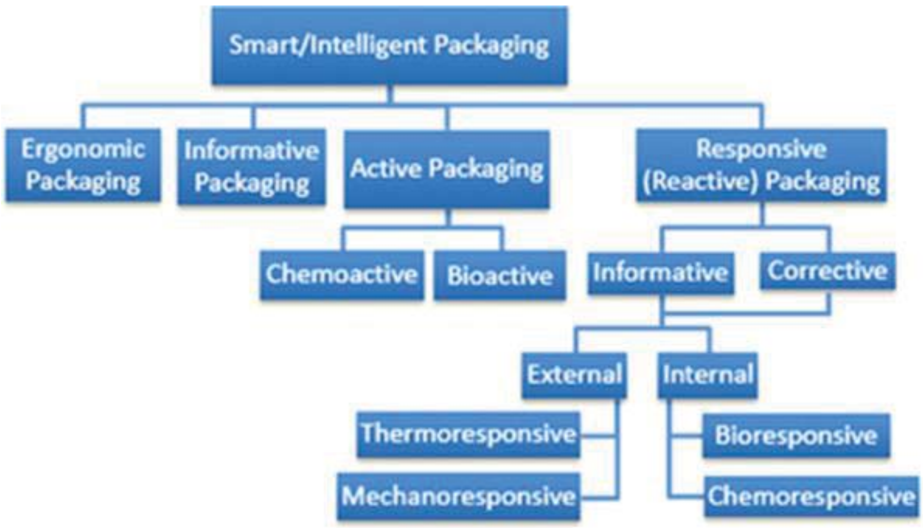
In order to lessen the confusion surrounding intelligent and smart packaging**; some authors consider that the two terms are synonyms that refer to any packaging systems that enhances the primary functions of packaging or adds new functionalities**

From an engineering perspective the synonyms smart and intelligent are generic descriptions that do not provide information on the designed functionality of a particular packaging

Comprehensive Reviews in Food Sci. and Food Safety, 2016, 15, 3-15

Introduction- Packaging Functions

## Classifications of smart/intelligent packaging




Comprehensive Reviews in Food Sci. and Food Safety, 2016, 15, 3-15



## Active packaging

**Active packaging** is defined as the incorporation of certain compounds into packaging systems to extend shelf life and maintain or enhace food quality and safety.

Active packaging is the deliberate changing of interactions with the packaging environment or conditions and includes additives and enhancers to preserve food quality

The nature **of active agents** is very diverse and includes: organic acids, enzymes, fungicides, natural extracts, antioxidants, ions and ethanol, among others

J. Sci. Food Agr. 2015, 95 2799-2810

Introduction-Active Packaging

**Active packaging applications can be classified in different categories:**

(1) Scavenging of oxygen, carbon dioxide, moisture, ethylene, UV light, taints and flavors
(2) Release/emission of ethanol, antioxidants, preservatives and sulfur dioxide
(3) Removal of food components (as lactose or cholesterol)
(4) Temperature control of the insulating materials, self-heating and self-cooling, temperature sensitive packaging and MW susceptors or modifiers
(5) Microbial and quality control

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# Active packaging

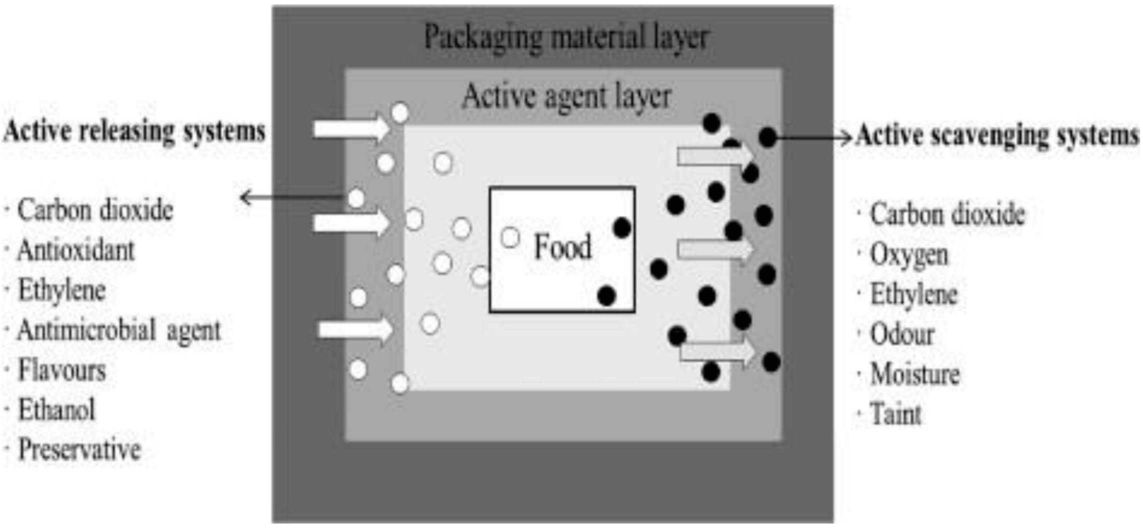


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**Table 1.** Examples of some currently known active packaging systems

| Type of active packaging system | Substances | Applications and advantages |
|---|---|---|
| Oxygen scavengers | Enzymatic systems: glucose oxidase, alcohol oxidase<br>Iron powder oxidation: powdered iron oxide, ferrous carbonate, metallic platinum<br>Ascorbic acid oxidation: ascorbic acid<br>Unsaturated fatty acids: oleic or linolenic acid<br>Immobilization of microorganisms in solid holders<br>Photosensitive dye oxidation | High-, intermediate- and low-moisture foods<br>Foods containing lipids<br>Refrigerated and frozen storage foods<br>Microwaveable food products<br>Reduce microbial growth and nutritional loss<br>Improve product quality and shelf life<br>Prevent discoloration and flavor change |
| Carbon dioxide absorbing/emitting | Iron powder/calcium hydroxide, ferrous carbonate/metal halide | Roasted ground coffee<br>Snack foods<br>Nuts and bakery products<br>Dried meat and fish products<br>Reduce respiration rate<br>Increase shelf life of product<br>Inhibit microbial growth<br>Absorbed by moisture or fat |
| Moisture absorbing | Silica gel, propylene glycol, polyvinyl alcohol, diatomaceous earth | Maintain food quality<br>Extend shelf life<br>Reduce microbial growth and degradation of texture, flavor and color |
| Ethylene scavenging | Activated carbon<br>Zeolites<br>Potassium permanganate | Fruits, vegetables and other horticultural products<br>Control concentration of ethylene<br>Improve quality of food |
| Antimicrobial releasing | Organic acids: sorbates, benzoates, propionates<br>Bacteriocins: nisin<br>Spice/herb extracts: rosemary, clove, cinnamon, thyme, mustard, horseradish<br>Chelating agents: EDTA<br>Inorganic acids: sulfur dioxide, chlorine dioxide<br>Anti-fungal agents: imazalil, benomyl | Fresh fruits and vegetables<br>Meat products<br>Maintain food quality<br>Inhibit microorganisms |
| Others | BHA, BHT, TBHQ, ascorbic acid, tocopherol, baking soda, active charcoal, biaxially oriented vinylon, compression-rolled oriented HDPE, encapsulated ethanol, low-toxicity fumigants (pyrethrins and permethrin) | Fresh fruits and vegetables<br>Meat products<br>Perishable foods<br>Maintain and improve food quality<br>Extend shelf life of food products |

J. Sci. Food Agr. 2015, 95 2799-2810



**Table 1** Commercially available active packaging systems

| Trade Name | Manufacturer | Principle | Type |
|---|---|---|---|
| Ageless | Mitsubishi Gas Chemical Co. Ltd., Japan | Iron based | Oxygen scavenger |
| Freshilizer | Toppan Printing Co. Ltd., Japan | Iron based | Oxygen scavenger |
| Freshmax, Freshpax, Fresh Pack | Multisorb Technologies, USA | Iron based | Oxygen scavenger |
| Oxyguard | Toyo Seikan Kaisha Ltd., Japan | Iron based | Oxygen scavenger |
| $Zero_2$ | Food Science Australia, Australia | Photosensitive dye | Oxygen scavenger |
| Bioka | Bioka Ltd., Finland | Enzyme based | Oxygen scavenger |
| Dri-Loc® | Sealed Air Corporation, USA | Absorbent pad | Moisture absorber |
| Tenderpac® | SEALPAC, Germany | Dual compartment system | Moisture absorber |
| Biomaster® | Addmaster Limited, USA | Silver based | Antimicrobial packing |
| Agion® | Life Materials Technology Limited, USA | Silver based | Antimicrobial packing |
| SANICO® | Laboratories STANDA, | Antifungal coating | Interleavers |
| Neupalon | Sekisui Jushi Ltd., Japan | Activated carbon | Ethylene scavenger |
| Peakfresh | Peakfresh Products Ltd., Australia | Activated clay | Ethylene scavenger |
| Evert-Fresh | Evert-Fresh Corporation, USA | Ativated zeolites | Ethylene scavenger |

J. Food Sci. Technol. 2015, 52 6125-6135

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Introduction-Active Packaging

## Active packaging- antimicrobial packaging systems

**Antimicrobial packaging** has been used to delay spoilage and improve the safety of food materials by integrating antimicrobial agents into packaging films to suppress the activities of besieged microorganisms

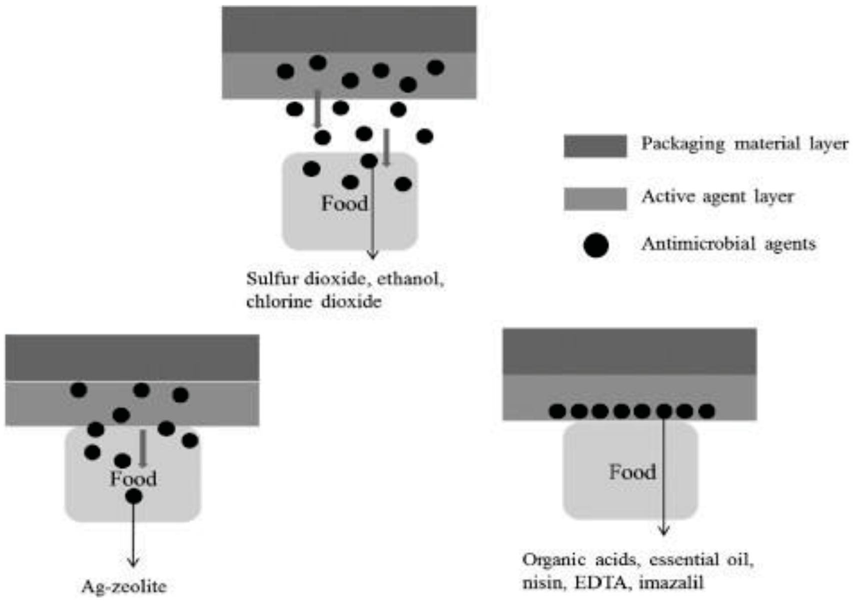
**The mechanisms for antimicrobials** in packaging can be classified:

**(1) Release mechanisms-** diffusion and decrease of effect over time

**(2) Contact mechanisms-** direct contact and surface-immobilizied substances

J. Sci. Food Agr. 2015, 95 2799-2810

## Active packaging- antimicrobial packaging systems




J. Sci. Food Agr. 2015, 95 2799-2810
Frontiers in Microbiology, 2015, 6, article 611



## Responsive Packaging

**Responsive packaging** is any package that elicits a curative or informative response as a result of a specific trigger or change occurring in the food product, packages, or the outside environment

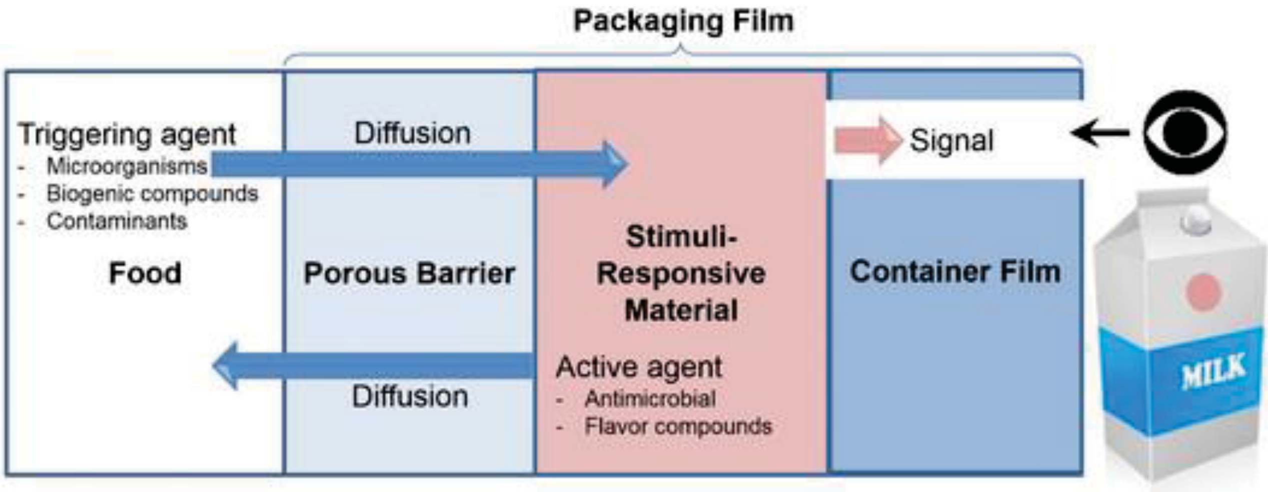
Current active packaging technology is based on passive diffusion or initial package modification;

Responsive packaging systems work differently by only reacting to a stimulus (based on the integration of a sensor or sensing interface)

Comprehensive Reviews in Food Sci. and Food Safety, 2016, 15, 3-15



# Responsive Packaging

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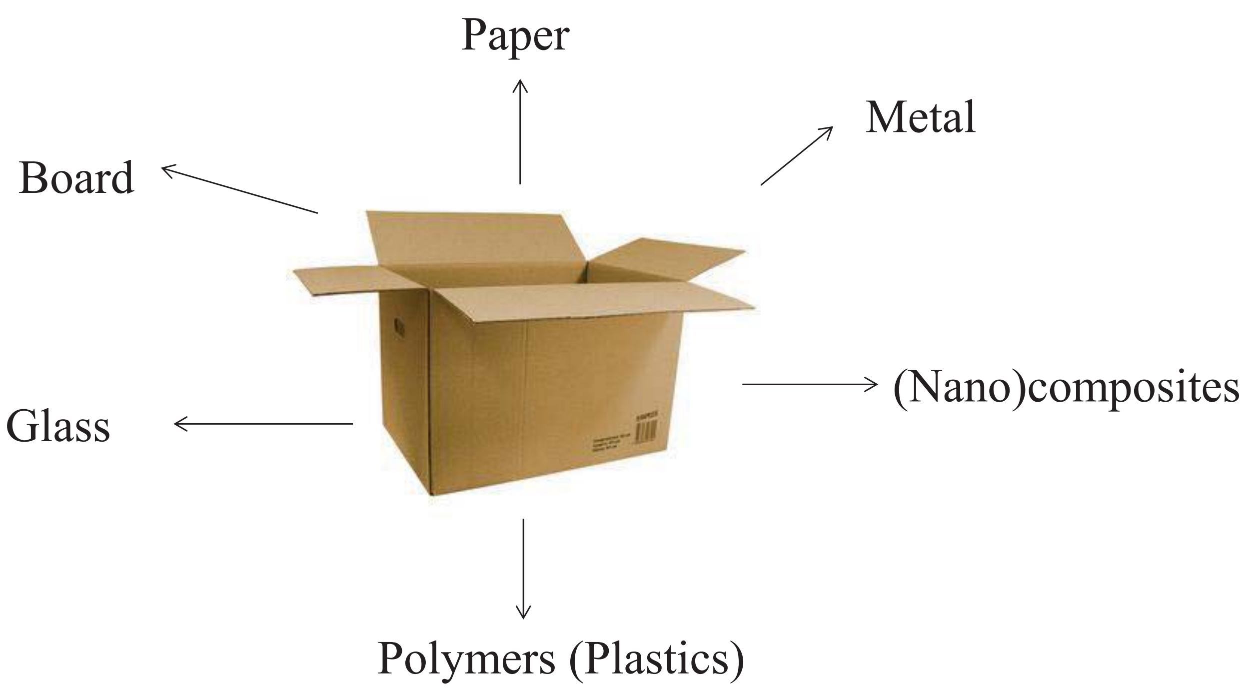
# Types of Materials used in Packaging

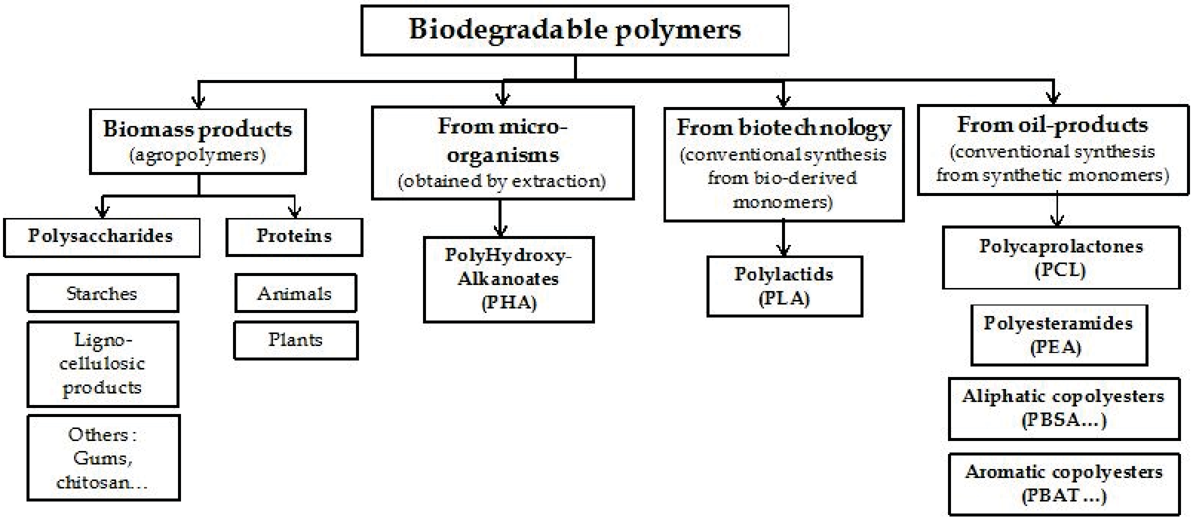



J. Sci. Food Agr. 2015, 95 2799-2810



## Biodegradable Polymers

Currently, biodegradable packaging has triggered great attention




Critical Reviews in Food Science and Nutrition, 2014, 54, 163-174





## Bio-based Packaging

**Bio-based Packaging** is defined as packaging containing raw materials obtained from natural sources, i.e. produced from renewable, biological raw materials (NATURAL POLYMERS; BIOPOLYMERS)

Biopolymers are environmentally-friendly and has the potential to improve the protection of food while maintaining its quality and safety

Shortcomes: weaker barrier and mechanical properties

Critical Reviews in Food Science and Nutrition, 2014, 54, 163-174



## Composites and Nanocomposites

**Nanocomposites Technology** has been shown to be useful for enhancing properties of biopolymer based materials

**Matrix**
"continuous phase"

**(bio)Polymers**

**COMPOSITE MATERIALS**

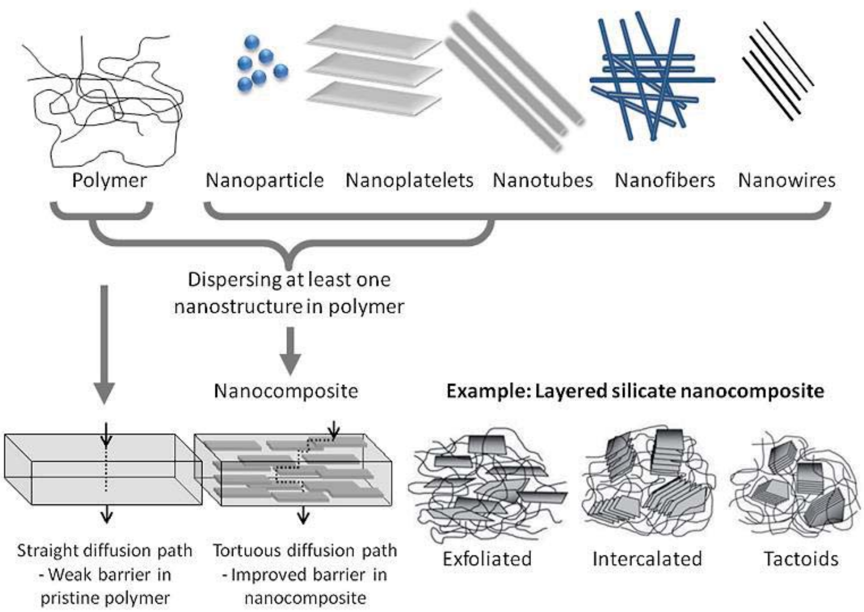
**Reinforcing Element**
"discontinuous phase

**Particles**
**Fibers**
**(clays, NPs, nanocellulose)**

Trends Food Sci. Technol., 2014, 40, 149-167

Introduction- Nanocomposites

## Composites and Nanocomposites




Trends Food Sci. Technol., 2014, 40, 149-167
J. Colloid Interface Sci. 2011, 363, 1-24

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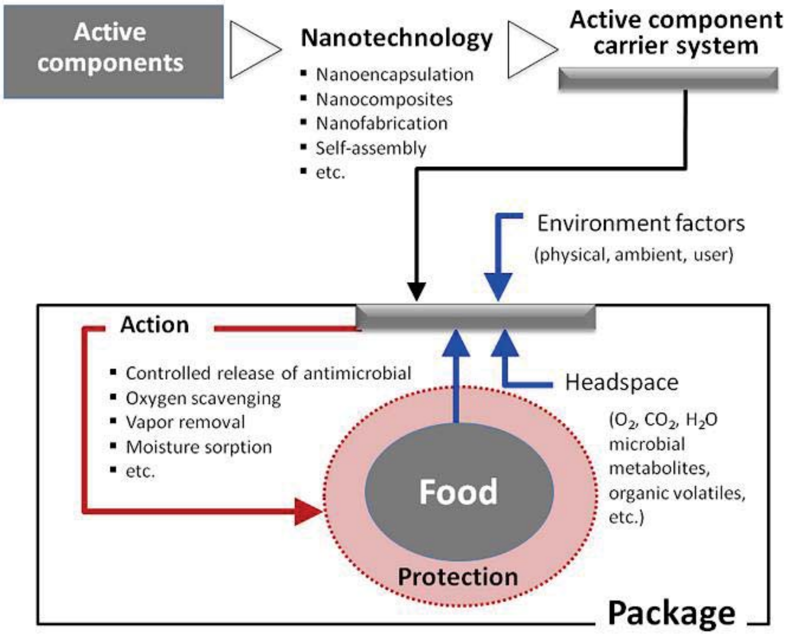
Introduction- Nanocomposites

# Composites and Nanocomposites




Trends Food Sci. Technol., 2014, 40, 149-167

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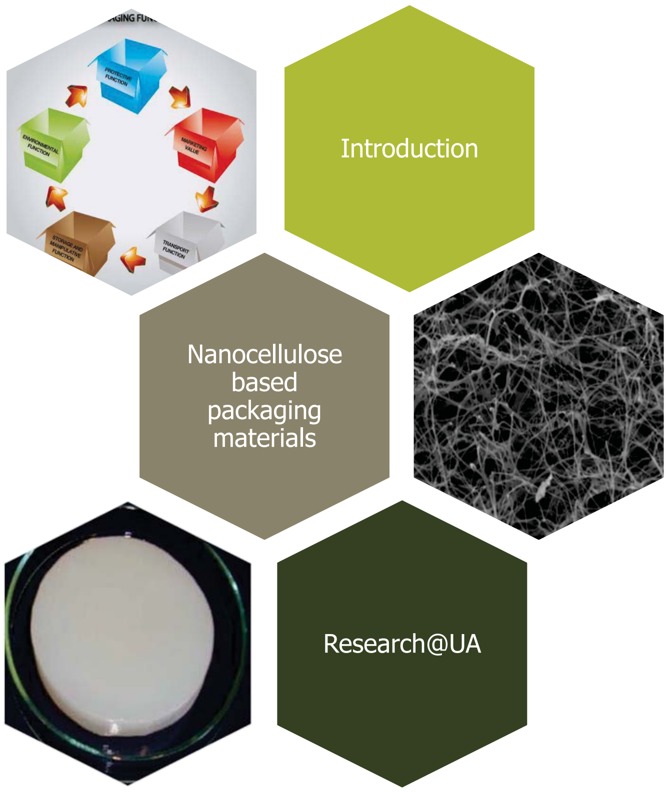
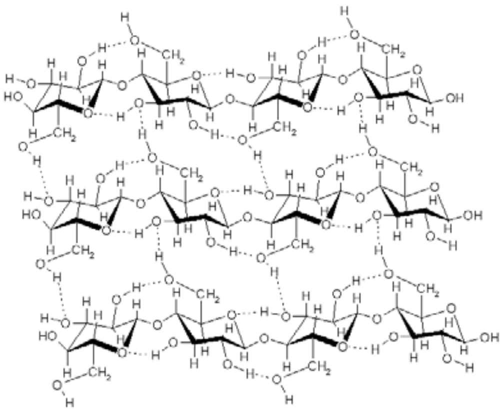
Lecture Outline

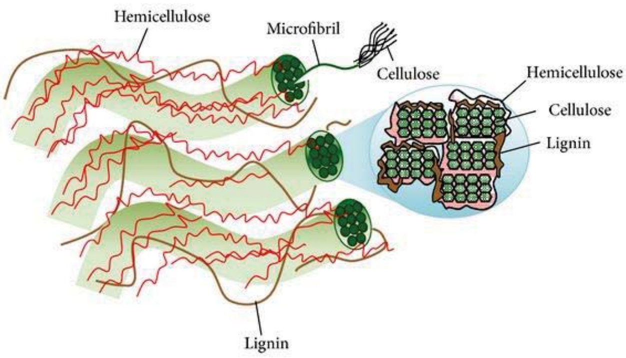




## Nanocellulose

Cellulose, the main component of plant cell walls, is the most abundant natural polymer






However, it is also produced by a family of sea animals called tunicates, several species of algae and some aerobic non-pathogenic bacteria

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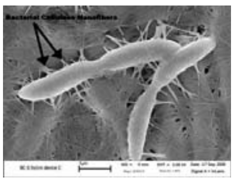
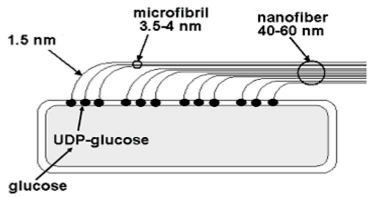
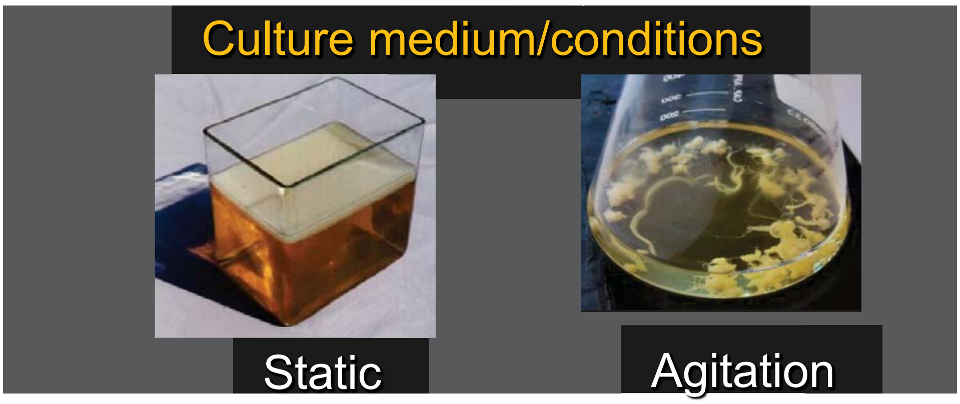
Nanocellulose based packaging materials

## Nanocellulose forms: Bacterial Cellulose



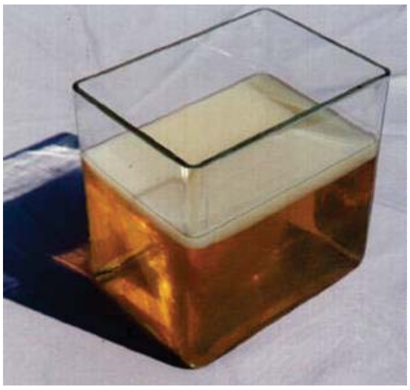



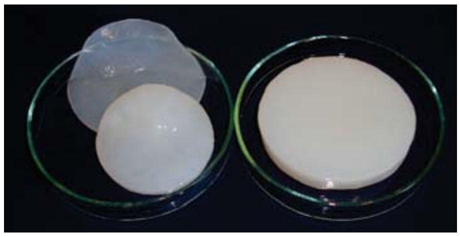

"Bacterial cellulose based nanocomposites: a roadmap for innovative materials. In Nanocellulose Polymer Nanocomposites: From Fundamental to Applications", V. K. Thakur(Ed.), Wiley –Scrivener, 2014, pg 17-64.

## BC production (static cultivation)

**Static cultivation** is the most common method, from which a highly hydrated BC membrane (or pellicle) on the air-culture media interface is obtained

As cellulose is synthesized, a membrane with increasing thickness is generated





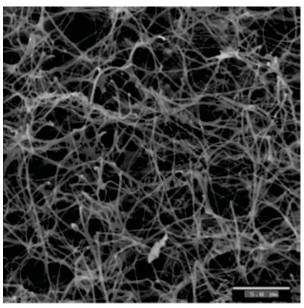


Nanocellulose based packaging materials

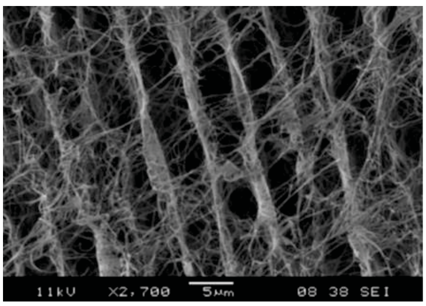

## BC properties

BC is obtained in a highly pure form, completely free of hemicelluloses, lignin and pectins

BC is characterized by an ultrafine network structure composed of ribbon-shaped fibrils with an average diameter 100 times thinner than those of plant cellulose fibers



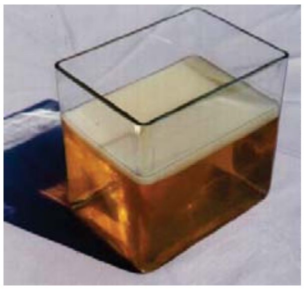
Surface

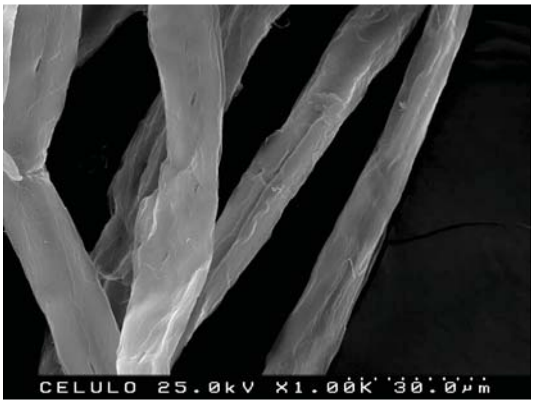



Cross-section

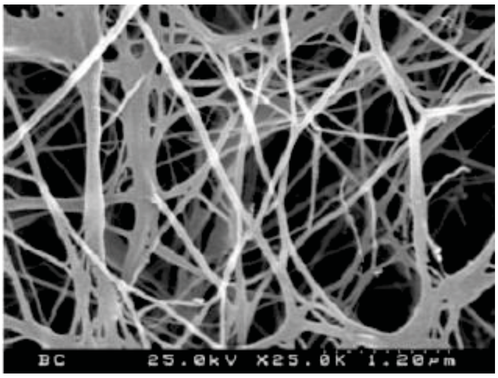


## BC properties






Plant fibers
~20-40 mm width, ~1-3(>) mm length




Bacterial cellulose
Nanofibrils 10-100 nm width, 3D network





## BC properties

- BC membranes are a highly porous material with substantial permeability for liquids and gases
- High water uptake (**water content >90%**)
- Low density
- High degree of polymerization (**about 2000-6000**)
- High crystallinity index (**60–80%**)



## BC properties

- High mechanical strength, with a **tensile strength of 200-300 MPa** and a **Young's Modulus of up to 15 GPa**
- High thermal stability **(Td ranging between 340-370°C)**.
- Biodegradable (not in human body, absence of cellulases)
- Biocompatible

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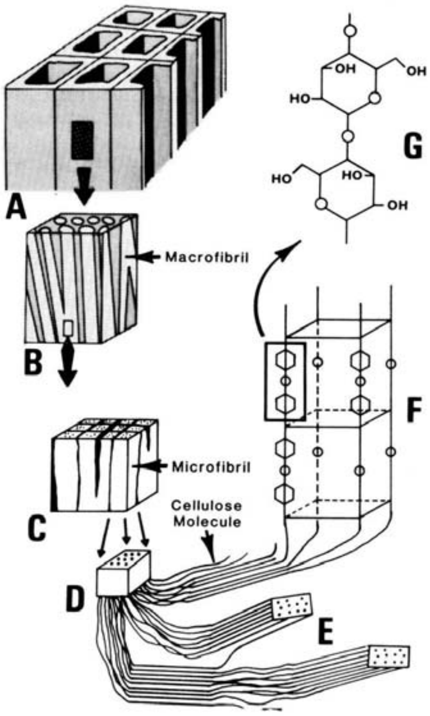
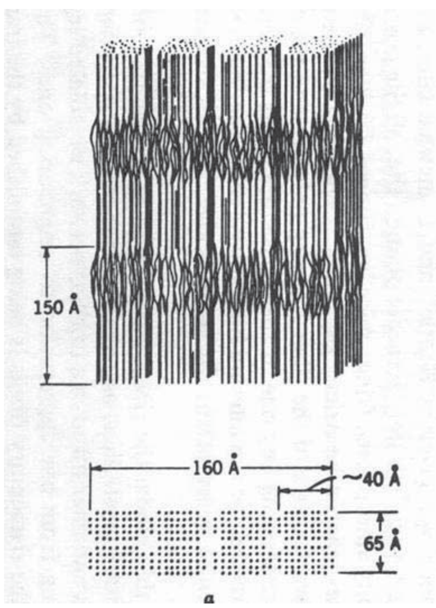
Nanocellulose based packaging materials

## Other nanocellulose forms: Nanofibrilated Cellulose (NFC)



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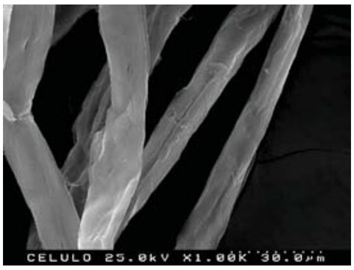
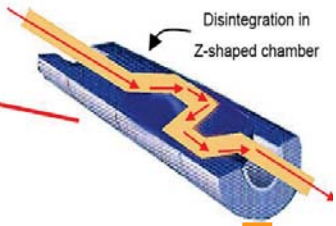
Nanocellulose based packaging materials

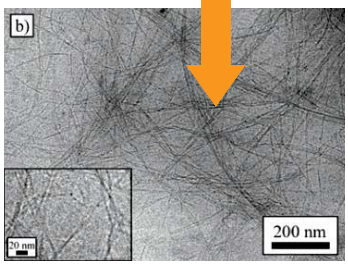
# Other nanocellulose forms: Nanofibrillated Cellulose (NFC)




-Multiple mechanical shearing

*-Enzymatic hydrolysis combined with mechanical shearing*




"Development and applications of cellulose nanofibers based polymer composites" (2016), In Advanced Composite Materials: Manufacturing, Properties, and Applications, De Gruyter Open (formerly Versita) (in press).

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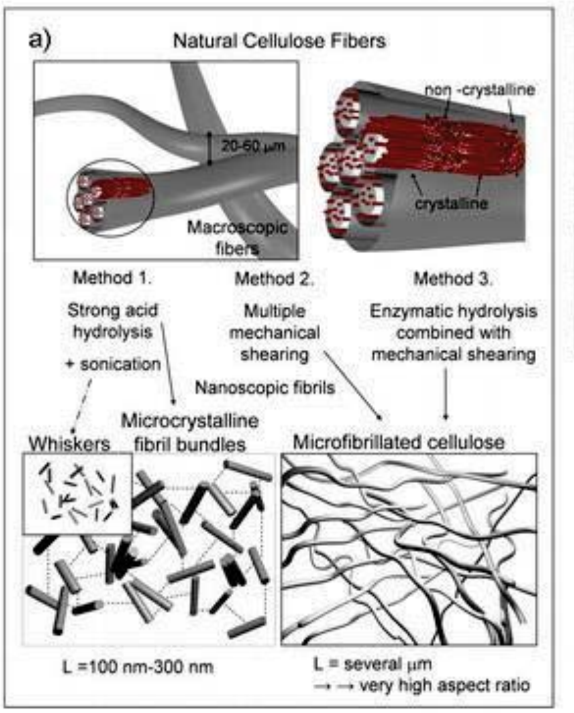
Nanocellulose based packaging materials

# Other nanocellulose forms: Cellulose Nanocrystals (CNC)



Nanocellulose based packaging materials

## Development of nanocomposite materials

The remarkable mechanical properties and reinforcing potential of nanocellulose fibers make it a perfect candidate **for polymer and hybrid nanocomposites development.**

In this sense, extensive research has been carried on the design of innovative nanocellulose nanocomposite materials with improved and functional properties, **by combination with several natural and synthetic polymers, as well as inorganic nanophases,** for a wide range technological applications; **Packaging**

Trends Food Sci. Technol., 2014, 40, 149-167

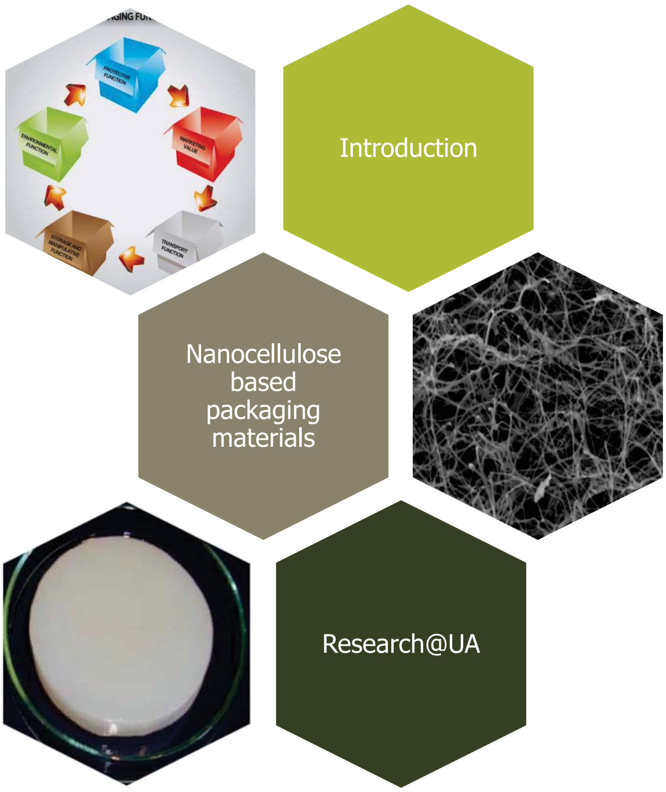
Nanocellulose based packaging materials

## Nanocellulose Packaging Materials

| EXPECTED PERFOMANCES | | | |
|---|---|---|---|
| Barrier $O_2$ | + | +++ | ++ |
| Barrier $H_2O$ | + | + | + |
| Mechanical | ++ | +/- | +++ |
| Surfaces properties | + | ++ | ++ |
| Optical | - | +/- | +/- |
| Safety | - | + | + |
| Economy | ++ | +++ | ++ |
| SOLUTIONS | FILLER | COATING | INDEPENDENT MATERIAL |
| TECHNOLOGY | EXTRUSION<br>MELT COMPOUNDING<br>ELECTROSPINNING | LAYER by LAYER<br>CASTING | CASTING<br>COMPRESSION<br>ALL CELLULOSE |
| CNs forms | MFC/NFC - CNC | MFC/NFC<br>CNC – TOCN | MFC/NFC - TOCN |
| | | NANO-CELLULOSE from | |
| RAW MATERIALS | BACTERIA<br>High purity and biocompatibility | PLANTS<br>Large availability | ANIMALS<br>Fundamental research |

Packaging Technology and Science, 2015, 28, 475-508

## Lecture Outline

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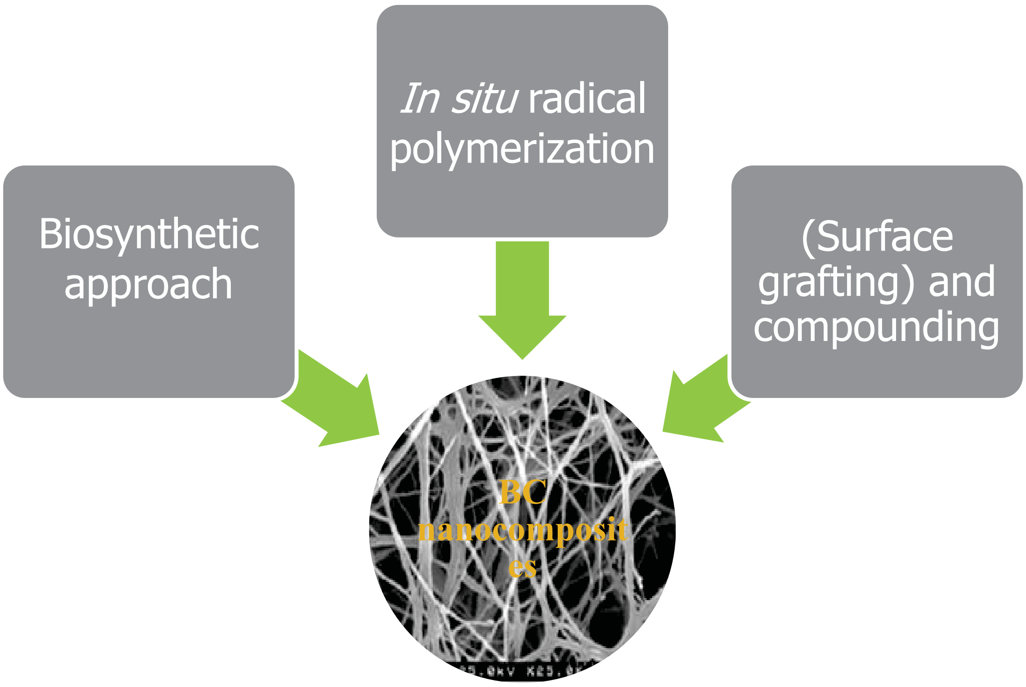
# Nanocellulose based Nanocomposite materials (Production strategies)



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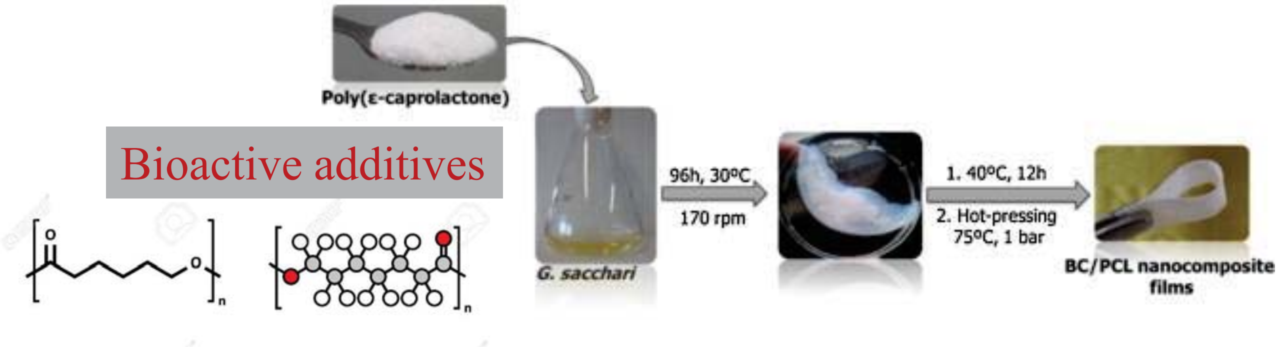
## Biosynthetic design of BC based composites

*In situ* biosynthesis of bacterial cellulose/polycaprolactone blends for hot pressing nanocomposite films production




Carbohydrate Polymers, 2015, 132, 400-408.

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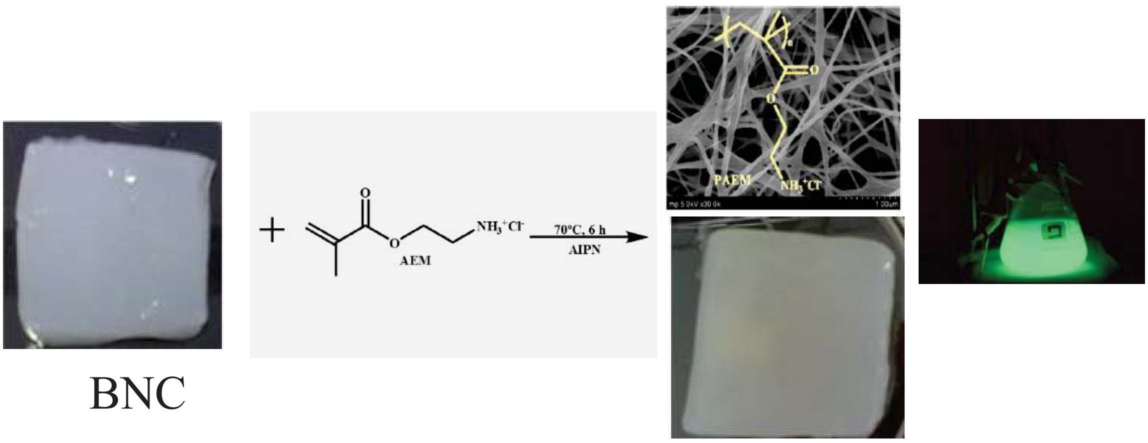
## *In situ* radical polymerization (BC/PAEM)

Antimicrobial bacterial cellulose nanocomposites prepared by *in situ* polymerization of 2-aminoethyl methacrylate

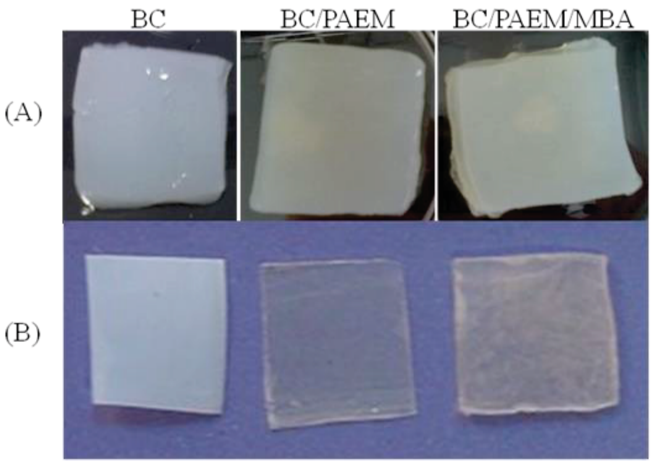



BNC

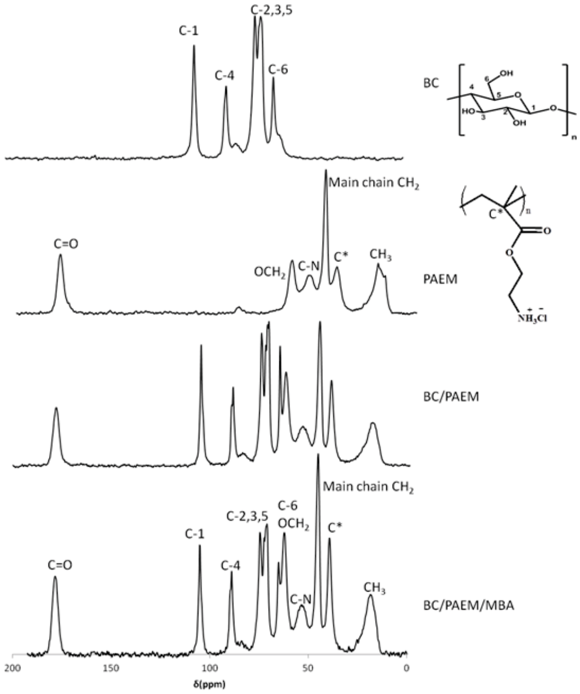
BNC/PAEM

Carbohydrate Polymers, 2015, 123, 443-453.


# *In situ* radical polymerization (BC/PAEM)




The success of the polymerization reaction inside BC membranes was confirmed by FTIR and <u>NMR</u> analysis

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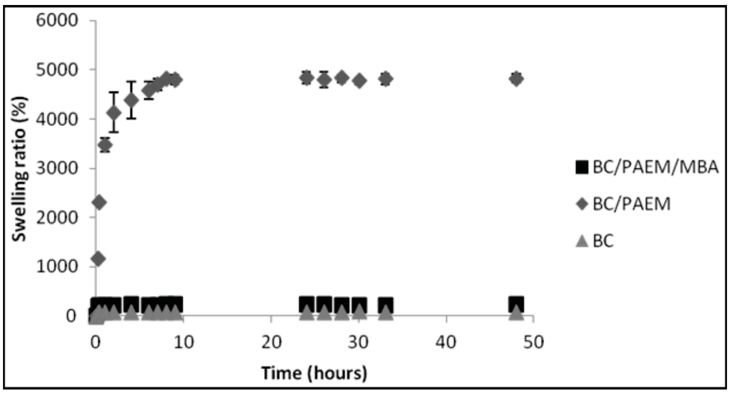
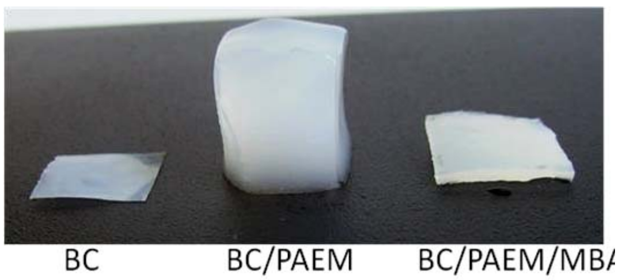
# *In situ* radical polymerization (BC/PAEM)



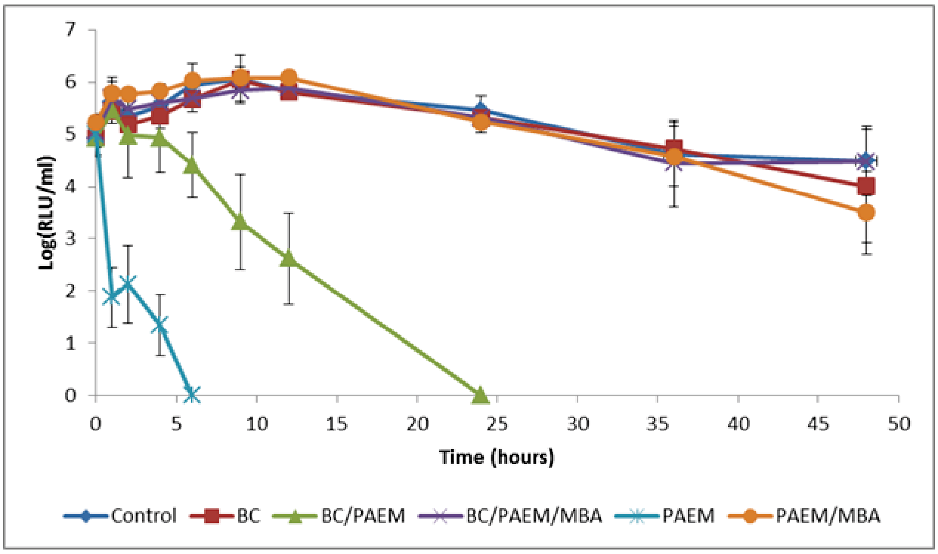




The studied samples showoed different swelling behaviours

The nanocomposite samples, particularly BC/PAEM, showed improved re-hydration ability



## *In situ* radical polymerization (BC/PAEM)




Only the BC/PAEM nanocomposites proved to have antibacterial activity

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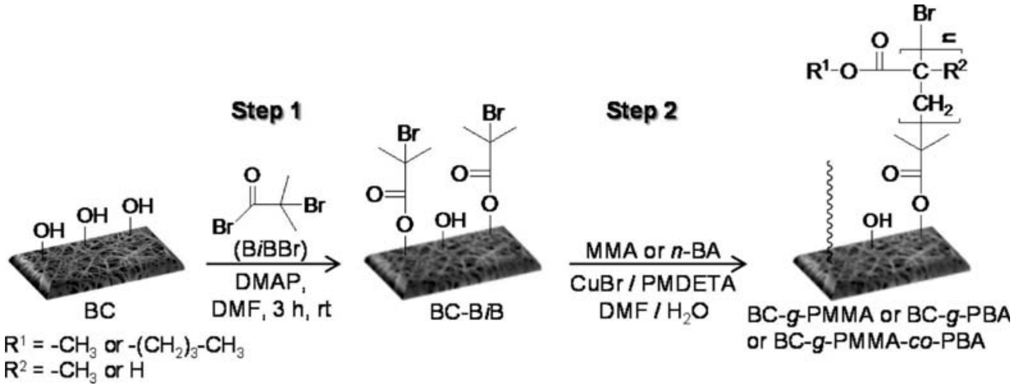
## *In situ* radical polymerization (ATRP)

Nanostructured Composites Obtained by ATRP Sleeving of Bacterial Cellulose Nanofibers with Acrylate Polymers




**Step 1- BC functionalization with the ATRP initiator**
**Step 2- ATRP grafting from the BC macroinitiator**

Biomacromolecules, 2013, 14, 2063-2073.

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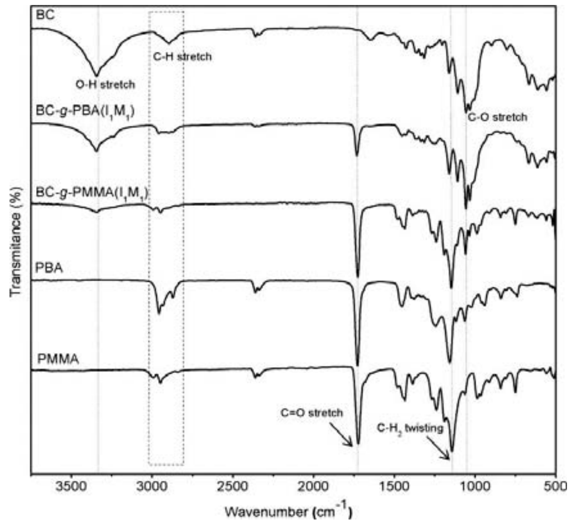
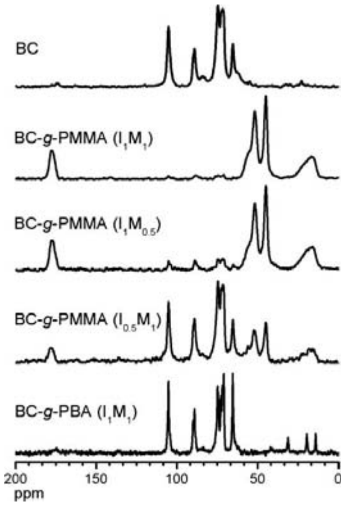
## *In situ* radical polymerization (ATRP)




The grafting of the polymers from BC macroinitiator was confirmed by FTIR and $^{13}C$ CP-MAS solid state

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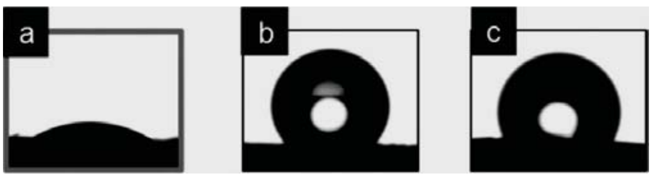
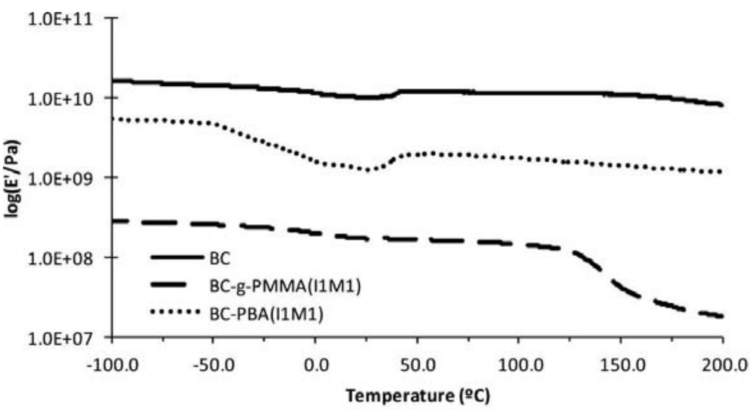
## *In situ* radical polymerization (ATRP)




Grafting PMMA or PBA yielded highly hydrophobic membranes.




The values of the elastic moduli across the whole temperature range are lower than that of the ungrafted BC membrane

Because acrylate polymers are more flexible than the BC nanofibrillar network

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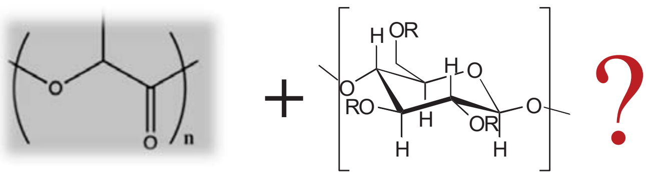
# Surface grafting and compounding

## Surface hydrophobization of nanocellulose fibers using ILs as solvent media and catalysts



The use of cellulose fibers in the development of (nano)composites with thermoplastic matrices requires its preliminary surface chemical modification

Green Chemistry, 2011, 13 (9), 2464 – 2470.

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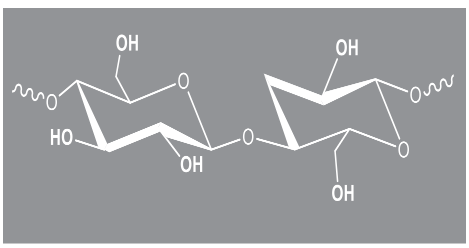
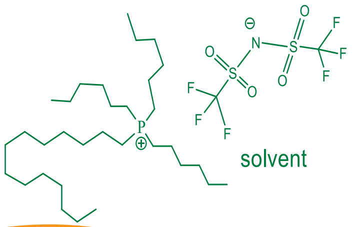
# Surface grafting and compounding

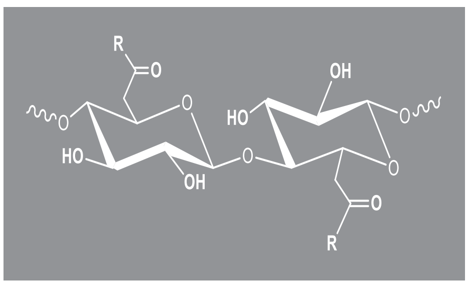





+

$H_2SO_4$ as catalyst

| Modification | Reaction time |
|---|---|
| Acetic Anhydride | 6 hours |
| Butyric Anhydride | 4 days |
| Hexanoic Anhydride | 11 days |
| Alkenyl succinic anhydrides | 15 days |
| Hexanoyl chloride | 24 hours |



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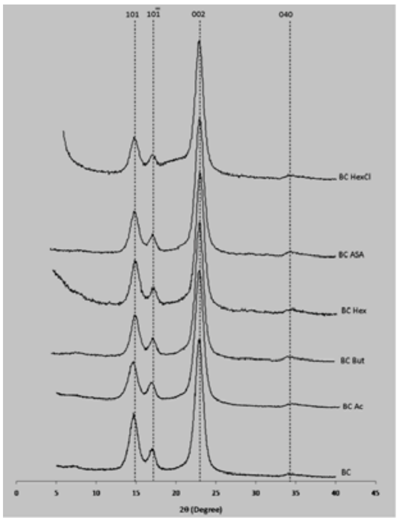
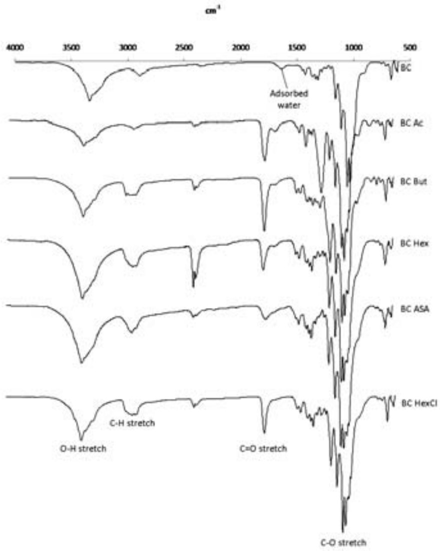
## Surface grafting and compounding




The modification reactions involved essentially the OH groups at the surface and the amorphous regions of the nanofibers

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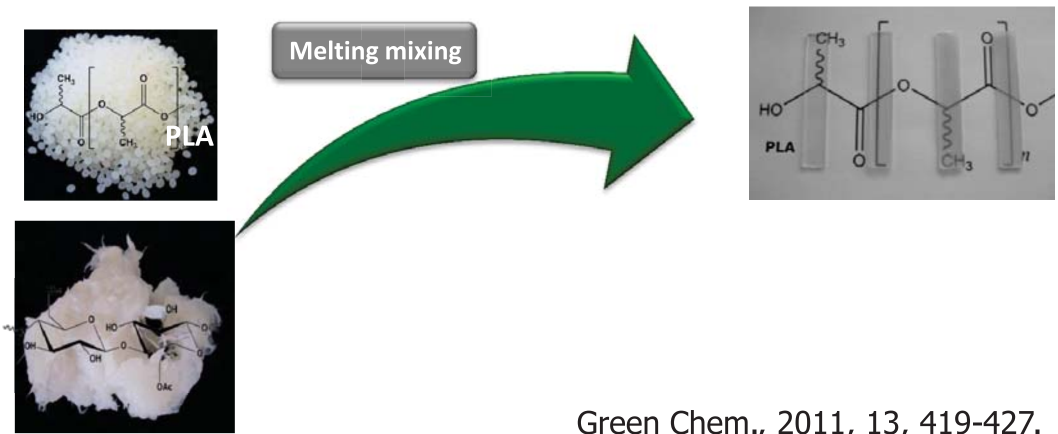
## Surface grafting and compounding (BC/PLA)

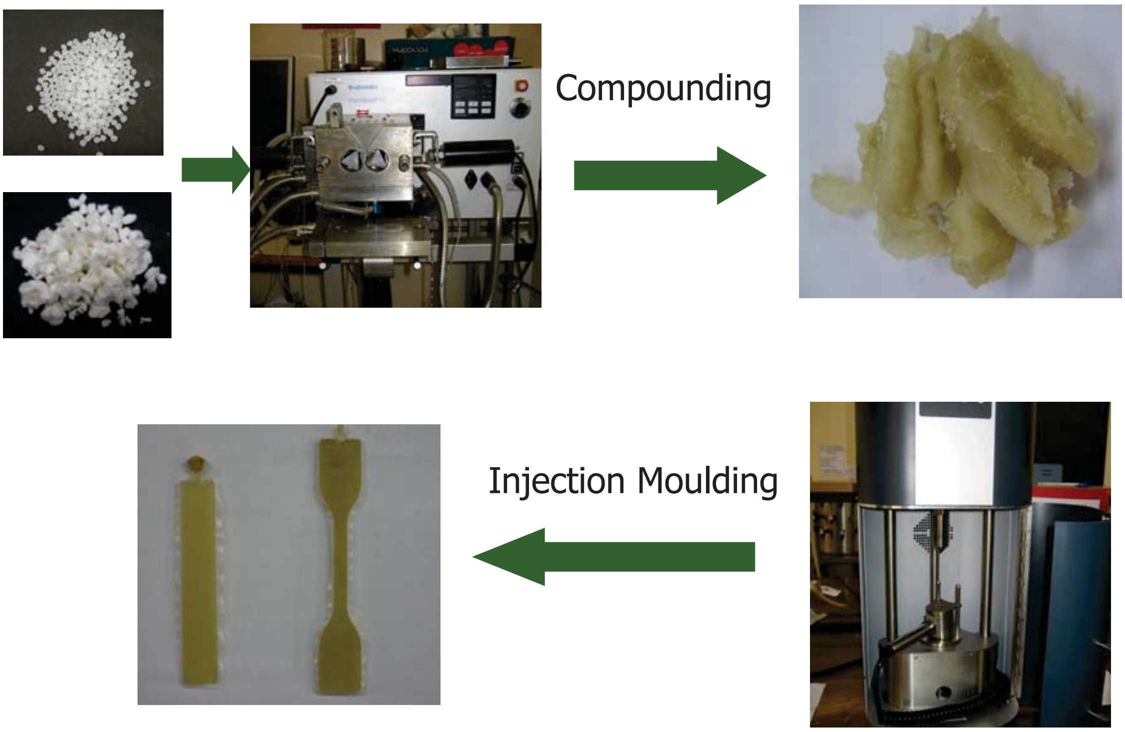
Transparent bionanocomposites with improved properties prepared from acetylated bacterial cellulose and poly(lactic acid) through a simple approach




**Acetylated BC** (DS = 0.02)

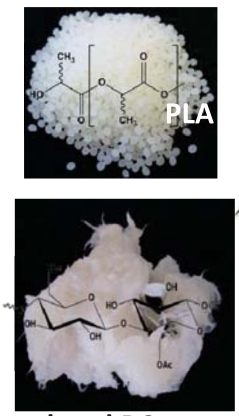
Green Chem., 2011, 13, 419-427.


## Surface grafting and compounding – processing of thermoplastic composites

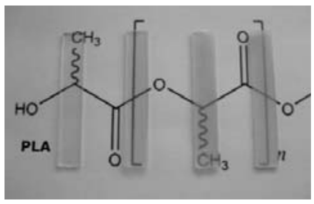




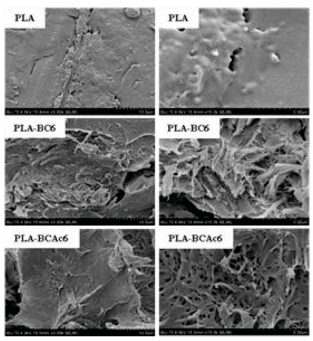
## Surface grafting and compounding (BC/PLA)




Acetylated BC (DS = 0.02)


- Higher homogeneity
- Thermal stability and
- Mechanical performance
- Low water up-take




**Applications:** packaging, biomedical products and devices, electronic devices etc.

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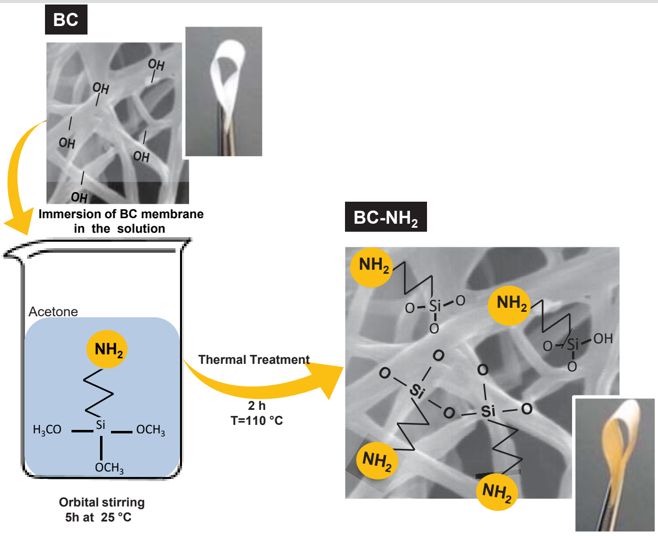
# Surface grafting as a strategy to produce functional BC membranes

## Bioinspired antimicrobial and biocompatible BC membranes obtained by surface decoration with aminoalkyl groups




ACS Applied Materials & Interfaces, 2013, 5, 3290-3297.

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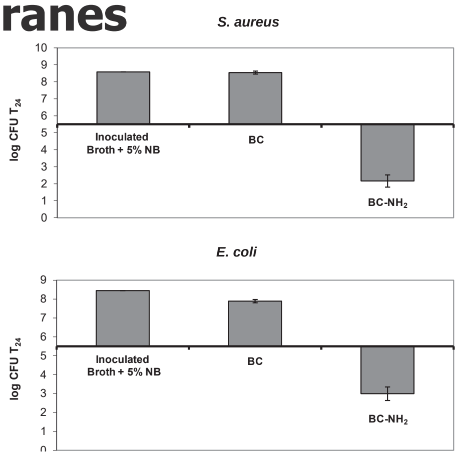
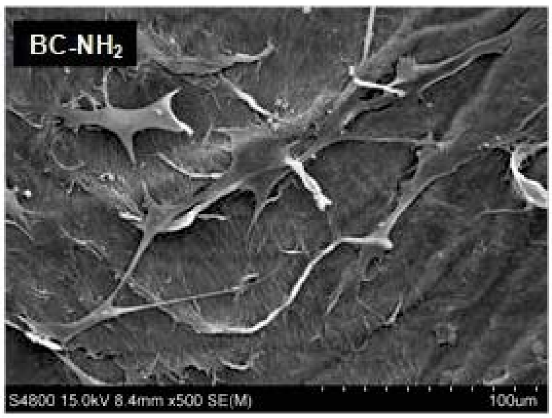
# Surface grafting as a strategy to produce functional BC membranes




- The nanostructured BC-$NH_2$ membranes were simultaneously **antimicrobial and biocompatible**

- In addition, these membranes also present improved mechanical and thermal properties. Applications: packaging, biomedical applications

The same strategy to producce active pullulan films

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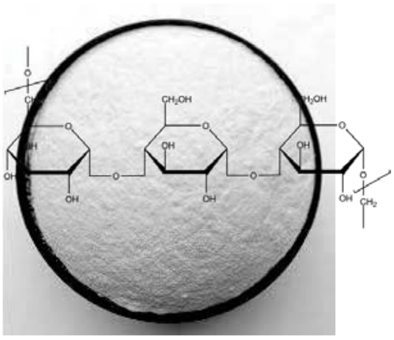
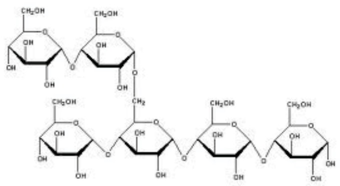
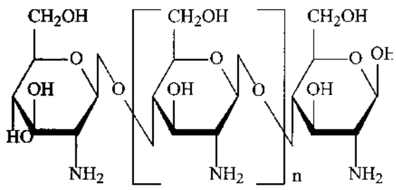
# Transparent nanocomposite films based on nanocellulose fibers and polysaccharides

**Chitosan**
**Starch**
**Pullulan**








Green Chem., 2009, 11, 2023–2029
Cellulose, 2012, 19, 729-737
Cellulose, 2013, 20, 1807-1818.

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# Transparent nanocomposites based on BC and chitosan

**LCH - WSLCH**
**HCH - WSHCH**
**1.5% (v/w)**

**NFC or BC (up to 40%)**

**Dispersion**
Ultra-Turrax
20 500 rpm
30 min.

**Degassing**

**Casting**
30ºC
ventilated oven
16 h


**HCH**

**HCHBC10**

## A fully green process

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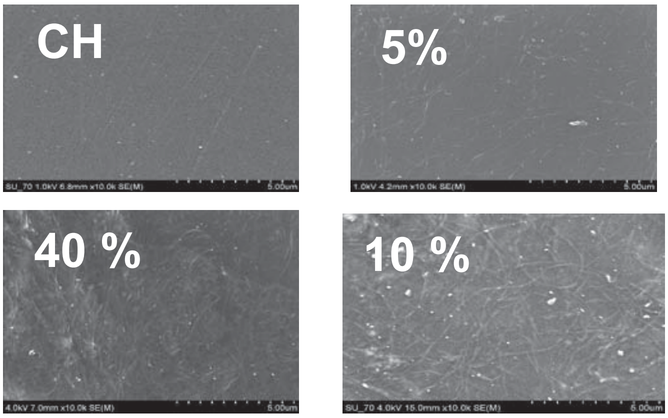
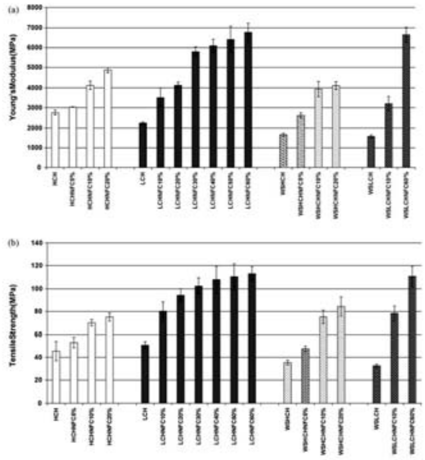
# Transparent nanocomposites based on BC and chitosan



- SEM images show the good dispersion of the NFC nanofibres at the surface of chitosan films
- The good dispersion together with the good interfacial adhesion of CH and cellulose gave rise to nanocomposites with improved mechanical properties

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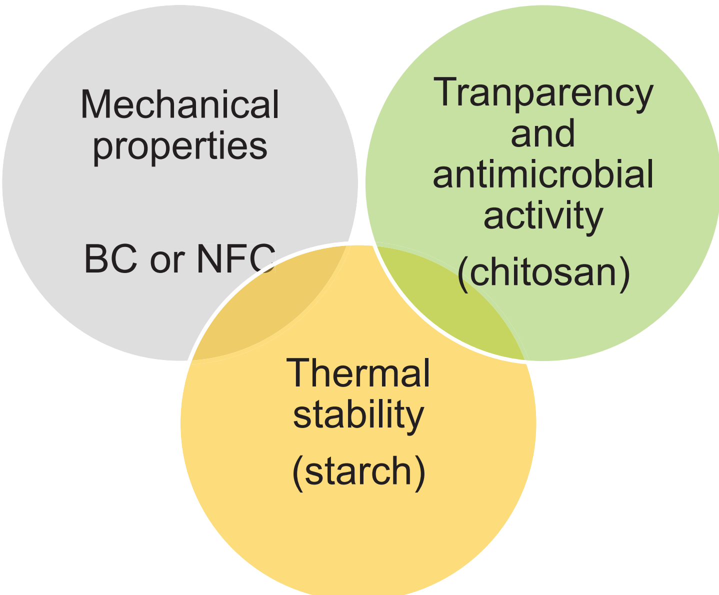
# The role of nanocellulose fibers, starch and chitosan on multipolysaccharide based films




Cellulose, 2013, 20, 1807-1818.

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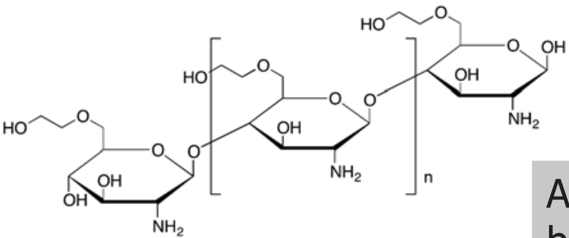
# Chitosan-algae extracts films (submitted for publication)


-Biomedical applications
- Packaging




Additional ongoing works: other filmogenic biopolymers and nanocellulose and phenolic extracts, ILs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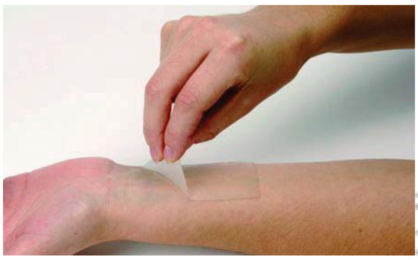
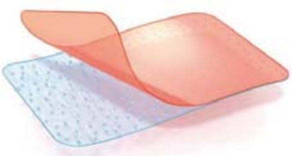
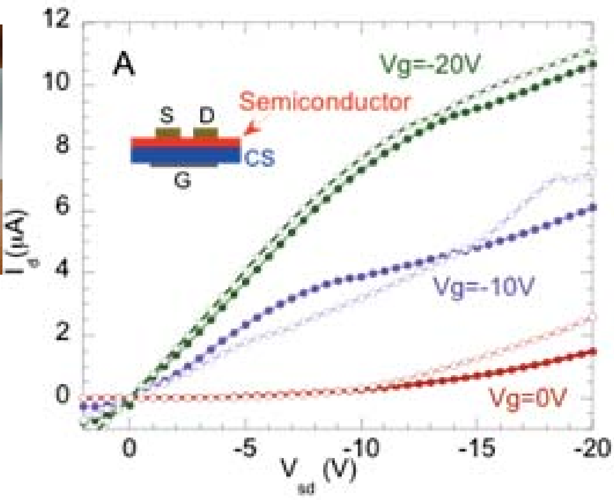
# Applications of transparent thin nanocomposite films: active packaging, biomedical applications (coatings, wound healing, drug delivery, etc.) organic electronics…







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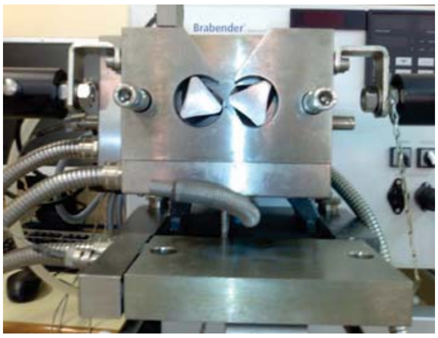
# Composites based on thermoplastic starch (TPS) and nanocellulose

**Plasticized starch (45% starch, 25% water, 35% glycerol)**
**+ Cellulose (VC or BC) AND ACTIVE COMPOUNDS**




**A GREEN PROCESS**

Compos. Sci.Technol., 2009, 69, 2163-2168.

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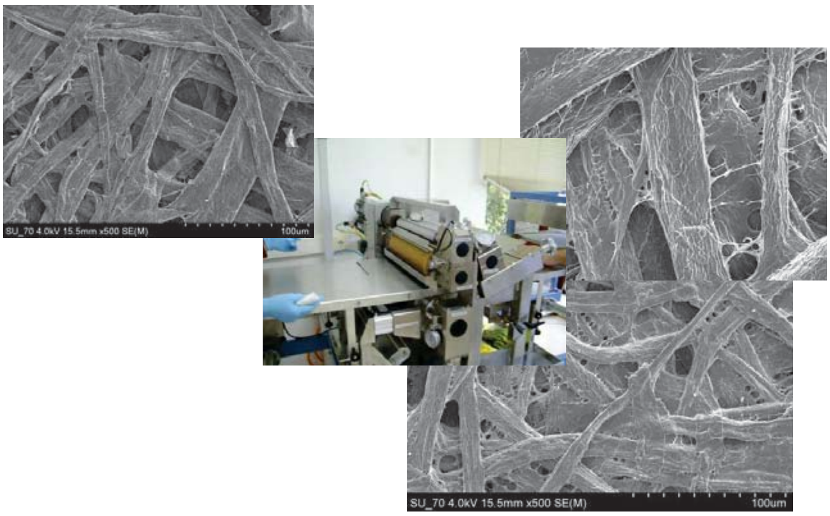
# Nanocellulose blends for paper coating




**Improved printability (gamut area, intercolour bleeding, etc.) and surface properties**

***Aqueous coating compositions for use in surface treatment of cellulosic substrates***
***WO 2011012934 A2***

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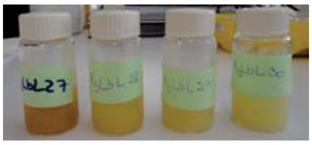
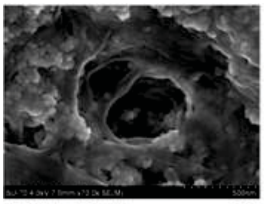
# NFC nanocomposites with Ag and ZnO NPs for antibacterial paper products



NFC
2.3 % solid content

LBL assembly



Paper coating

**(1) Assembly of NFC and ZnO or Ag NPs using polyelectrolytes (PDDA, PSS) as macrolinkers**

**2) Application of the obtained NFC/ZnO or NFC/Ag nanofillers in paper coating starch based formulations (16 % solid content)**

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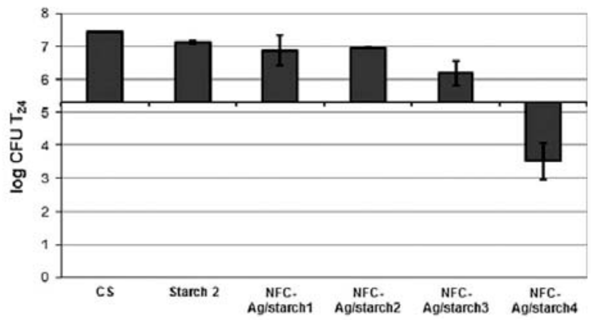
# NFC nanocomposites with Ag and ZnO NPs for antibacterial paper products

| Paper sample | Brightness (%) | Air Permeability (nm/Pa. s) | Burst Index (KPa.m²/g) | Tensile index (N.m/g) MD [a] | CD [b] |
|---|---|---|---|---|---|
| CS | 95.21 ± 0.07 | 11.49 ± 0.4 | 2.62 ± 0.30 | 83.7 ± 3.81 | 23.7 ± 1.2 |
| Starch 1 | 94.78 ± 0.10 | 10.82 ± 0.5 | 2.74 ± 0.20 | 77.5 ± 2.70 | 23.2 ± 0.9 |
| Starch 2 | 94.44 ± 0.12 | 10.76 ± 0.5 | 2.86 ± 0.14 | 81.1 ± 2.46 | 25.2 ± 0.9 |
| NFC-PE/starch 1 | 94.76 ± 0.10 | 9.12 ± 0.3 | 3.15 ± 0.23 | 85.6 ± 2.16 | 24.7 ± 0.8 |
| NFC-PE/starch 2 | 94.62 ± 0.10 | 4.00 ± 0.4 | 3.46 ± 0.21 | 86.7 ± 2.14 | 27.2 ± 0.9 |
| ZnO/starch 1 | 94.44 ± 0.11 | 10.81 ± 0.5 | 3.00 ± 0.18 | 85.3 ± 3.53 | 24.7 ± 0.9 |
| ZnO/starch 2 | 94.38 ± 0.17 | 9.17 ± 0.3 | 3.17 ± 0.18 | 86.7 ± 3.11 | 24.7 ± 0.6 |

a) MD = machine direction
b) CD = cross-machine direction




SUNPAP
Scale-up Nanoparticles in Modern Papermaking

Cellulose, 2012, 19, 1425-1436
Colloids and Surfaces A, 2013, 111-119.

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## Final Remarks

**NanoCellulose based Packaging Materails...**

**...Multitude of properties and opportunities**

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## Final Remarks

## Acknowledgements

**All co-authors**
**colleagues, PostDoc PhD and MSc students**

**University of Aveiro and CICECO**

**Funding Agencies and projects**

afore

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COMPETE
PROGRAMA OPERACIONAL FACTORES DE COMPETITIVIDADE

PORTUGAL 2020

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