



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group   
Color & Comfort

---

# Inks and Printing Methods for Biosensors



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



Color & Comfort

# Outline of Presentation

- Manufacturing flow diagram
- Substrate materials
- Transducers - what role do they play
- Materials used in printed biosensors
- Application techniques – screen printing and others



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

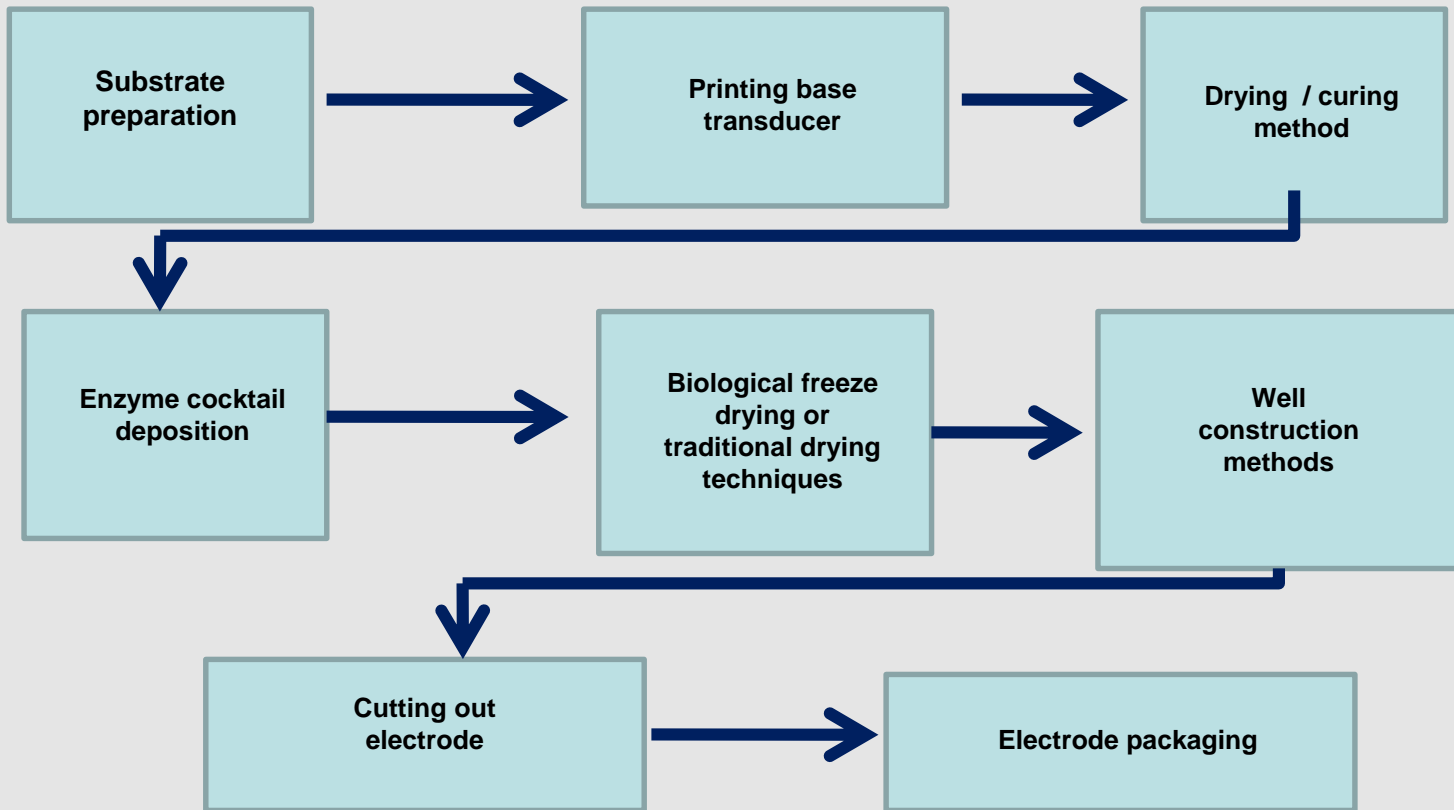
Part of:-

**SunChemical®**

a member of the DIC group



# Manufacturing protocol flow diagram





GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



Color & Comfort

# Printed Transducer

- Definition – power transforming device for which the input and output are of different kinds of energy
- In an electrochemical biosensor chemical energy is transformed into electrical energy



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical**<sup>®</sup>

a member of the DIC group



# What's So Special about Materials for Electrochemical Transducers

- Electrochemistry is a surface technique - for electrochemical reactions to occur the surface of electrode materials must be clean and have active materials available.
- All material systems must have active material at the surface i.e. not coated with polymers
- Inks are formulated to allow this to happen but screen printing and other physical properties are sacrificed to achieve this



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of-

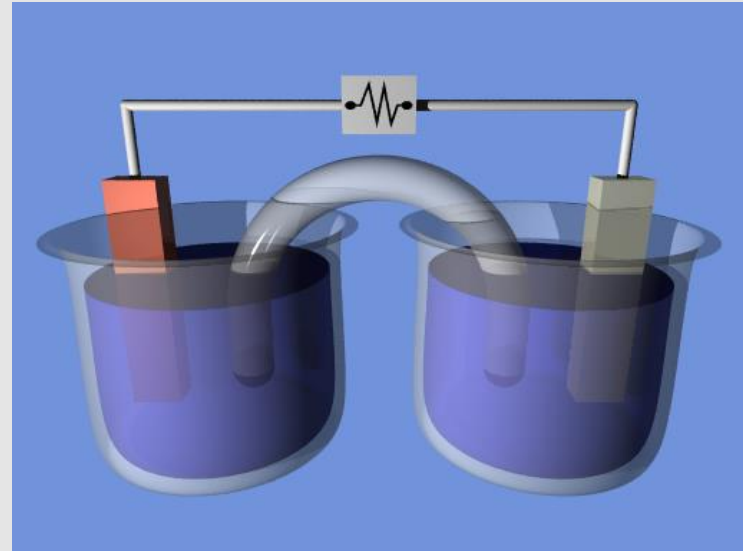
SunChemical®

a member of the DIC group



# Batteries and biosensors

- A demonstration electrochemical cell setup resembling the [Daniell cell](#). The two half-cells are linked by a salt bridge carrying ions between them. Electrons flow in the external circuit.





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



Color & Comfort

---

# Substrates Used in Base Transducers

- Polyester
- PVC
- Polycarbonate
- Polystyrene
- Alumina



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of-

SunChemical®

a member of the DIC group



# PET Polyester

- Is the most commonly used substrate thickness of substrate from 90-500 microns
- Most common thickness 350 to 500 microns
- Highest cure temp how long?
- Normal 120 to 130 °C





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of-

**SunChemical®**

a member of the DIC group



Color & Comfort

# Major Ink Systems

- Particulate
- Organo-Metallic
- Precious Metal
- Base Metal
- Ceramic
- Carbon
- Polymer
- Dielectrics



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical**<sup>®</sup>

a member of the DIC group  **DIC**  
Color & Comfort

---

# Major Application Methods

- Screen Printing
- Ink Jet
- Syringe
- Spraying
- Other printing methods  
(not yet)



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



---

# Screen –Printed Materials Commonly Used in Disposable Biosensors

- Carbon – graphite mixes
- Silver conductors
- Silver/silver chloride reference electrode materials
- Insulators / Dielectrics
- Adhesives



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Differences between functional and graphic inks

## Graphic ink

- Polymer 15-25 pbw
- Filler 35-10 pbw
- Solvent 50-65 pbw

## Functional carbon ink

- Polymer 5-09 pbw
- Filler 38-42 pbw
- Solvent 57-49 pbw

**Why manufacturers make poor printing inks**



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

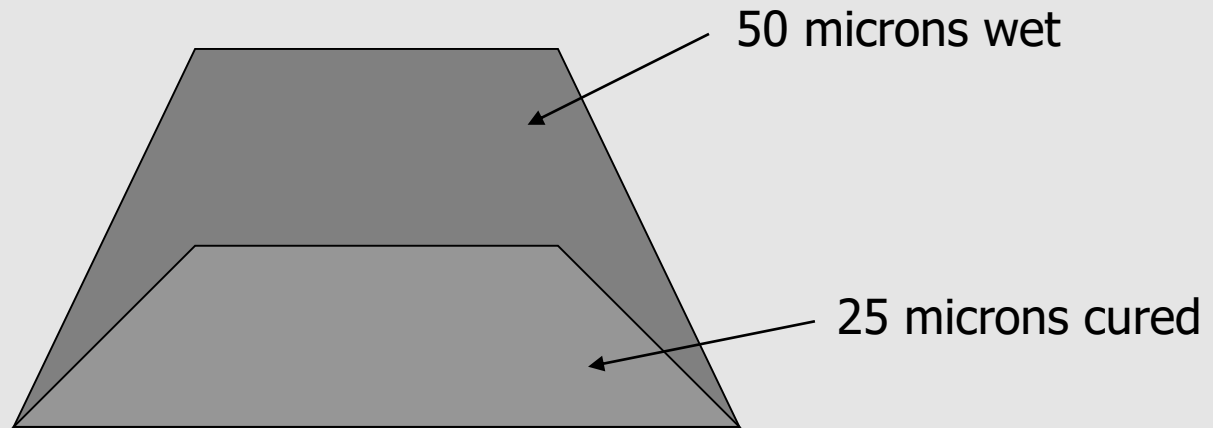
**SunChemical**<sup>®</sup>

a member of the DIC group



# Major Constituents of Carbon Inks

- Functional phase: 38 to 42 parts by weight
- Polymer carrying system: 4 to 9 parts by weights
- Solvents usually 3 different: 11 to 58 parts by weight





GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Materials and their roles

- Carbon black and synthetic graphite

Role: Carry the current

- Polymers

Role: Adhere material to substrate

- Solvents

Role: Lower viscosity for application method



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



# Major constituents of carbon inks and their roles

- Base polymer system consists of a thermoplastic polymer and solvents; to adhere to base substrate
- Functional filler carbon black and graphite; to conduct electrons and interface with ions
- Mixed solvent system; to allow printing and drying without disrupting print film



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



Color & Comfort

---

# Vehicles (polymers + solvents)

- Almost all polymers used are thermoplastic
- 2 or 3 different solvents are used of differing evaporation rates
- Dispersed together to form the base system
- Thermoset polymers are used in conjunction with sensors needing membranes





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical**<sup>®</sup>

a member of the DIC group  **DIC**  
Color & Comfort

---

# Solvents and their role

- Viscosity modifier for polymer vehicle
- Controls viscosity of printing ink
- Allows drying without cracking film of electrode



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

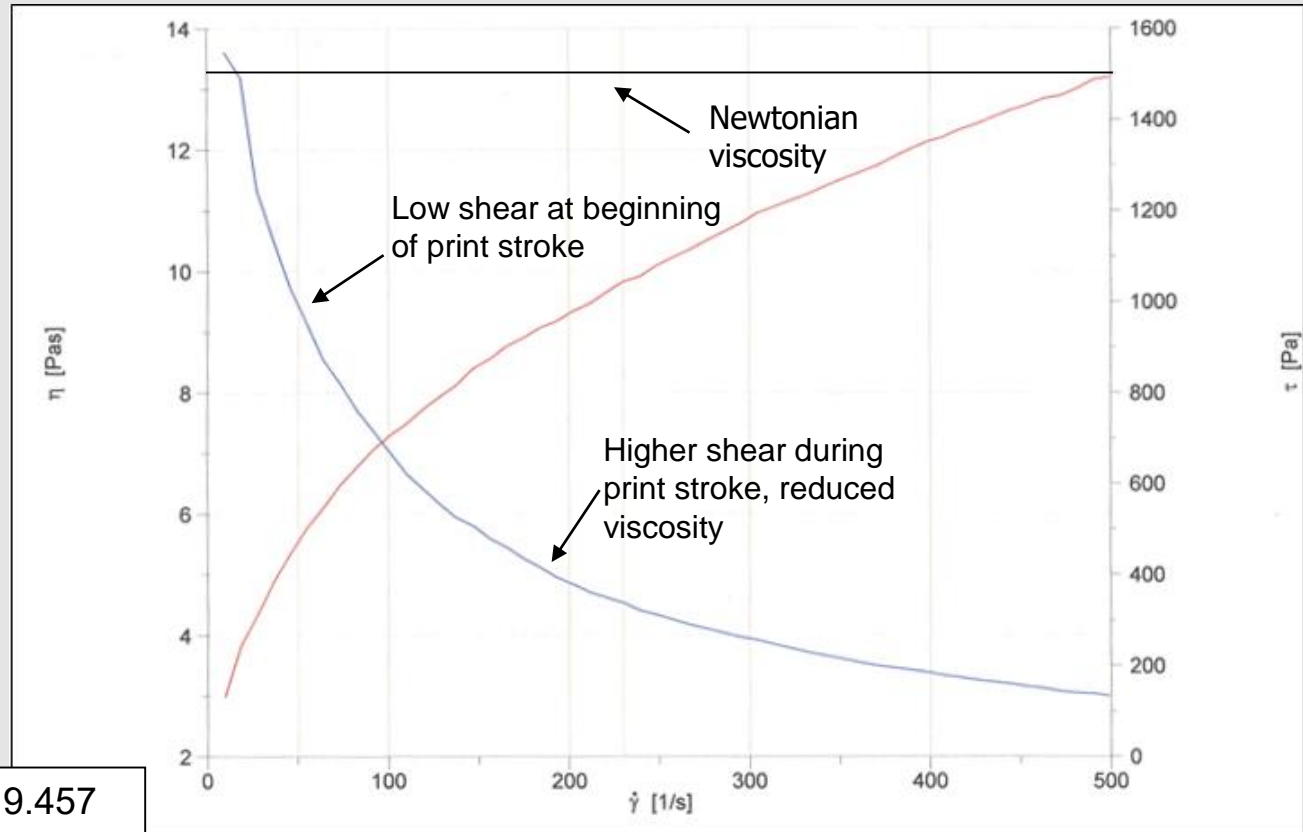
**SunChemical®**

a member of the DIC group



Color & Comfort

# Plot of Viscosity



$\dot{\gamma}$ [1/s]	50.0	$\eta$ [Pas]	9.457
$\dot{\gamma}$ [1/s]	100.0	$\eta$ [Pas]	7.045
$\dot{\gamma}$ [1/s]	200.0	$\eta$ [Pas]	4.863
$\dot{\gamma}$ [1/s]	230.0	$\eta$ [Pas]	4.536
$\dot{\gamma}$ [1/s]	300.0	$\eta$ [Pas]	3.942
$\dot{\gamma}$ [1/s]	400.0	$\eta$ [Pas]	3.379



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Ink dispersion methods

- Dispersing particulate ink is a 2 stage process
- 1<sup>st</sup> low shear mixing
- 2<sup>nd</sup> high shear mixing
- Mixing technology similar to cake baking



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



# Dispersion a 2 stage process



Planetary mixing low shear  
process



3 roll mill high shear process



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Testing functional systems

- The vast majority of commercial systems are based on measuring current
- As ink manufacturers we are unaware of customers individual needs



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

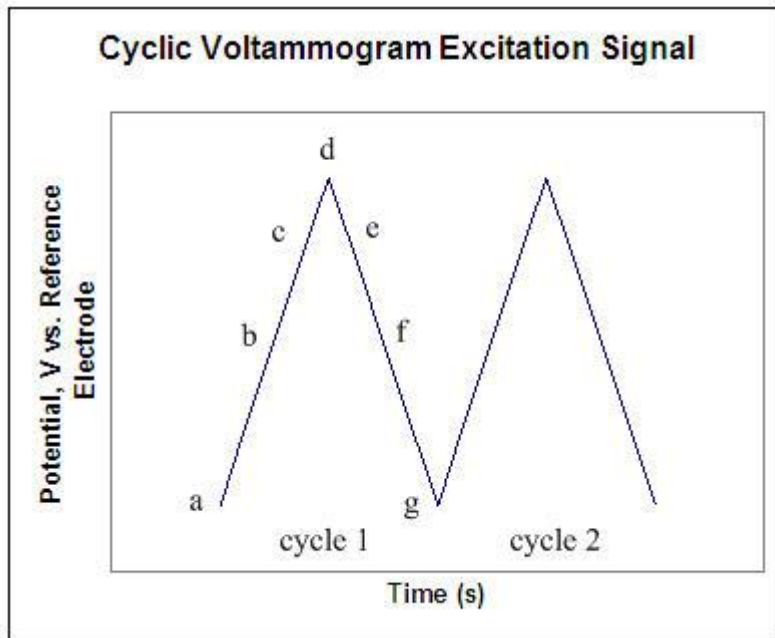
Part of:-

SunChemical®

a member of the DIC group

# Cyclic voltammetry

- **Definition:** a method for determining the kinetics of electrode processes. CV is performed by cycling the potential of a working electrode, and measuring the resulting current.





GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group

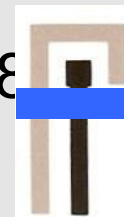


Color & Comfort

# Cyclic Voltammetry

Method employed to determine the oxidation potential of  
Carbon/Graphite pastes

Print Electrodes Design No. BE2031028



Buffered Ferricyanide Solution – 0.5mM Potassium  
ferricyanide in 0.1M buffer and KCl, pH7.5

Cyclic voltammetry performed using ferricyanide solution  
from +0.8V to -0.4V to +0.8V at 10mV/s

Interested in the position of the oxidation peak and the  
CV% of the triplicate tests



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of-

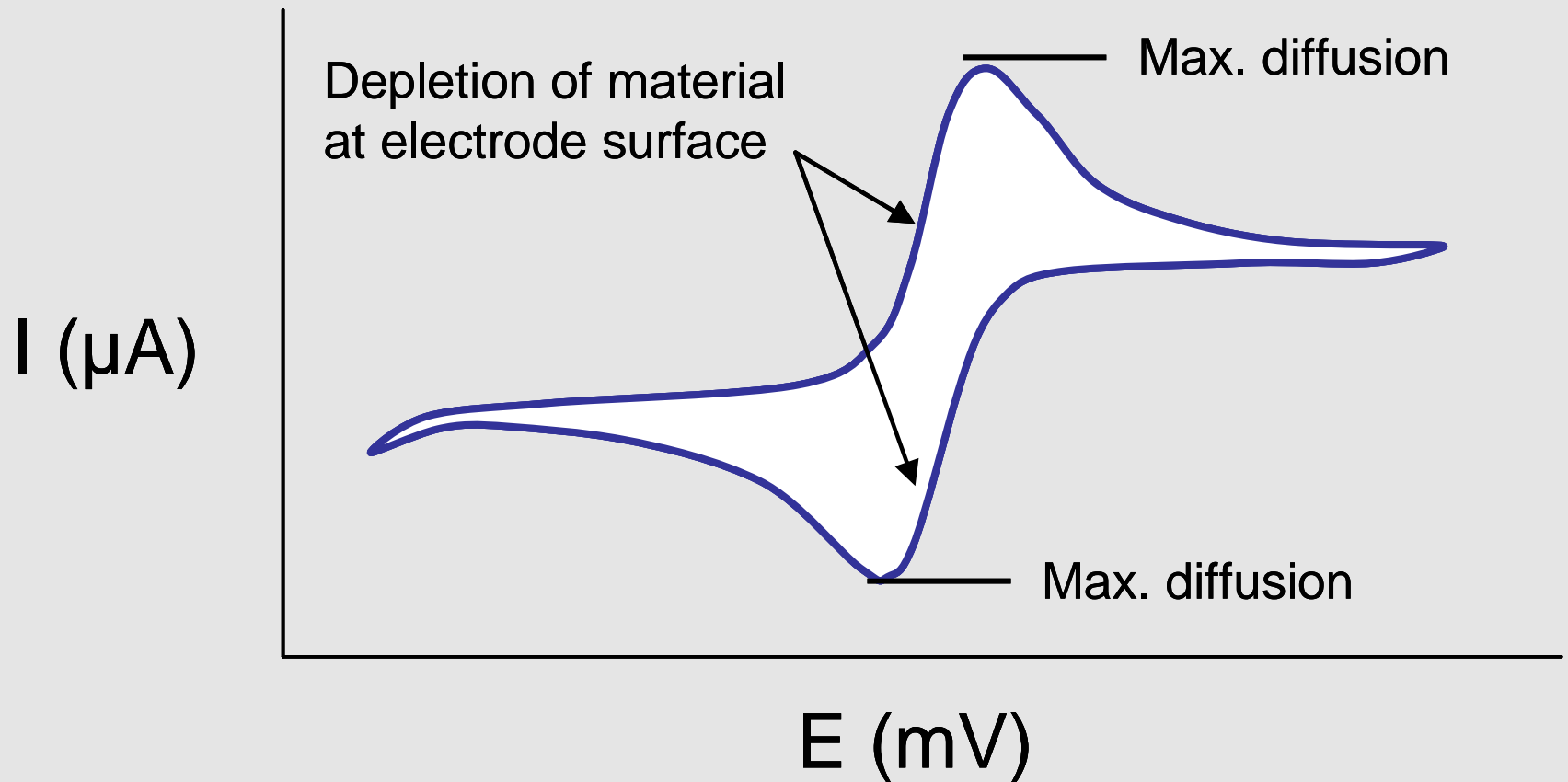
SunChemical®

a member of the DIC group



Color & Comfort

# Cyclic Voltammogram







GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

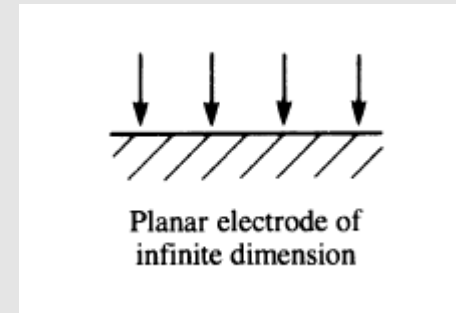
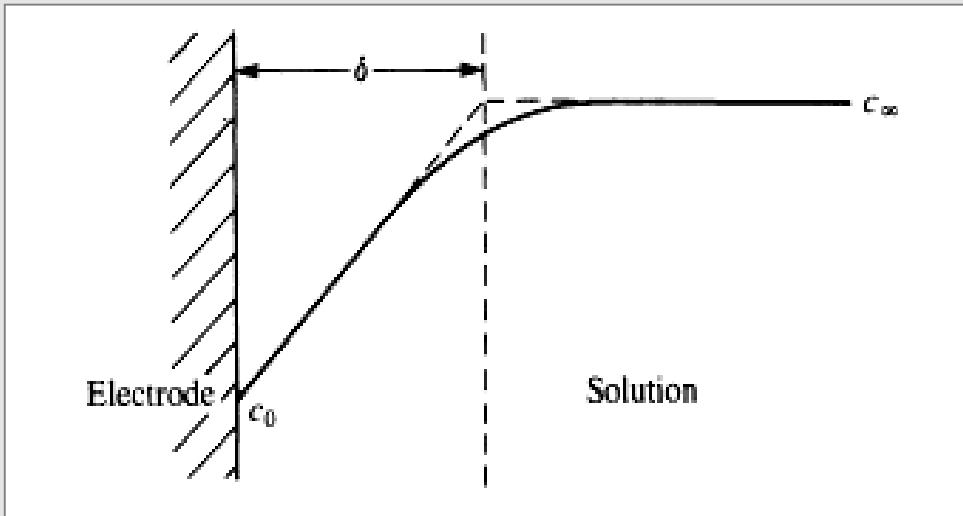
Part of-

SunChemical®

a member of the DIC group



# Diffusion layer at macroelectrode



- Diffusion layer is the concentration gradient at the electrode surface until it reaches the bulk concentration.
- The size of the diffusion layer depends on the mass transfer coefficient and is time related.



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Electrochemical cell and the role of each electrode

A typical electrochemical cell is formed of three electrodes:

- Working electrode: the electrode at which the electrochemical reaction takes place. It is usually made of carbon/graphite, mediated carbon, gold, platinum etc.



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of-

**SunChemical®**

a member of the DIC group   
Color & Comfort

---

# Counter (auxiliary) electrode

---

- It is collecting and transferring the current generated at the working electrode. It has to be highly conductive and chemically inactive and has to be in the close proximity of the working electrode; material used preferable platinum but carbon and silver are good options.



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of-

SunChemical®

a member of the DIC group



# Reference electrode

- It has to provide a good reference potential for the working electrode.
- Examples of reference electrodes: Ag/AgCl, saturated calomel, hydrogen electrode (the 0V reference electrode), carbon as pseudo-reference electrode.
- When using carbon pseudo-reference electrodes is important to ensure the potential is established through a different way. In the case of the glucose biosensor the potential is established by using a high concentration of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  mediator.



# Electrochemical cell and the role of each electrode

GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

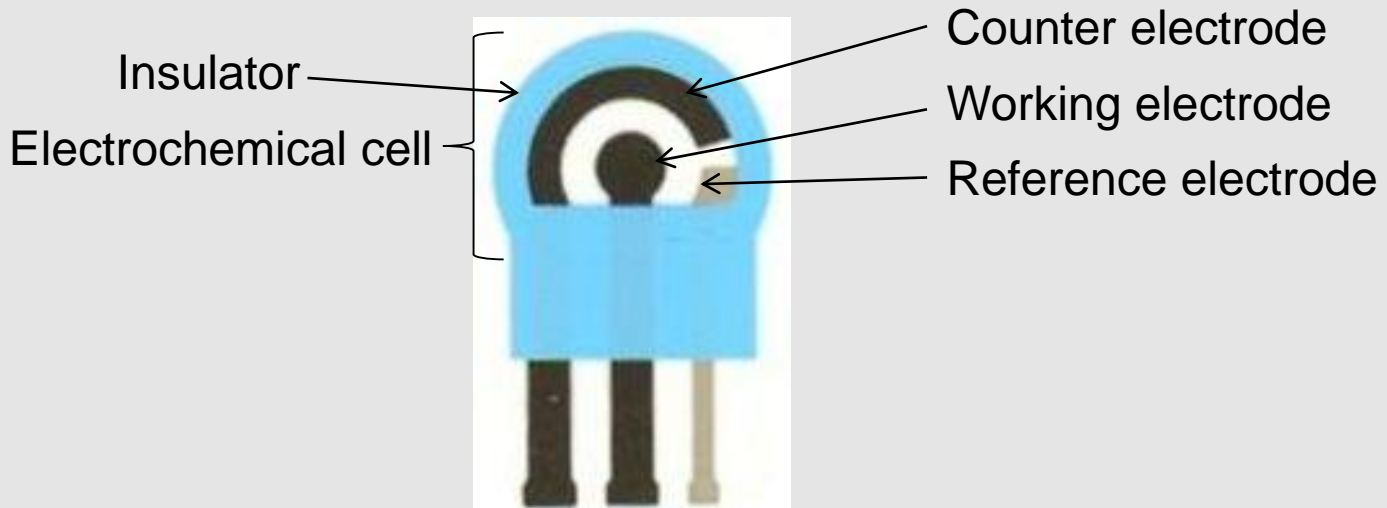
Part of:-

SunChemical®

a member of the DIC group



- The potential is applied between the reference and the working electrode hence the importance of having a good reference electrode
- The current is measured between the working and the counter electrodes





GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

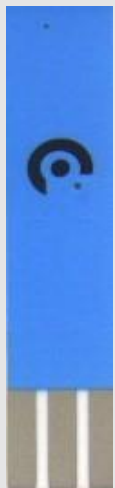
SunChemical®

a member of the DIC group

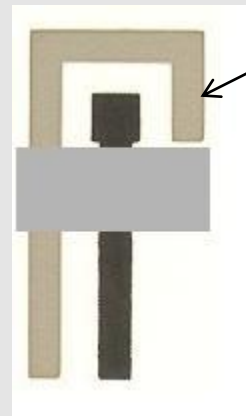


# Electrochemical cell and the role of each electrode

- When the measured currents are relatively high (nA or rather  $\mu\text{A}$ ) the counter and the reference electrodes can be combined as one electrode. This is the case for screen printed electrodes with Ag/AgCl or carbon combined reference and counter electrode.



Three electrode system



Two electrode system



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



Color & Comfort

# Enzyme based inks

- Some commercial manufacturers print a discrete enzyme layer
- This only for GOX based biosensors
- Others use liquid deposition equipment for bio-cocktail systems



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Enzyme solutions

- Stabilised enzyme solutions are commercially available
- Most manufacturers customise these systems to meet their own requirements
- Other stabilised enzyme solutions are available





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



# Materials Available for Special Applications

- Cross-linked systems suitable for membranes (polar or strong solvents) and FIA applications
- High temperature systems available for ceramic substrates (alumina)
- Gold, Platinum, Palladium, Rhodium in both polymeric and high temperature systems
- Other metals such as Nickel and Copper if needed



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Why is Screen-Printing Popular

- Cheap for small volumes - less than 1 billion sensors per year
- Film thickness can be high ( $>40\mu\text{m}$ )
- Other printing techniques give lower weights of deposit



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



# What About Other Methods?

- Flexographic and Gravure printing lower weight of deposit
- Web based printing for volumes over 1 billion and expensive set-up costs
- Rotary screen printing needs different viscosity inks
- Liquid dispensing needed for enzymes other than glucose oxidase
- Dot on demand ink jet pico litre drop sizes and production cycle time issues will be used for smaller structures



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



# Sensor Design and Application Techniques

- The limit of traditional screen printing was 70 micron lines and spaces
- The new limit is 20 micron lines and 100 micron spaces
- With new inks this is the new limit of the screen printing technique
- A new screen is needed for each printed layer
- Art work needs to be generated for each screen



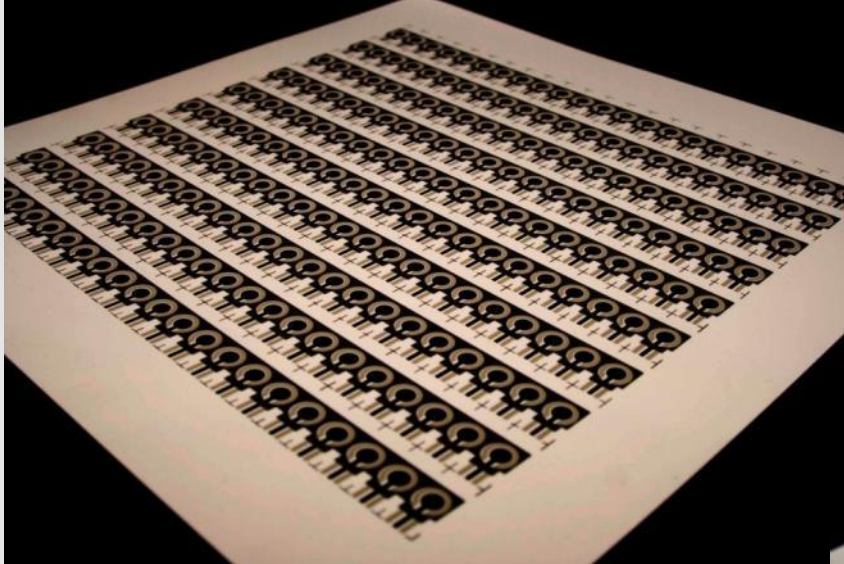
**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

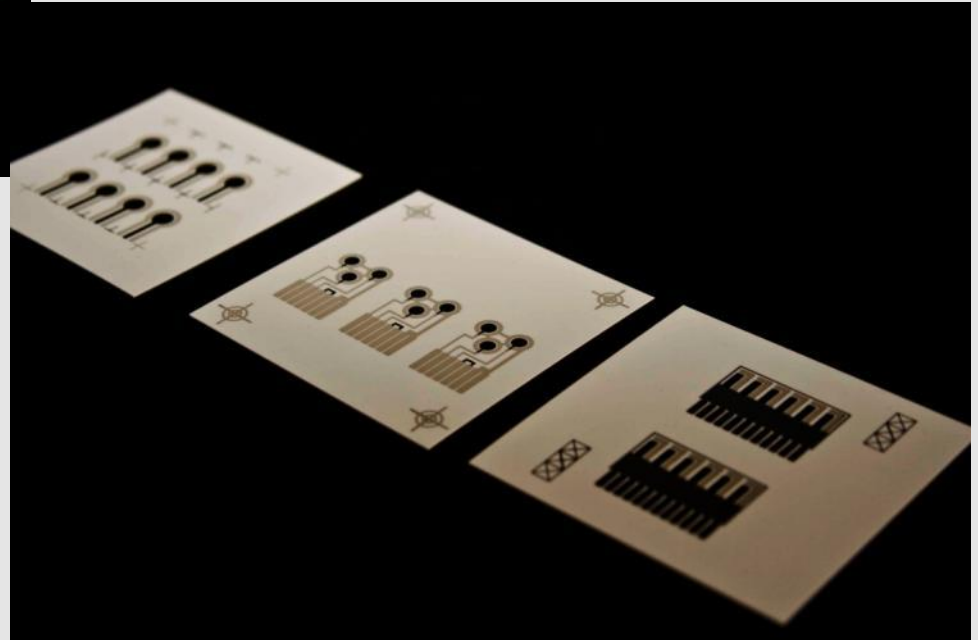
**SunChemical®**

a member of the DIC group 

# Screen Printing



**Printing speed:**  
**60 -1500 sheets per hour**





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of-

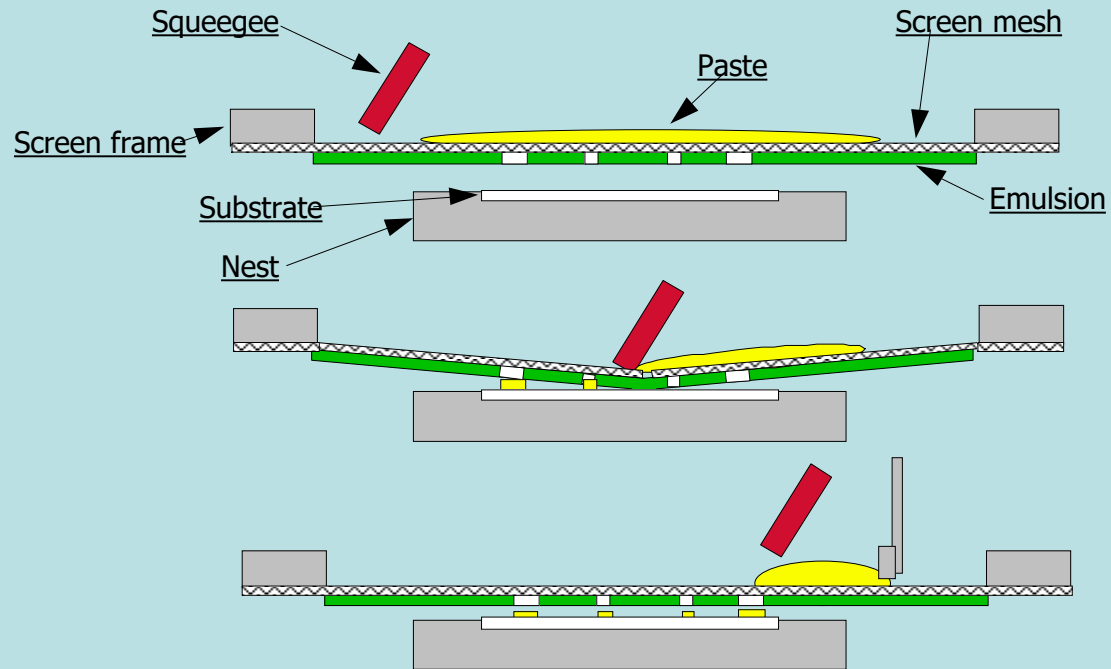
**SunChemical®**

a member of the DIC group



# The Screen Printing Process

[Fig 1 The basic screen print process](#)





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

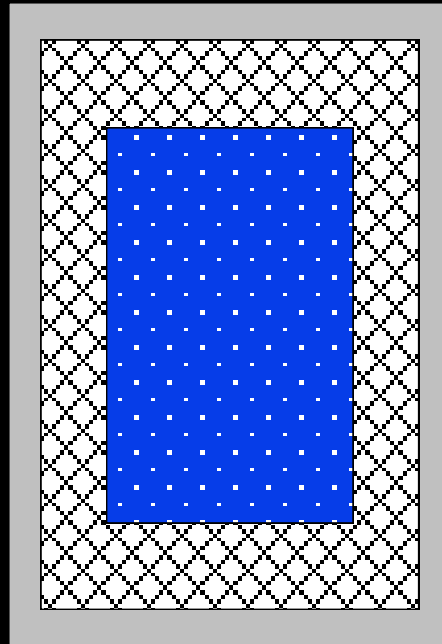
**SunChemical**<sup>®</sup>

a member of the DIC group



# Screen Frame Size Relative to Working Area

Fig 2 Screen / image size



Normal printing  
2/3 of  
screen  
area can  
be used

For high  
definition  $\frac{1}{2}$   
of screen  
area can be  
used



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



# Curing of Printed Electrodes

- For a few prototypes simple oven curing is acceptable - temperature ranges will depend upon the substrate used for most grades of polyester 60-110 deg C can be used.
- For production quantities a IR belt furnace is often used; the temperature of drying can be reduced if air flow is increased
- Some manufactures use rotary wicket driers in an attempt to save production space





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



Color & Comfort

# Electrode Polymer Curing Unit





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



Color & Comfort

# Dek248 Production Printer





GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Screen printing & manufacturing volumes

- Low volume production ( 3.5 Million per month)
- High Volume (100 million per month)
- Volumes made by flat bed printing
- Higher volumes use web printing
- Higher accuracy use optical printing



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

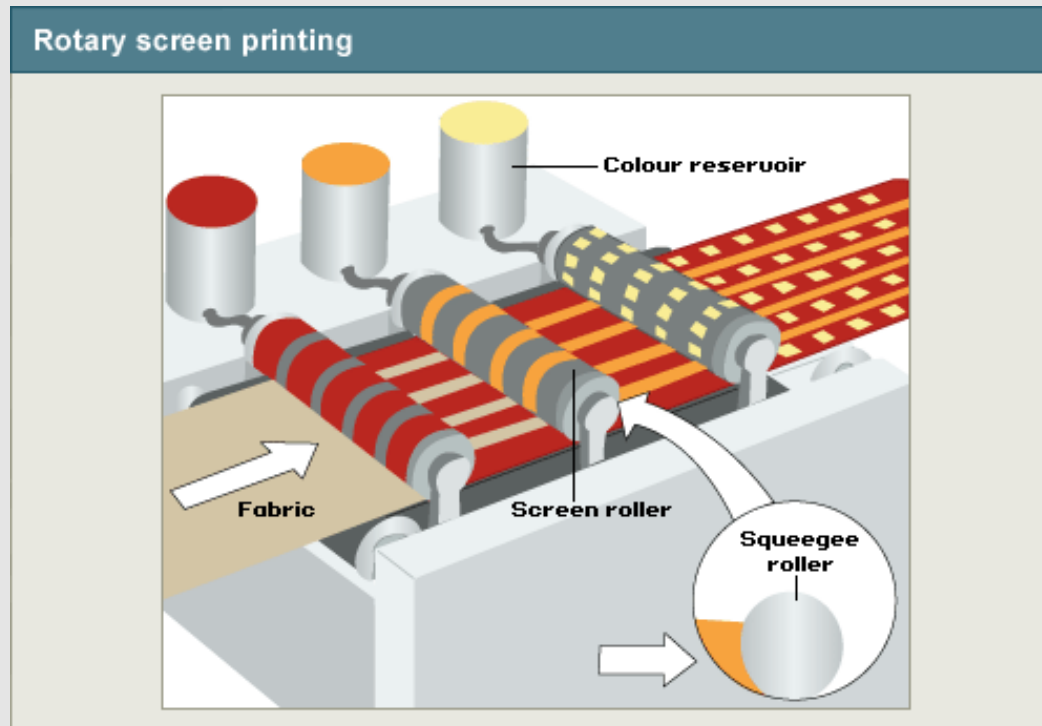
**SunChemical®**

a member of the DIC group



Color & Comfort

# Rotary Screen Printing





GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of-

SunChemical®

a member of the DIC group



# Sensitivity and Limits of Detection

- Screen printed electrodes can measure analytes in the nanomolar range.
- Many environmental applications require low ppb limits of detection.



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group   
Color & Comfort

# Finer lines and pitch

- The limits of screen printing in production is 100 microns track and gap
- Many research projects are being carried out to print finer details
- GEM are working to develop new techniques in this area



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

# Print Limitations

Part of-

**SunChemical®**

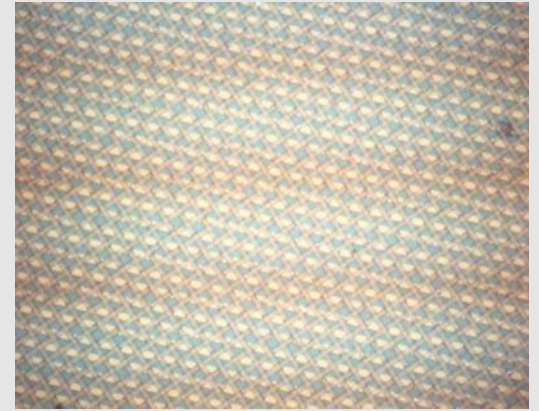
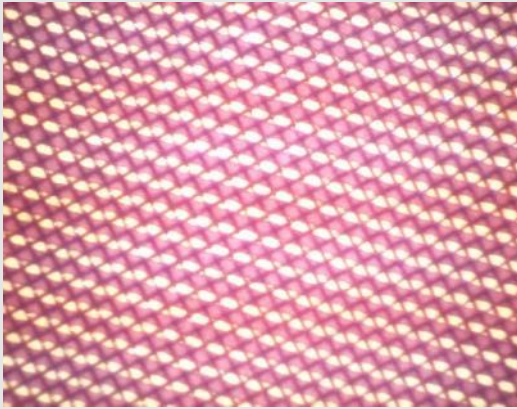
a member of the DIC group



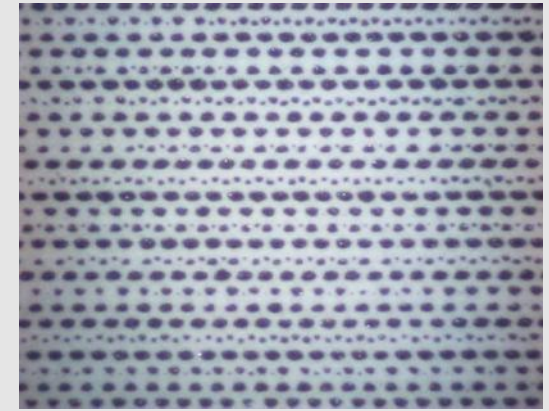
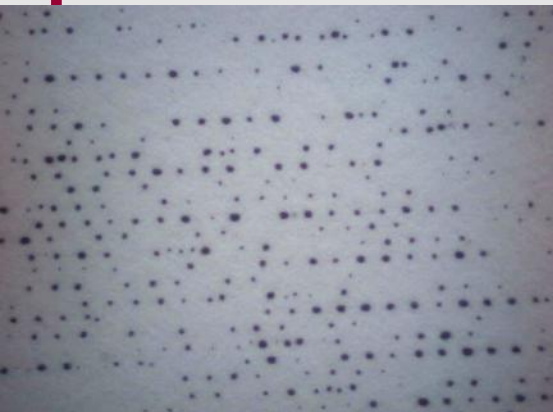
300SDS 40μm

400UT 40μm

V330 40μm



C2090903R3 76% Pt





**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

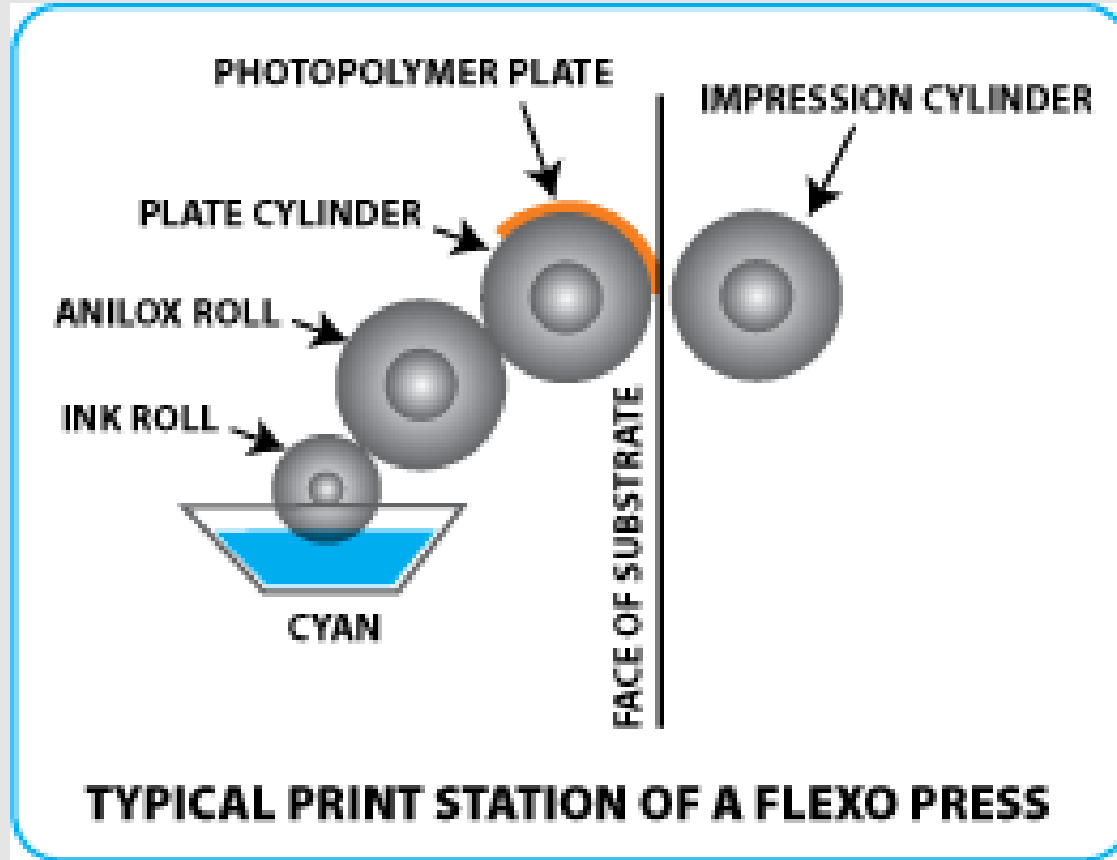
Part of:-

**SunChemical®**

a member of the DIC group



# Flexography







**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group   
Color & Comfort

# Recap on printing speeds

- Flat bed printing 50 to 1500 sheets per hour
- Web based systems 9 to 15 metres per min
- Flexo printing 40 to 120 metres per min
- Some history early 1990's flat bed production
- 2000 web based systems



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of:-

SunChemical®

a member of the DIC group



# Technology and production

- Practical- lets assume a 10 second production period.
- Flat bed 200 prints per hour - half a sheet of electrodes printed
- Web based systems 10 metres/min - 1.7 metres of electrodes printed
- Flexo 60 metres/min – 10 metres of electrodes printed



GWENT GROUP  
ADVANCED MATERIAL SYSTEMS

Part of-

SunChemical®

a member of the DIC group



# Application Methods for Biomaterials

- The only enzyme system commonly printed is Glucose Oxidase
- Many enzyme systems cannot be applied with ink jet systems
- The more sensitive systems are applied using liquid dispensing methods



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



# Conclusions

- Screen-printing is the most commonly used application method for base transducers
- Screen-printing can be used with enzymes
- A variety of application techniques can be used with bio-systems
- The limit for small structures in the future will be ? lines and spaces



**GWENT GROUP**  
ADVANCED MATERIAL SYSTEMS

Part of:-

**SunChemical®**

a member of the DIC group



---

# Gwent Electronic Materials Ltd

Address: Monmouth House  
Mamhilad Park  
Pontypool  
Torfaen  
NP4 0HZ  
United Kingdom

Tel: +44 (0) 1495 750505

Fax: +44 (0) 1495 752121

Email: [sales@gwent.org](mailto:sales@gwent.org)

Website: [www.gwent.org](http://www.gwent.org)