Functional Polymer Composites: innovative platform for lifetime insurance in Organic Electronics

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Advanced Course on
"ORGANIC ELECTRONICS :
principles, devices and applications"
Milano (italy), 23rd to 27th November, 2015

saes group

making innovation happen, together

Outline

- SAES Group
- OLED degradation phenomena
- Types of Encapsulation
- Functional Polymer Composites

70 years of World Wide leadership

For more than **70 years**, our **technology** has been supporting **innovation** in the:

- Information and Displays industry,
- Lamp industry,
- Vacuum and Ultra-high Vacuum applications,
- Vacuum tubes and electronic devices industry,
- Ultra-high gas purification,
- Renewable Energies area.

Since 2004 our **NiTi smart materials solutions** have been innovating:

- the Medical devices industry,
- the Consumer electronics industry,
- the Automotive industry,
- the White Goods and Domotic industries.

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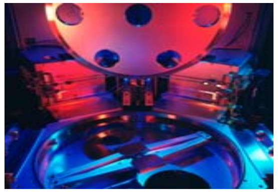
Core Business

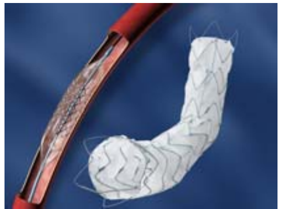
Some applications for SAES Group products:

LAMPS: fluorescent lamps (linear, circular, compact), high intensity discharge (HID), LED and OLED lamps for: industrial, domestic, medical and automotive applications



GAS PURIFICATION: From small to very large scale Gas Purification Equipment for Semiconductor, LEDs, Display (LCDs, OLEDs), Fiber Optics and Solar Industries

VACUUM DEVICES, SENSORS & MICRO-SENSORS: X-Ray tubes, power microwave and vacuum interrupters, accelerometers and gyroscopes, IR and pressure sensors, frequency meters, etc. for: consumer electronics, industrial, medical, domestic, automotive , telecom and avionics applications



MEDICAL TOOLS & DEVICES (NiTiNol based): medical implantable devices (stents, spinal clips, cardiac valves, etc.), guide wires and components for medical applications like cardiovascular, orthopedic, endoscopic surgery

HIGH AND ULTRA HIGH VACUUM SYSTEMS: particles accelerators, colliders, analytical equipment for scientific and industrial applications that need excellent and stable ultra high vacuum conditions

ACTUATORS (Shape Memory Alloys based): innovative miniaturized and high performance actuators, both thermostatic and electro-mechanical, for industrial, consumer electronics and automotive applications

THERMAL INSULATION: vacuum insulated panels for construction and white goods, vacuum insulated tanks and pipes for: scientific, consumer and industrial applications, solar collectors

ORGANIC ELECTRONIC DEVICES & MATERIALS: consumer electronics (OLED), lighting, automotive, medical instruments, advanced packaging markets

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A Customer-focused Approach

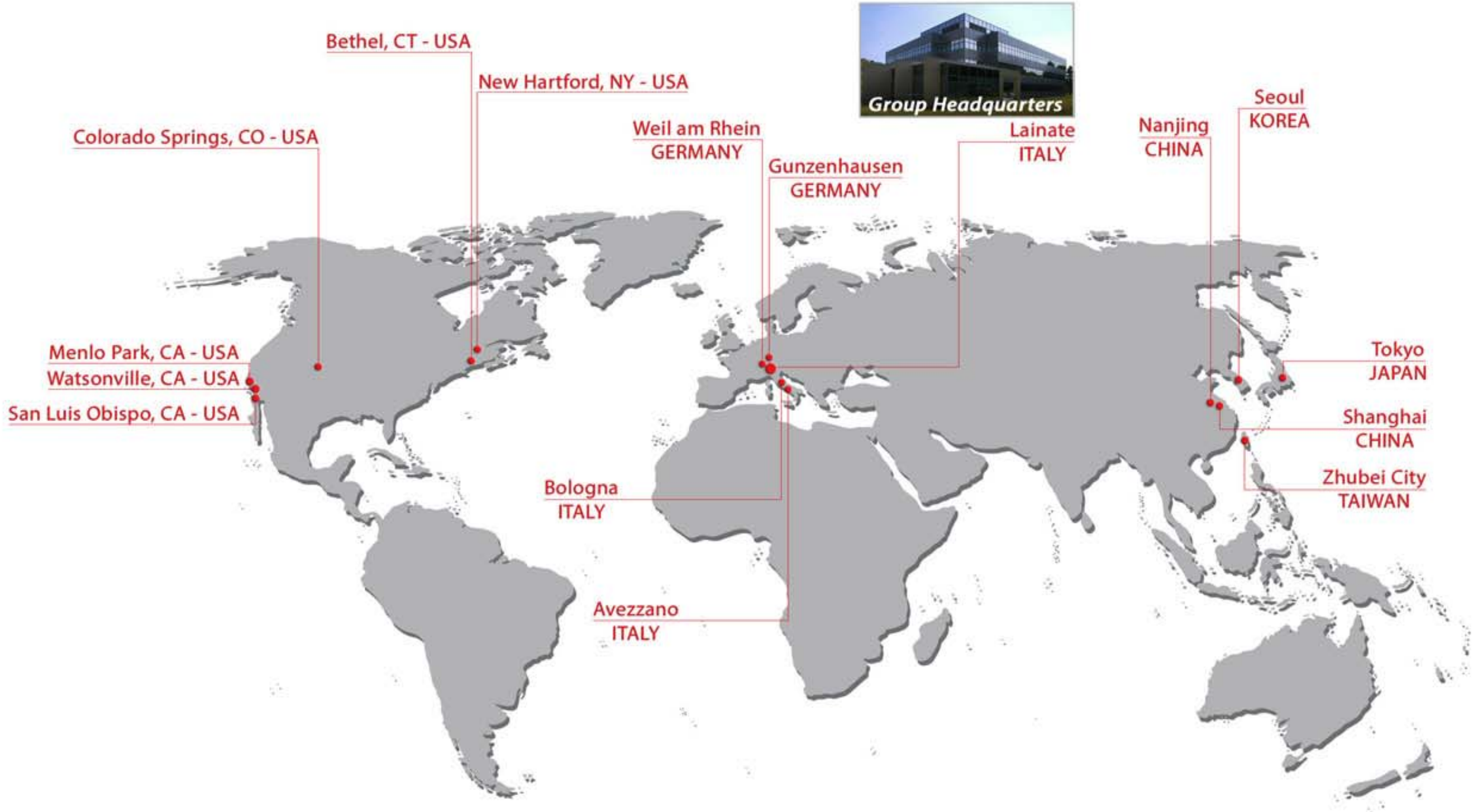
Nearly **2,000 active customers in 5 continents**, spanning from blue chip companies to business start-ups, Universities and R&D centers

More than 70 years of expertise in partnering with customers for the engineering **of fully customized solutions**

High flexibility in product development, fine-tuning and manufacturing, to foster emerging and **forefront application technologies**

Technical service network and CRM structure **supporting customers' innovation** 24 hours a day

Global Presence



- SAES Group has a worldwide presence thanks to its subsidiaries located in Europe, USA and Asia
- The company is headquartered in Lainate (Milan), Italy
- The Group has 10 manufacturing facilities: six in the USA, two in Italy and two in Germany
- In Asia the Group can count on subsidiaries located in Japan, China, South Korea and Taiwan
- The worldwide presence of the Group is also ensured by a number of authorized distributors

Our Research and Innovation

Key Figures

- **10%** of net sales allocated to R&I every year
- State-of-the-art corporate laboratories covering a surface of over 3,300 sq. m.
- More than 150 highly skilled people engaged in RDI activities world-wide. Almost 17% of the total workforce of the Group:
  - about 50% are graduated (mainly in Physics, Chemistry, Engineering and Material Science)
  - 20% of graduated are PhD
- 233 Scientific Papers and Conference Proceeding published in the last 20 years
- Strong cooperation with Universities and R&D centers

SAES Core

Key Core Competences

- Surface Science
- Advanced Metallurgy
- Gas-Solid Interaction
- Macro-molecular Chemistry

↓

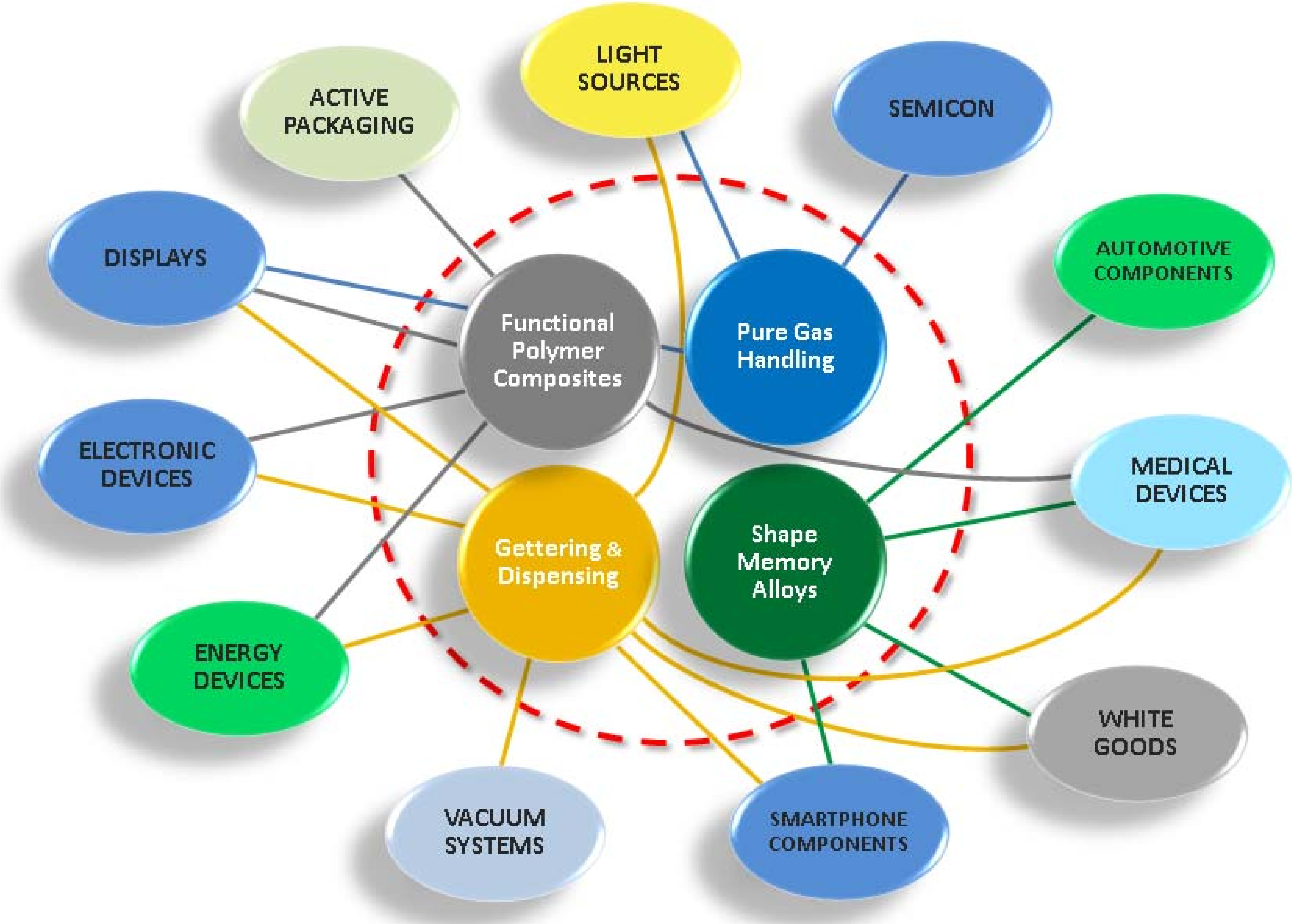
ADVANCED FUNCTIONAL MATERIALS

↓

Core Technological Platforms

- GETTERING & DISPENSING
- SHAPE MEMORY ALLOYS
- PURE GAS HANDLING
- FUNCTIONAL POLYMER COMPOSITES

Core Technological Platforms Main Applications



  making innovation happen, together

Collaborative Projects

LABOHR
Lithium-Air Batteries with Split Oxygen Harvesting and Redox Processes

MAC-TFC
MEMS Atomic Clocks for Timing, Frequency Control and Communications

PHOTO-FET
Integrated Photonic Field-Effect Technology for Bio-Sensing Functional Components

SEVENTH FRAMEWORK PROGRAMME

APPLES
Advanced, High Performance, Polymer Lithium Batteries for Electrochemical Storage

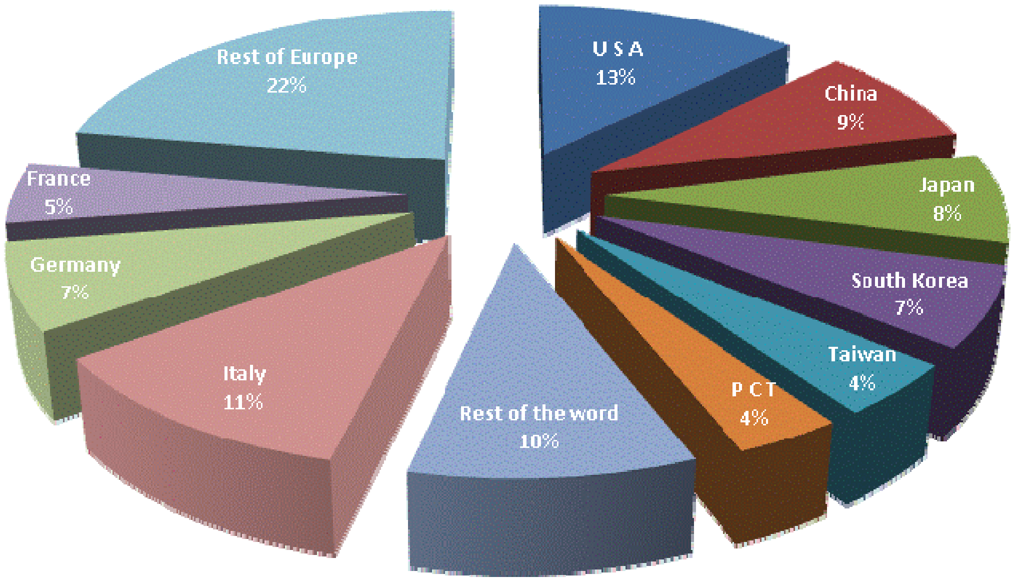
SNIFFLES
Artificial Sniffer Using Linear Ion Trap Mass Spectroscopy

SUNFLOWER
Sustainable Novel Flexible Organic Watts Efficiently Reliable

SAES IP Portfolio

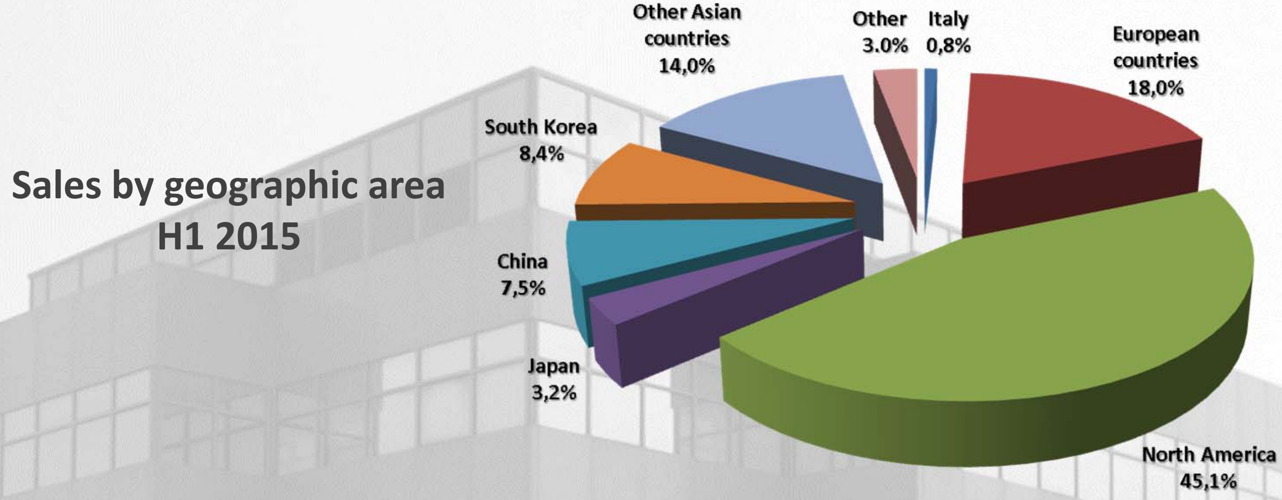
- About 8-10 new inventions per year are protected by patent application filings
- Over 300 inventions (SAES case/Patent Families) in 70 years

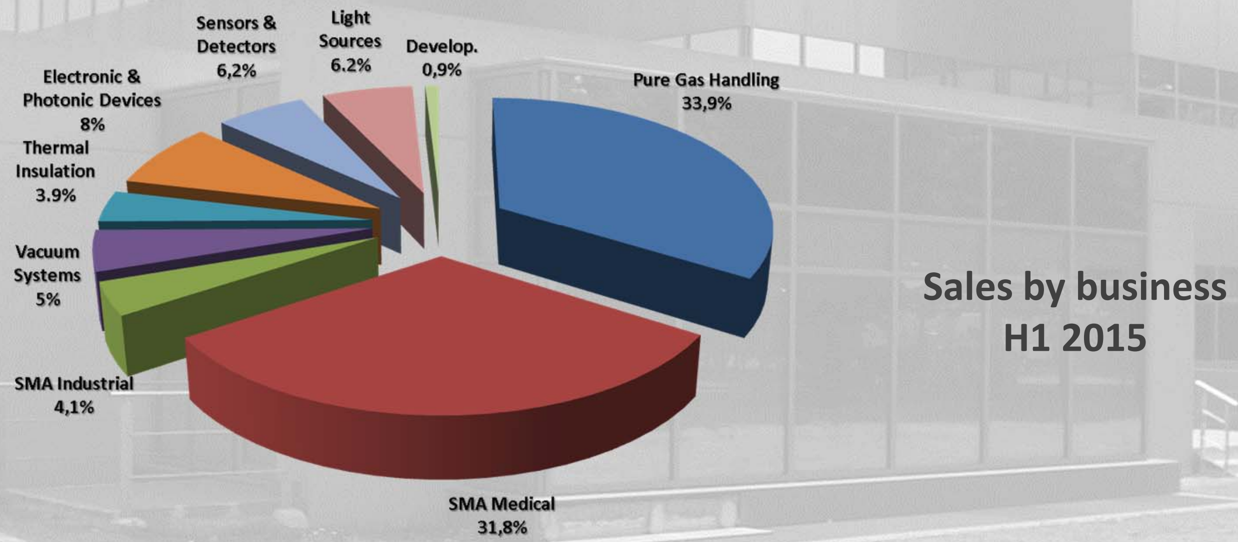
Patents & Applications by Geographic Area



- At present about 1300 "live" elements (Granted Patents and Patent Applications)
- About 70 Trademarks protected in SAES history, 38 still "alive".
- About 1-2 requests of registration for new trademark(s) per year.

SAES Group Consolidated Sales





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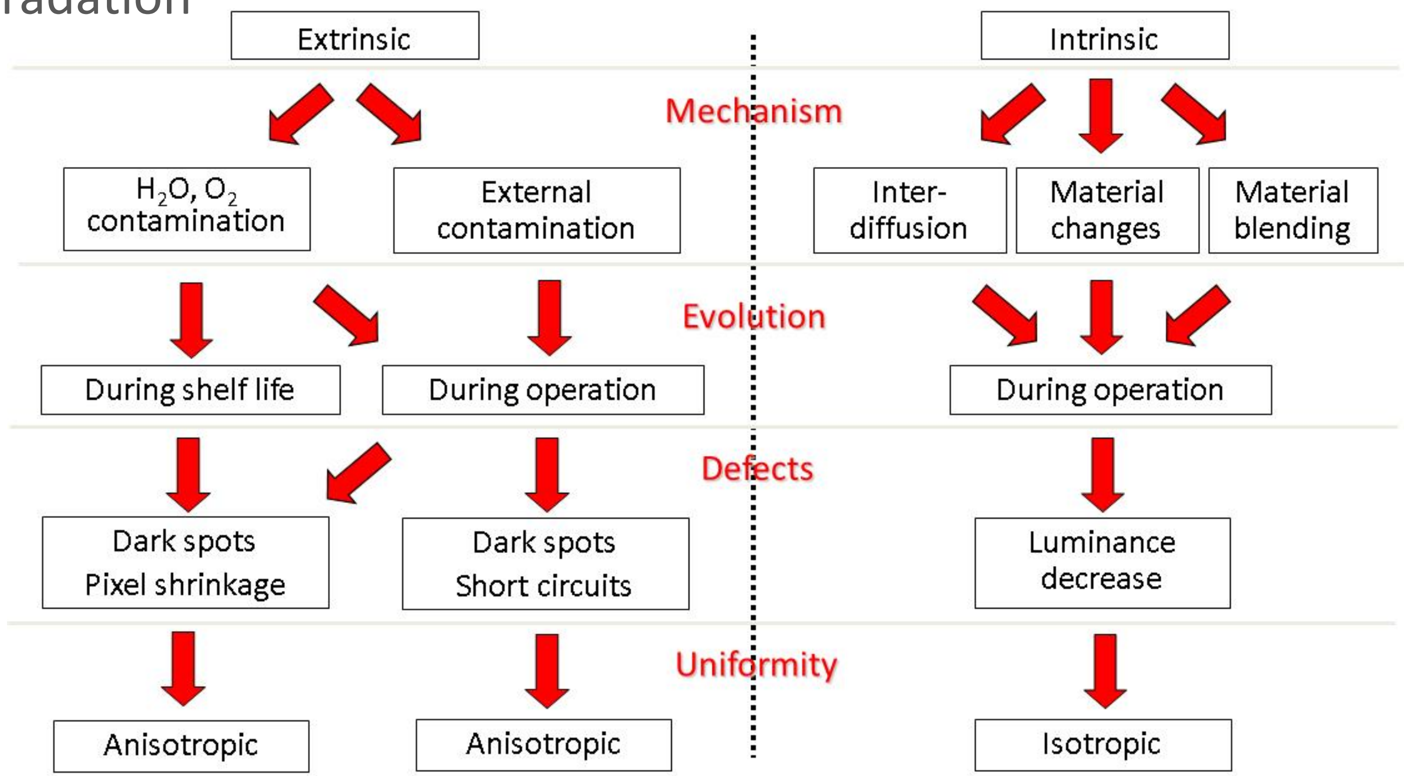
- OLED degradation phenomena
- Types of Encapsulation
- Functional Polymer Composites

Degradation phenomena

- Intrinsic degradation is mainly related to excited states of emitter molecules (charge-transport and injection properties)
- Extrinsic degradation factors include mechanical damage, reactions with harmful gases or liquid chemicals, light-induced degradation

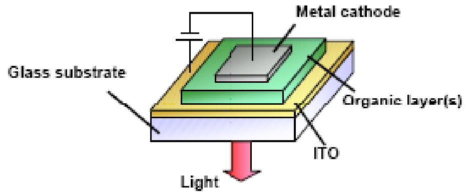


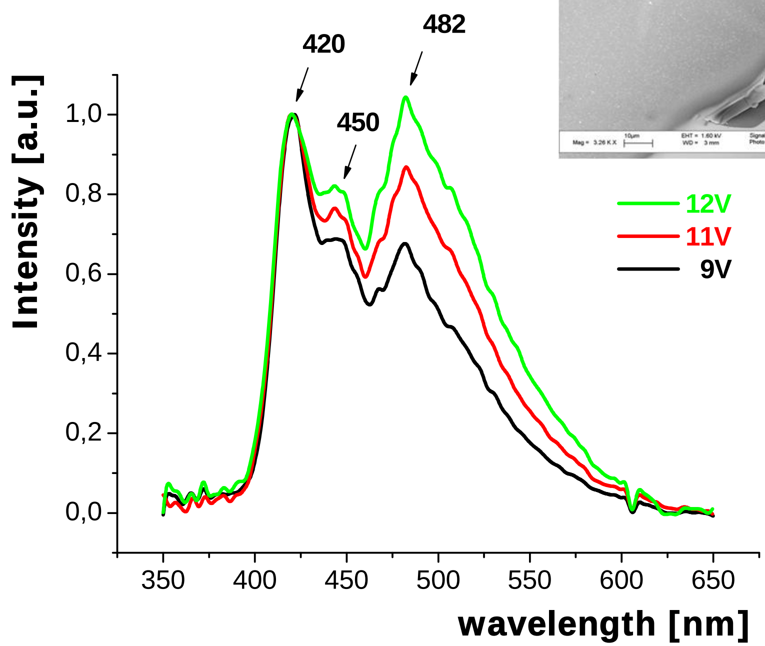
Deagradation in Organic Electronics

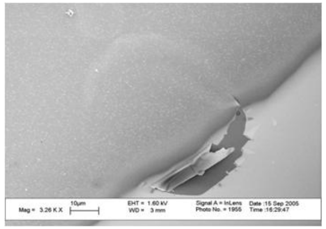
- Extrinsic degradation of Organic Electronics devices primary occurs at cathode level
  - Device structures usually include highly reactive low work function metals as cathode
  - Degradation proceeds through the primary metal oxidation -> causing injection/extraction barriers for charge carriers -> performances degradation

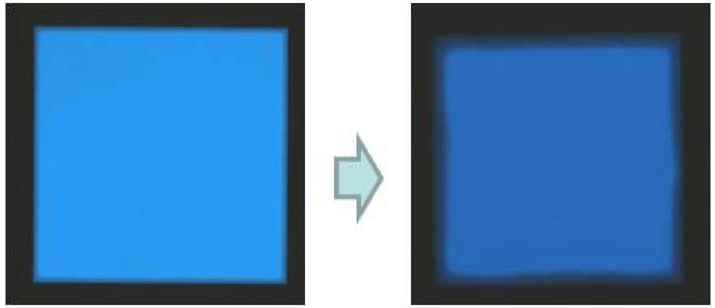
Examples of OLED degradation

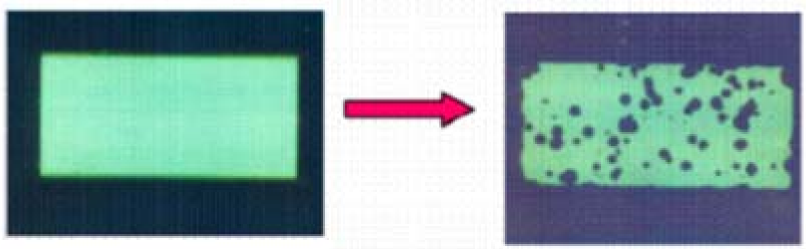
PhD Thesis "TECHNOLOGY AND ELECTRO-OPTICAL CHARACTERIZATION ON ORGANIC SEMICONDUCTOR DEVICES" P. Vacca





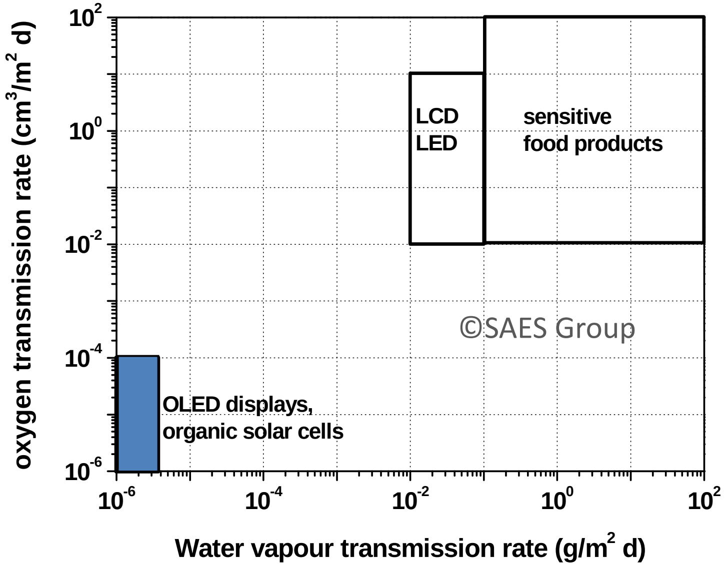






Device Encapsulation

- Device Encapsulation describes the packaging of devices to protect them against damage caused by the environment (extrinsic factors)
- Encapsulation thereby refers to both the packaging materials (e.g. sealants, substrate, getters) and the packaging processes (e.g. lamination, deposition)
- Therefore a major task of the encapsulation is to prevent water vapor and oxygen from reaching the device



WVTR & OTR

- The water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) are used as quantity to describe maximum allowed amount of water to reach an organic device before device failure
- These values (WVTR and OTR) describe a mass of water or volume of oxygen permeating through the encapsulation system per time unit and area (commonly one square meter)
- $[WVTR] = g/(m^2 d)$
- $[OTR] = cm^3/(m^2 d\ bar)$.
- They are not material constants but depend on the environmental conditions (mainly temperature and relative humidity) at which they are measured.
  - indoor use (23°C - 50%RH)
  - outdoor use in tropical conditions (up to 38°C - 90%RH)

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- Functional Polymer Composites

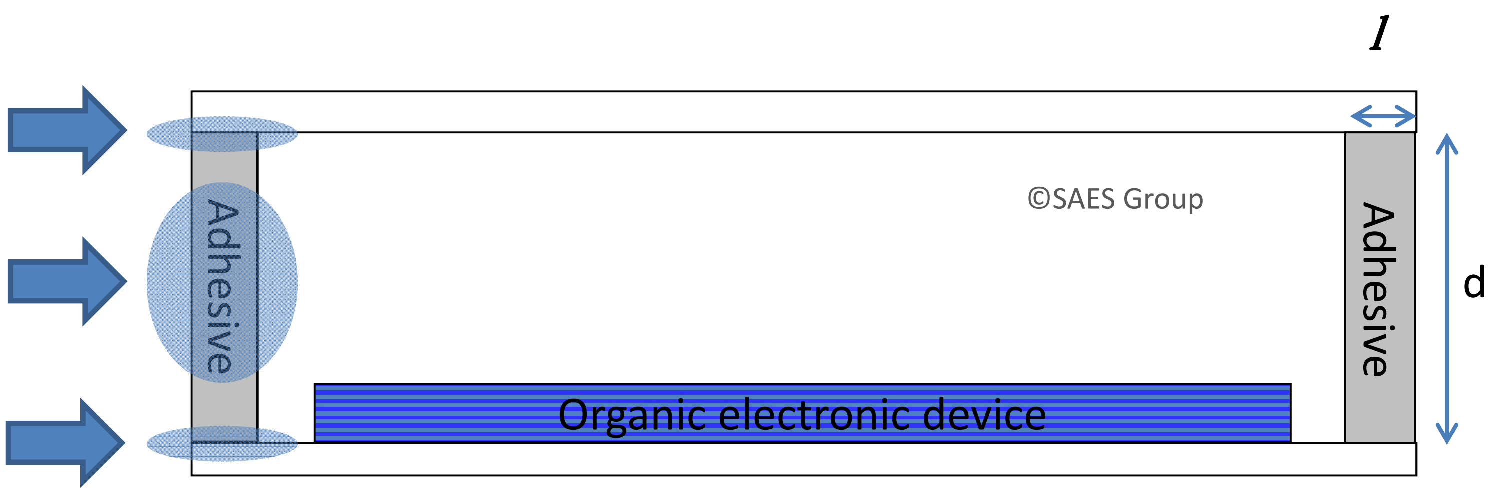
Types of encapsulation

- Different encapsulation approaches may be chosen depending on:
  - the desired lifetime
  - the inherent stability of the system
  - the target market for the organic device

- Encapsulation types:
  - Glass-to-glass encapsulation
  - Lamination of barrier films
  - Thin film encapsulation

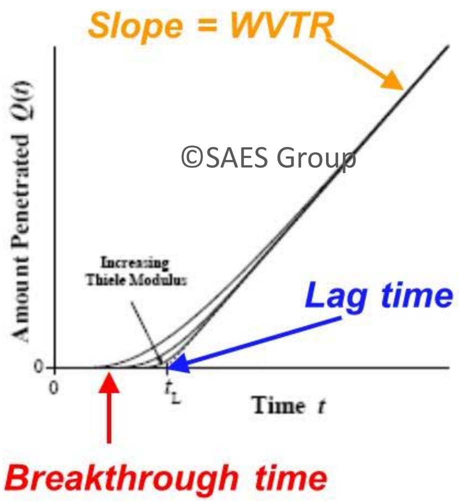
Glass to glass encapsulation

- Glass sheets are practically a perfect barrier against oxygen and moisture
- The weak point of this encapsulation approach is the permeation through the connection of the two glass slides: the adhesive
- Two main mechanisms:
  - permeation through the adhesive
  - the permeation at the interface between the glass and the adhesive and through any coated thin layer

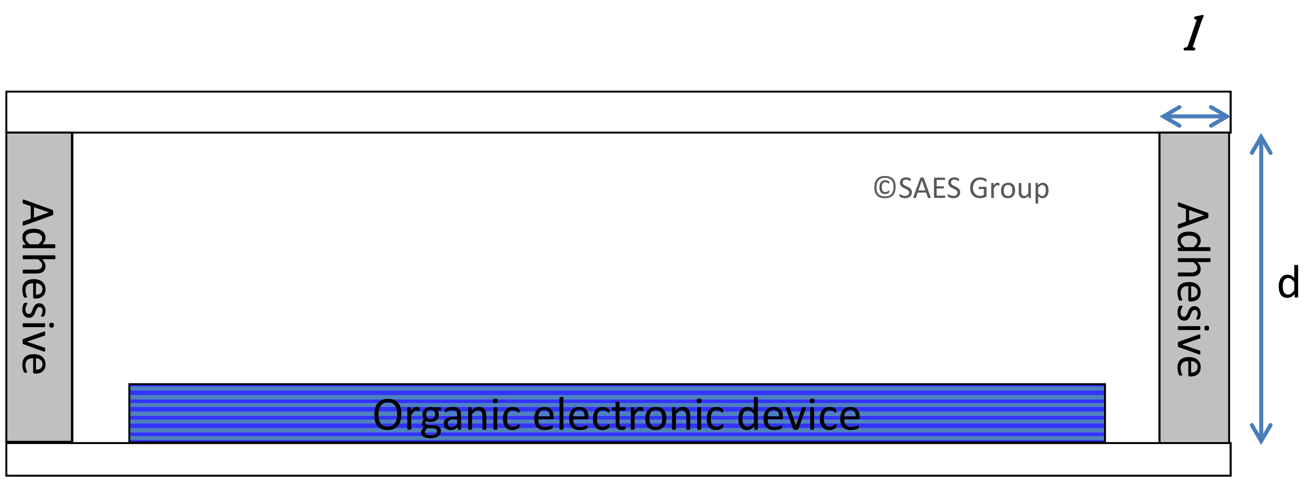


Passive adhesives

- Moisture permeation depends only on its diffusion through the adhesive
- Working on the adhesive bulk properties, different WVTR can be obtained
- Low WVTR is not enough to ensure a suitable lifetime

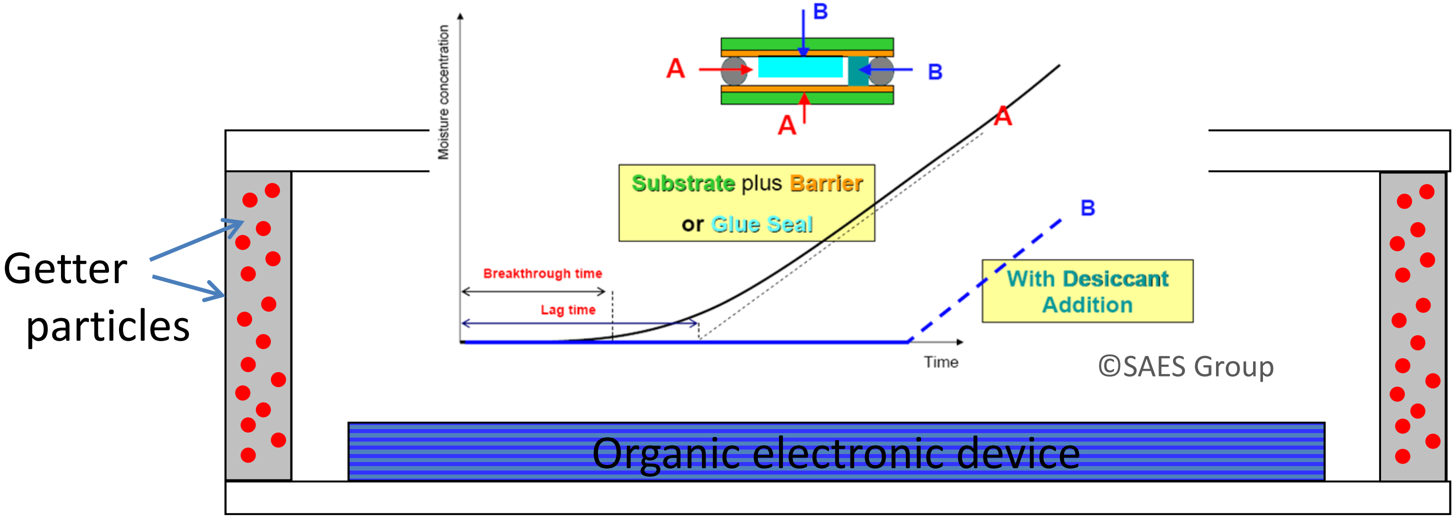


$$t_{lag} = \frac{l^2}{6D}$$



SAES Active adhesive approach

- The integration of getter materials in adhesive materials is able to solve "weak points" issue of rigid encapsulation
- The development of active adhesive based on the efficient integration of engineered getter particles in epoxy resins strongly increase the package lag time and the resulting device lifetime

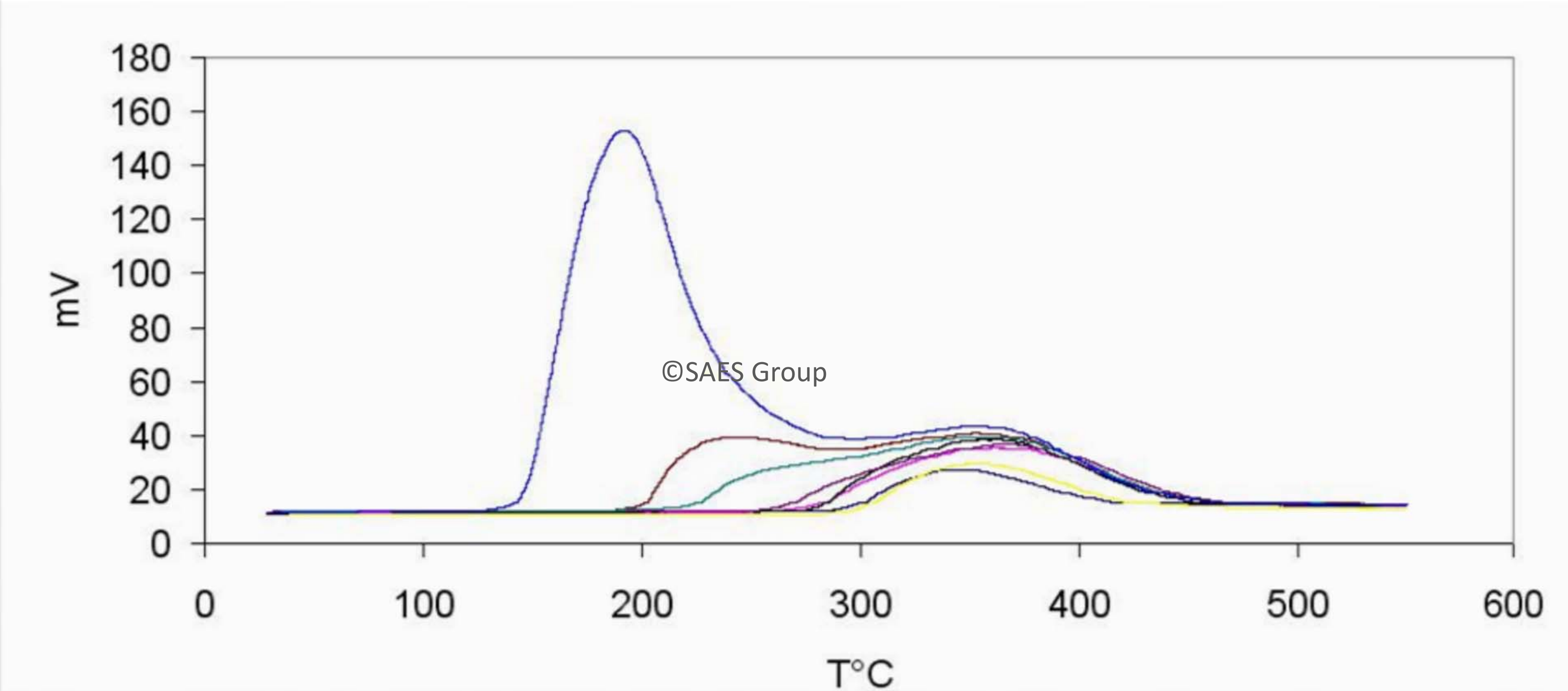


Active adhesive: nano-composites based on nano-sized zeolites

- Main properties
  - no phase segregation due to chemically tailored particle surface (class-I materials from non-reactive capping agents, class-II hybrid materials from reactive capping agents)
  - no leaking pathways within the substrate/scavenger interphase due to particles wetting
  - good sorption properties (capture rate, capacity, energetics: low H_2O vapour pressure)

Zeolites: why?

- Fast kinetics and high sorption capacity for H_2O

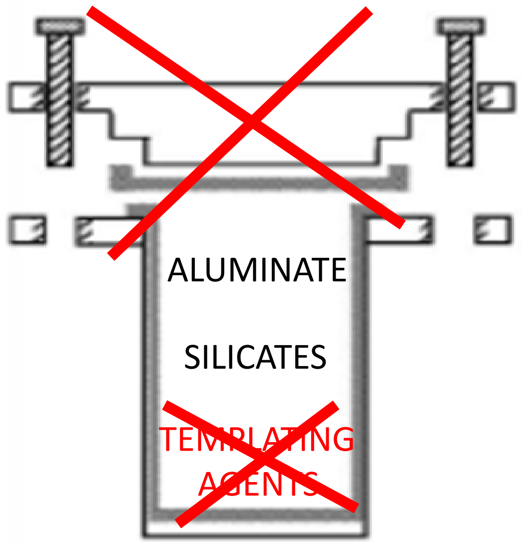


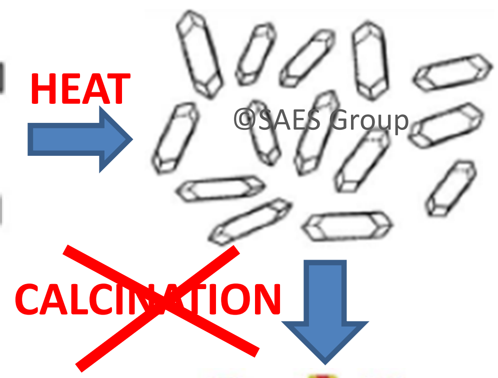
- Reversible getter but irreversible up to high temperature (180-200°C)
- Available at nanometric scale ← SAES technology
- Additonal gettering features ← SAES technology
- Chemically tailored particle surface ← SAES technology

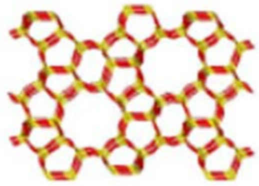
Zeolite – *state of the art* approach

SOL-GEL HYDROTHERMAL SYNTHESIS FOR NANOZEOLITES

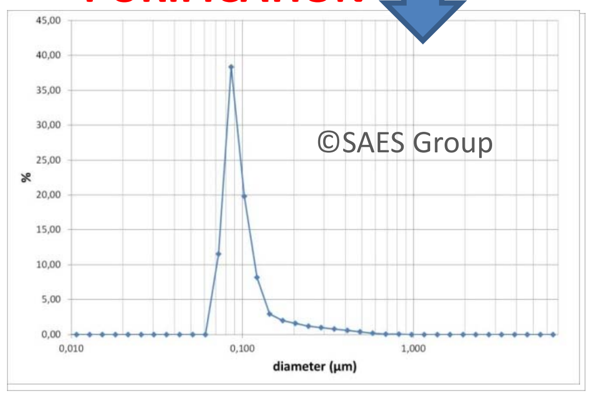
- **low T and atmospheric pressure**
  - no need of high-T autoclave
- **no need of templating agent**
  - No calcination
  - process step reduction
- **purification**
  - effective filtration
  - agglomerate-free drying



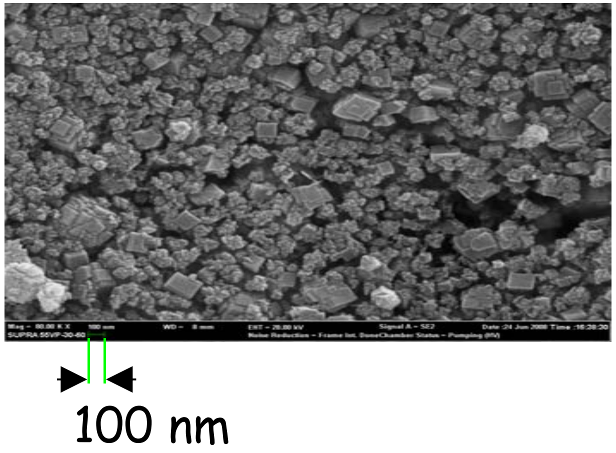


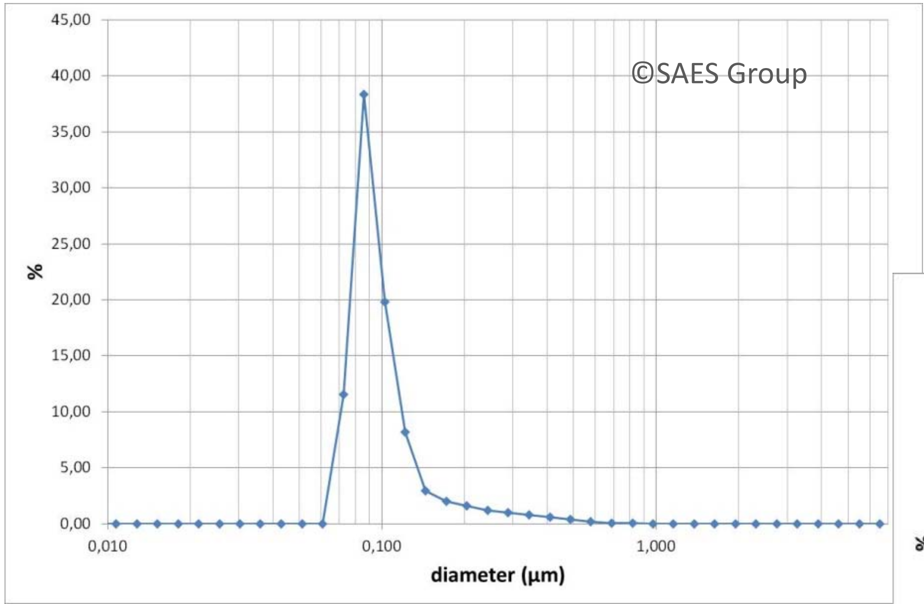


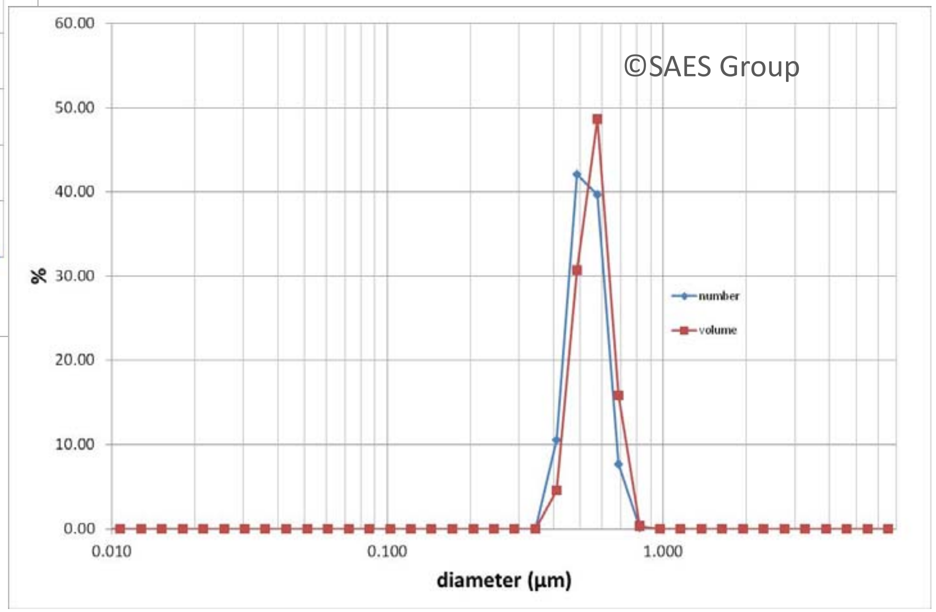
narrow distribution of sub-micrometer-sized primary particles



SAES nanozeolites – particle size distrib.

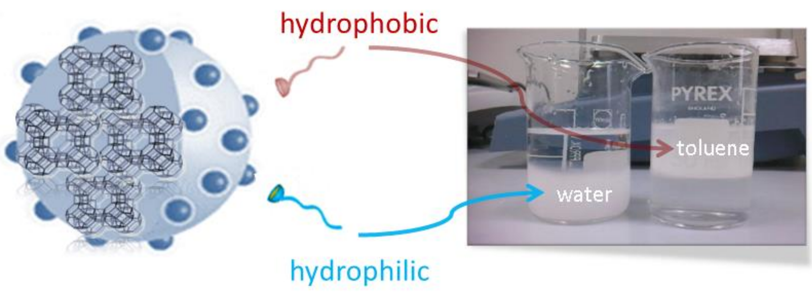


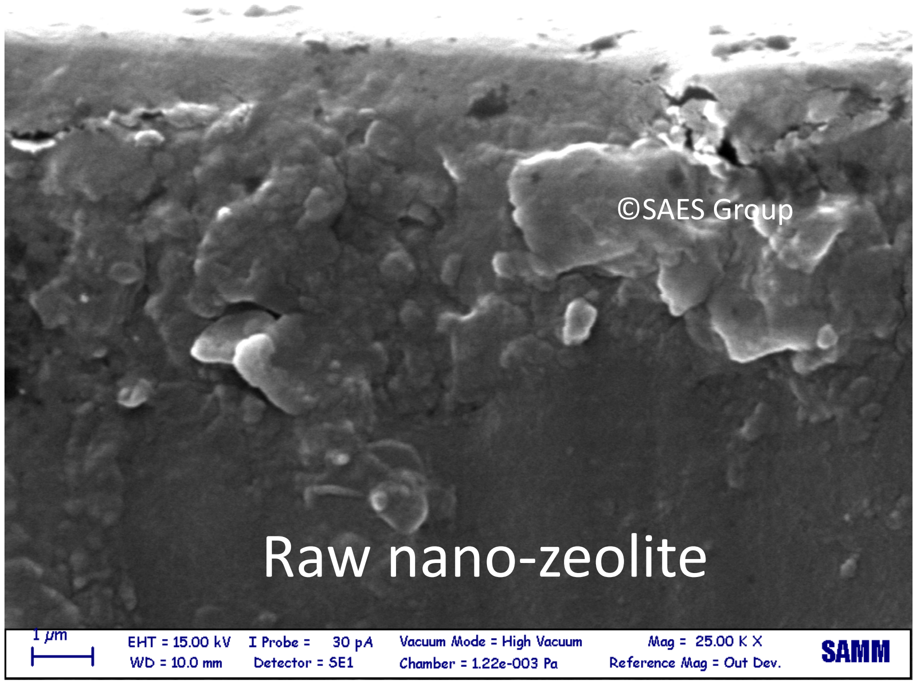


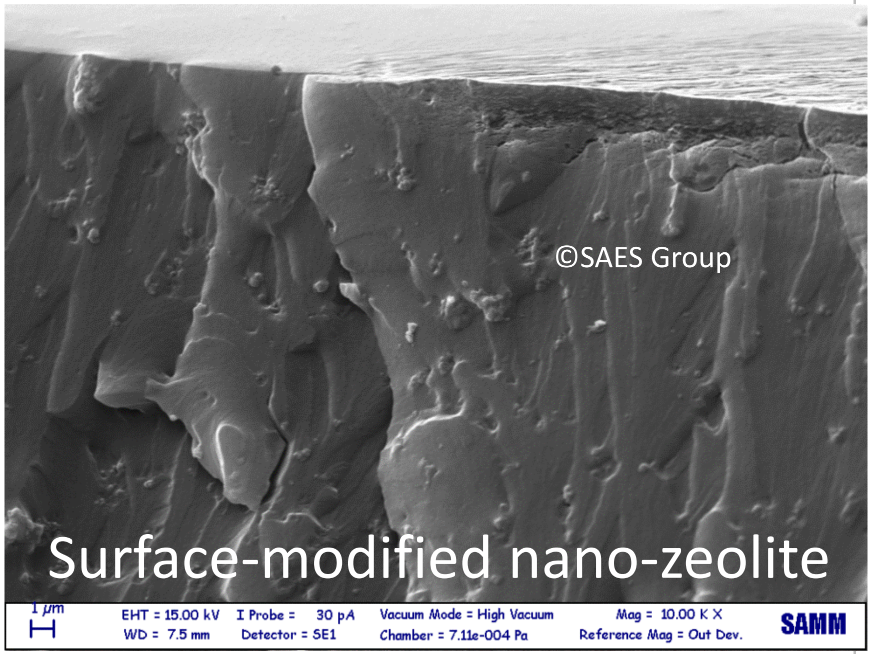


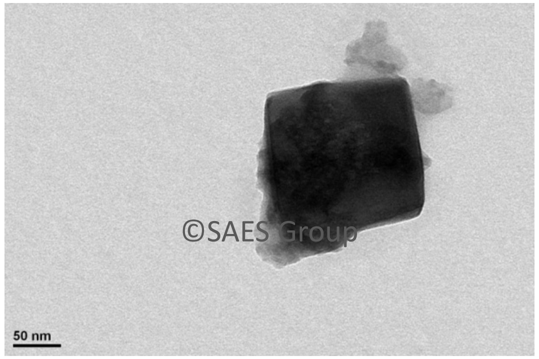
- mean particle size: 100-300 nm
- very sharp particle size distribution

Modified nano-zeolite in organic matrices



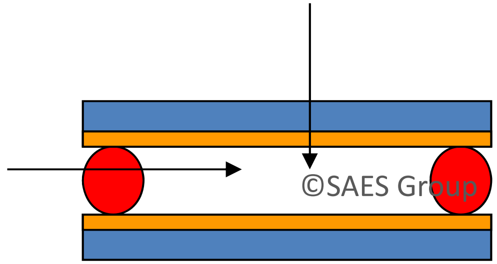


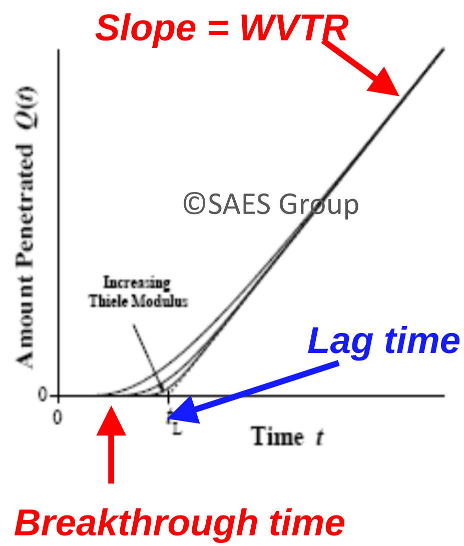


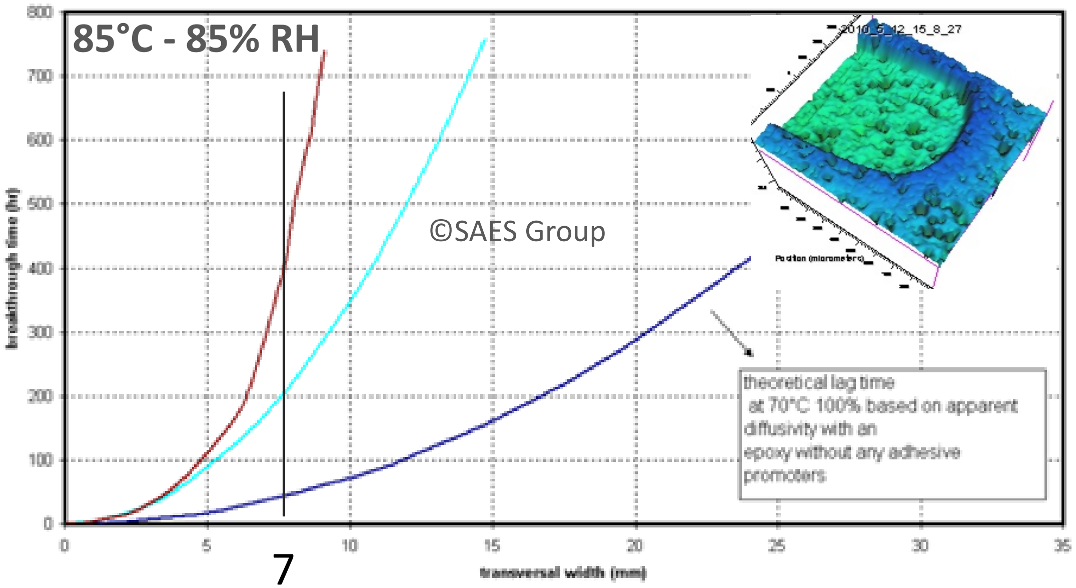


Active sealant based on nanozeolite

- Active sealant are produced by dispersing modified nano-zeolite in an epoxy-polymer matrix
- Active adhesive looks like a whitish liquid
- It is designed to work as an active edge sealant







- Moisture concentration increases rapidly, even with a “good” WVTR

How to support an active barrier?

- After getting the active barrier lag time, the moisture concentration will tend to increase
- The integration of a getter material in the encapsulation package is able to maintain very low the moisture conc. for long time
- The right combination of active adhesive and getter materials can ensure a H_2O pressure below ~ 0.1 ppm limiting dark spot area growth and pixel shrinkage below values significantly affecting the device

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Getter materials

- Key properties of getter materials are:
  - kinetics of the capture process (adsorption, absorption, chemical reaction)
  - capacity (weight of specific chemical species captured by unit weight of getter)
  - partial pressure of a specific chemical species in equilibrium with getter

$$G + g \rightleftharpoons G \cdot g$$

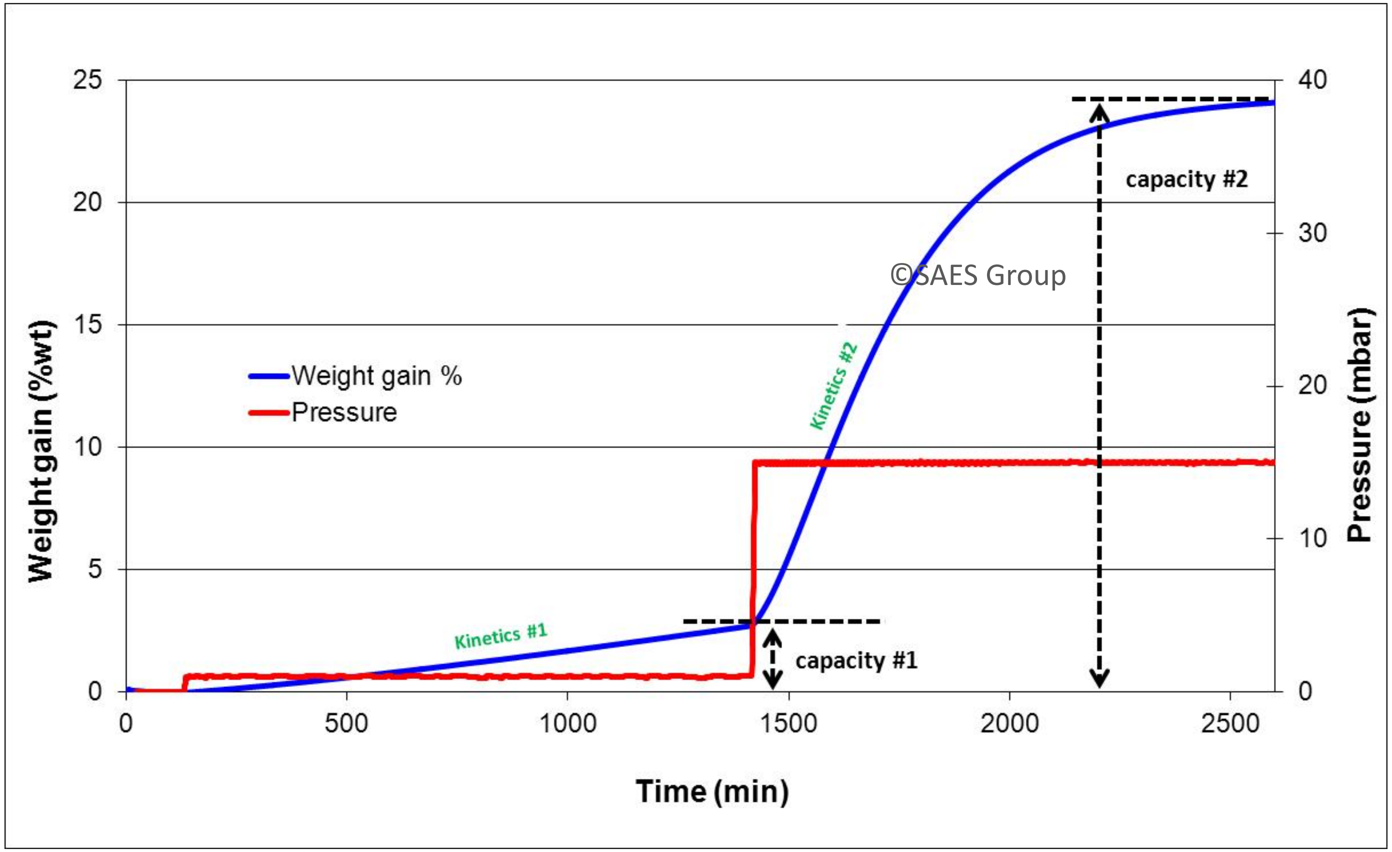
irreversible / reversible

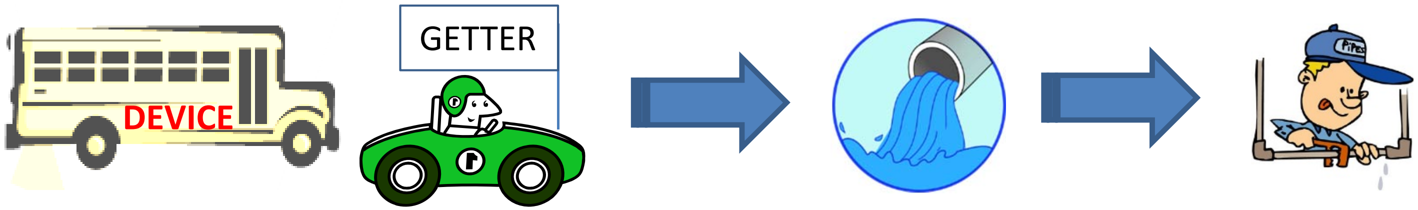
- Getter materials are :

pure metals (Ba, Ca, Ti):	evaporated thin films
metal alloys (ZrVFe, ZrCo, TiNi, etc.):	bulk and thin coatings
inorganic, non metal:	bulk and thick coatings
hybrid organic-inorganic:	<u>Functional polymer composites</u>

Getter materials:key characteristics

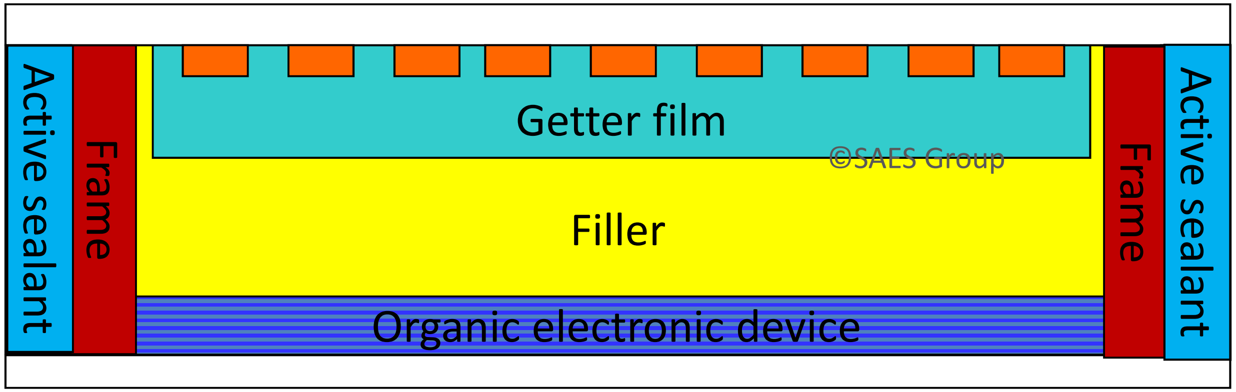
➢ Kinetics, capacity, gas partial pressure





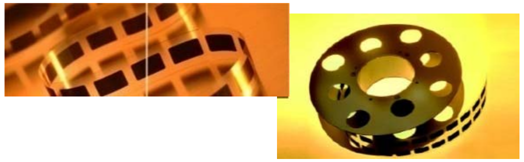
Getter encapsulation configuration

- ☐ Edge sealant
- ☐ Getter (pattern)
- ☐ Frame
- ☐ Getter (film)
- ☐ Filler

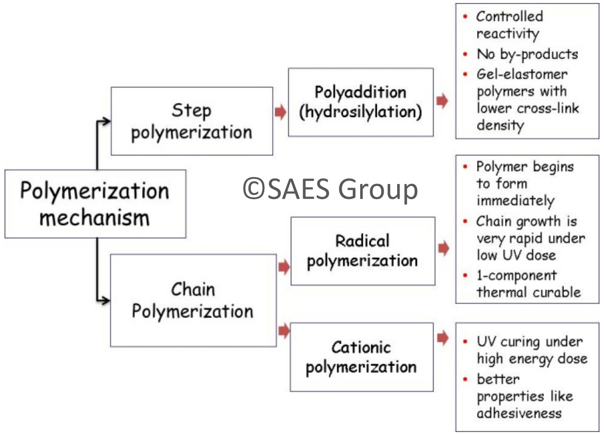


In order to limit dark spot area growth and pixel shrinkage below values significantly affecting the display uniformity: maximum H_2O pressure inside OLEDs ~ $1.1x10^{-4}$ Torr or ~ 0.1 ppm

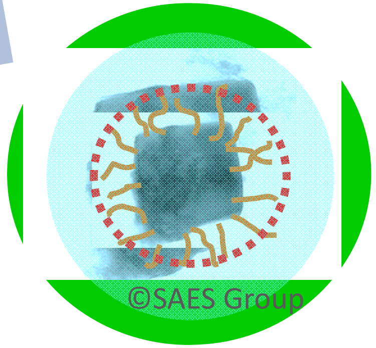
Functional Polymer Composites platform



Macromolecular Chemistry



Getter technology



Mixing Technologies

- Technology
  - Particle Material
  - Particle size
  - Surface modifier
  - Organic matrices

Getter composites: new systems

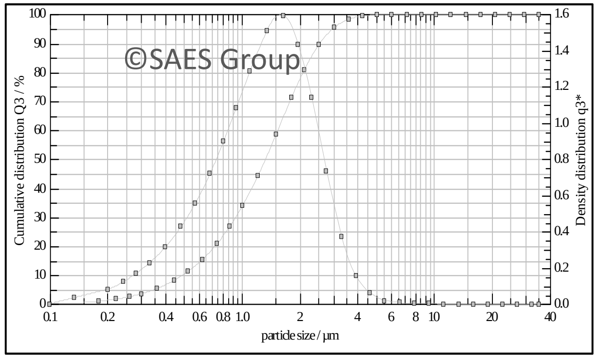
- Polymer-matrix micro- and nano-composites based on metal oxides
- Liquid getters based on perfluoropolymers and nanozeolites
- Polymer-matrix solid solutions of inorganic hydrophilic salts

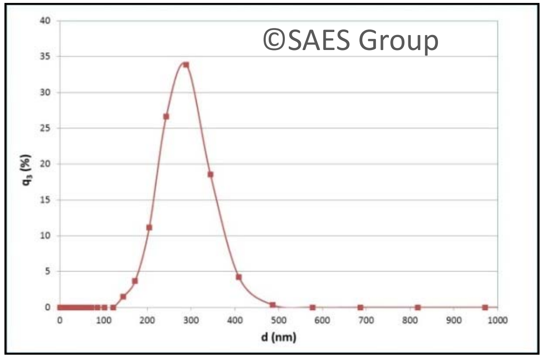
DryPaste® products family

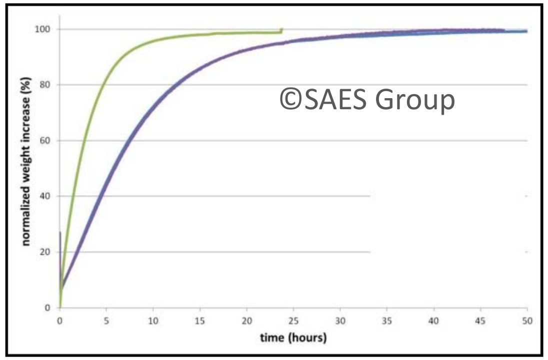
- All formulations are solventless formulations
- Consolidation process (when available) is promoted trough a polymerization mechanism
- No solvent evolution during heating treatment
- Purified formulations in order to low the VOC content
- For not-curable formulations, very long shelf life is assured

micro & nano Metal Oxide

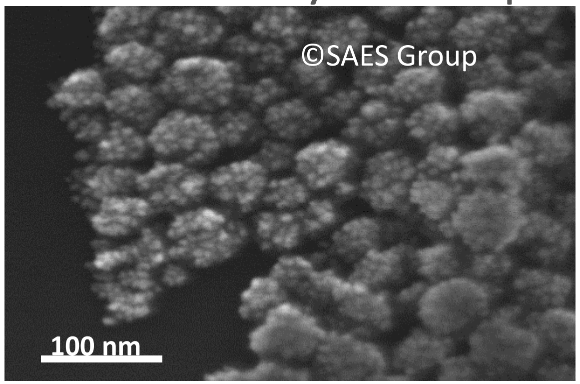
- Top-down approach by microsizing processing
  - Tuned reactivity and particle sizes control down to hundreds nanometers

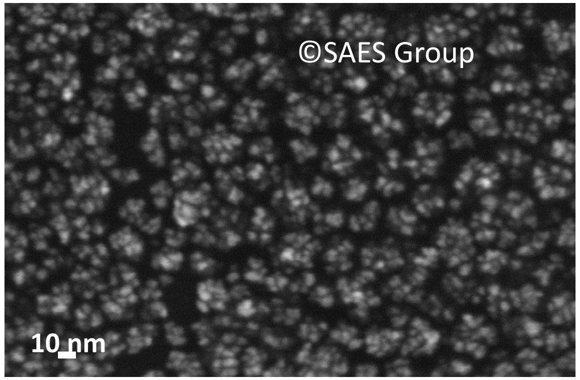


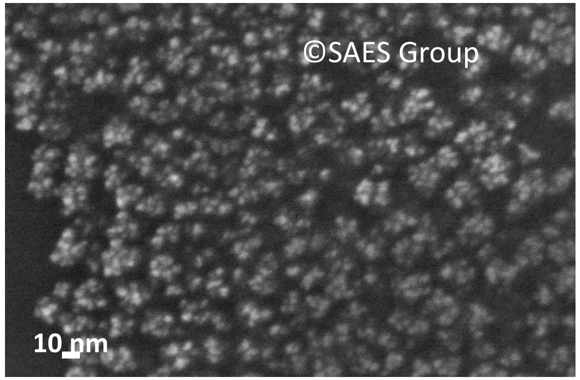




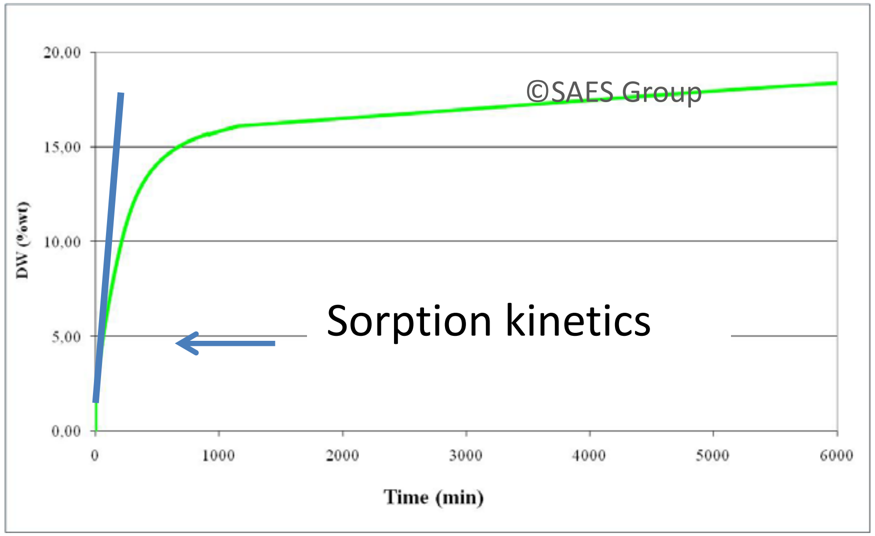
- Bottom up approach by colloidal synthesis
  - Particle size control through precursors characteristics and synthesis parameters

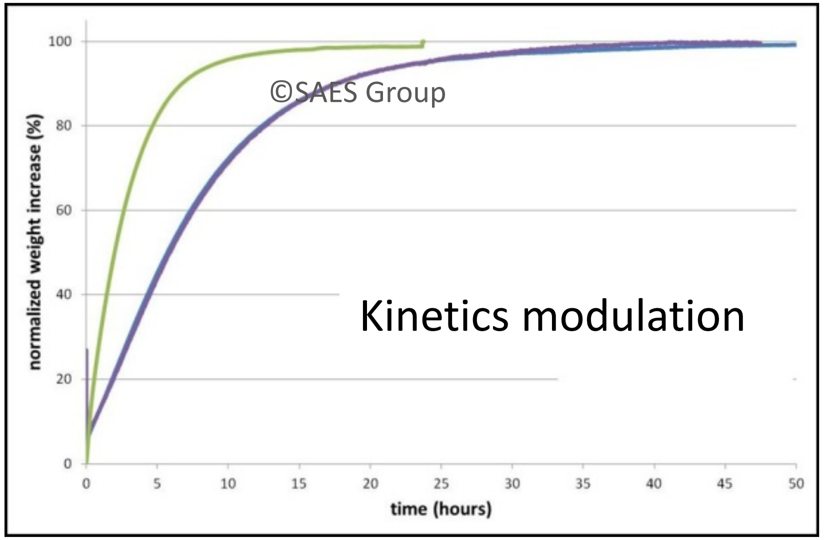


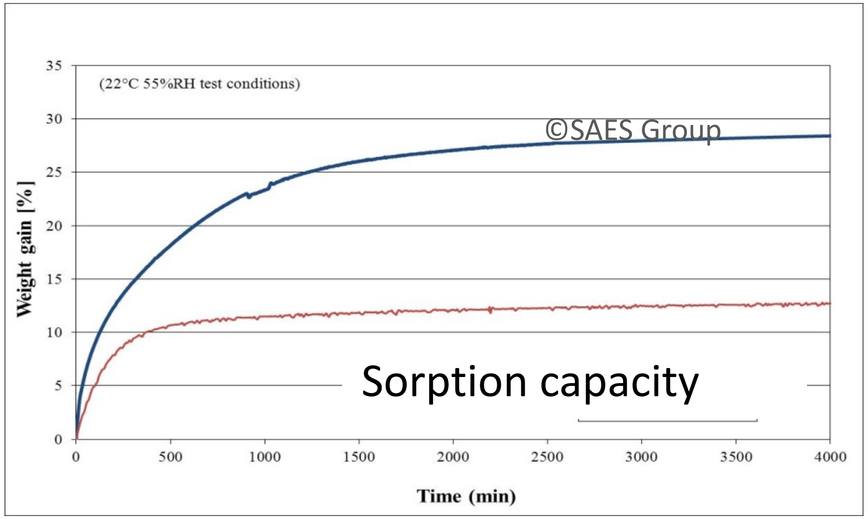


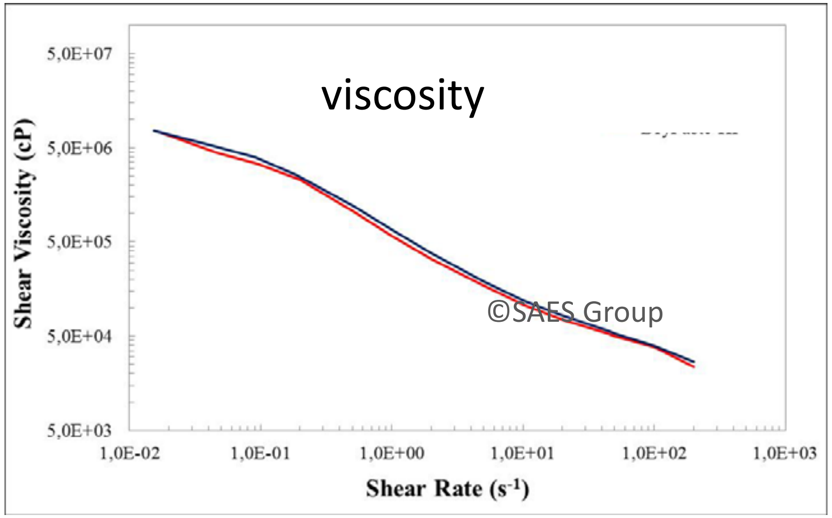


Properties modulation

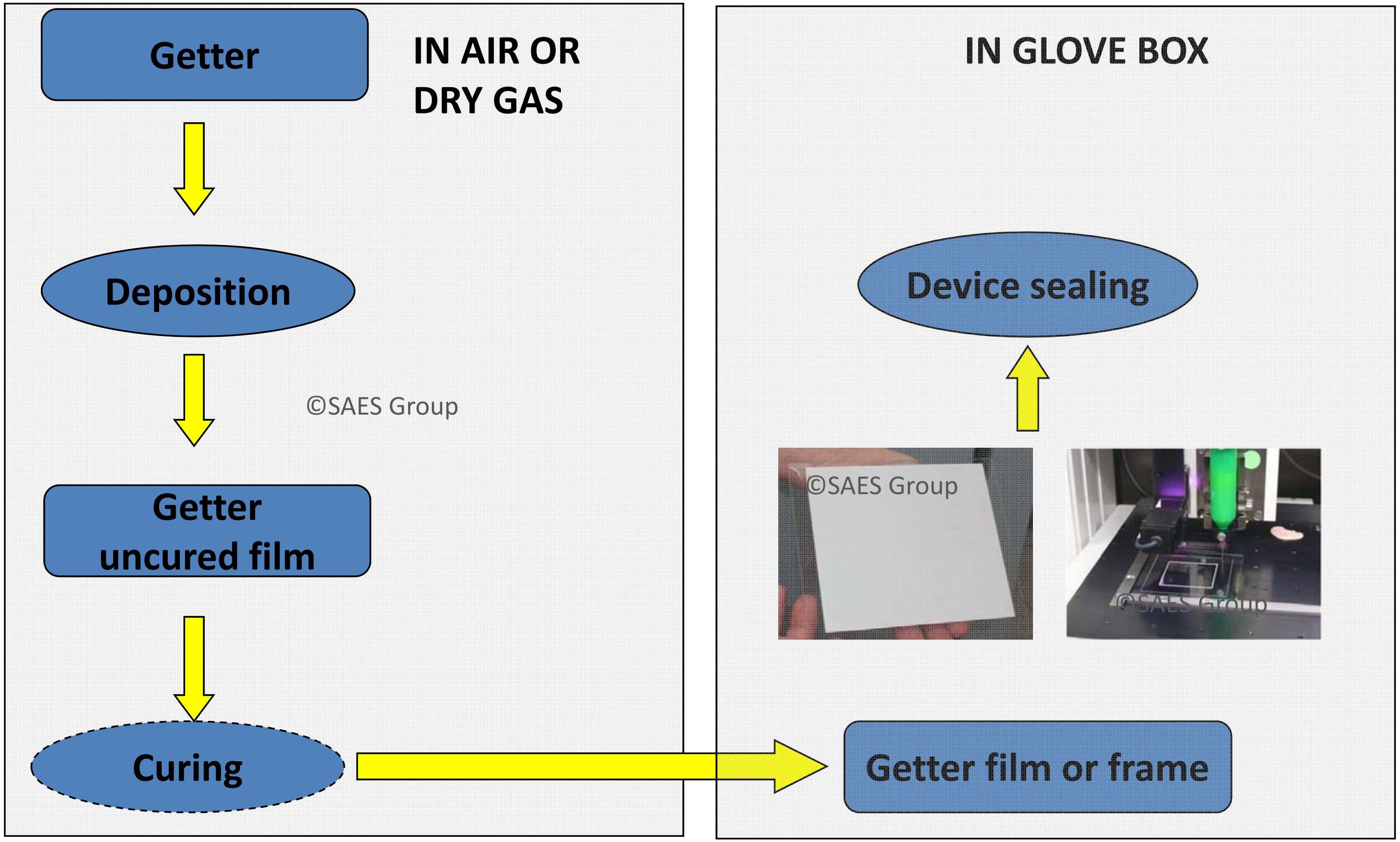








Process Flow



DryPaste® : datasheet

DryPaste - G

Dispensable Dryer

Product description

DryPaste-G is a high capacity, solventless, thermally curable, dispensable dryer, designed for use in OLED, Organic Electronics and other sophisticated applications. Due to its viscosity it can be applied by syringe or blading.

DryPaste-G films work as irreversible moisture getter.

DryPaste-G Moisture Sorption

Calculation example
Sorption capacity in air: 16% of dry weight
1cm x 1cm x 50 µm= 0,005 cm^3 x 1,3 g/cc= 0,0065 g= 6,5 mg
Moisture capacity = 6,5 mg x 16% = 1,04 mg

Material Property	Typical value	
	Paste	Cured Film
Appearance	white-brown paste	White film
Viscosity at 25℃ (cP) (*)	> 90.000	NA
Density (g/cm^3)	1,3	1,3
Filler load (%)	50	50
Weight loss at 100℃	NA	< 0,1 %
Moisture capacity (wt %)	16	16
Maximum particle size (µm)	5	NA
Storage temperature (℃)	2 – 40	-30 – + 170
Shelf life (months)	6	NA
Storage atmosphere	Dry if bag is opened	Dry

(*) at a shear rate of 5 s^{-1}

saes group

eDRY™: datasheet

eDry

Product description

eDry is a high capacity, solventless, thermally curable, dispensable dryer, designed for use in semiconductor, microelectronic, and opto-electronic packaging applications and other sophisticated applications. Due to its viscosity it can be applied by syringe or blading.

eDry films work as irreversible moisture getter.

eDry Moisture Sorption

Calculation example
Sorption capacity in air: >24% of dry weight
1cm x 1cm x 50 μm= 0,005 cm^3 x 1,3 g/cc= 0,0065 g= 6,5 mg
Moisture capacity = 6,5 mg x 22% = 1,4 mg

Material Property	Typical value		
	Paste	Cured film after 8h air-exposure	Uncured film after 8h air-exposure
Appearance	gray-brown paste	gray-brown	gray-brown
Viscosity at 25°C (cP) (*)	> 350.000	NA	NA
Density (g/cm^3)	1,3	1,3	1,3
Filler load (%)	50	50	50
Weight loss up to 200°C	NA	< 1 %	< 1 %
Moisture capacity (wt %)	> 24	> 22	> 20
Max. particle size (μm)	< 50	< 50	< 50
Storage temperature (°C)	5	-30 / +250	-30 / +250
Shelf life (months)	1**	NA	NA
Storage atmosphere	dry if bag is opened	dry	dry

(*) at a shear rate of 5 s^{-1}

Liquid getters based on perfluoro polymers

Perfluoro polyether

L → L → L

- Low volatility
- Chemical inertness
- Low surface
- High oxidative and thermal stability
- Wide temperature range stability
- High volume resistivity

ZetaFill^{TM}-F (not curable)

- One-component, low hygroscopic active filler
- Dispersion of SAES proprietary engineered nano-zeolites
- Active filler looks like a slightly translucent liquid
- Active filler shows liquid features

	ZetaFill-F3/LV-N/
Organic matrix	Perfluoro Polyether
Average particle size (nm)	300
Viscosity @ 5s-1 (cP)	3.000
Density (g/cm3)	1,90
Curing conditions	-
Moisture sorption capacity (%wt)	1,0
Organic matrix optical T%	n.a.
VOC (ppm)	**< 2 ,0**

saes group

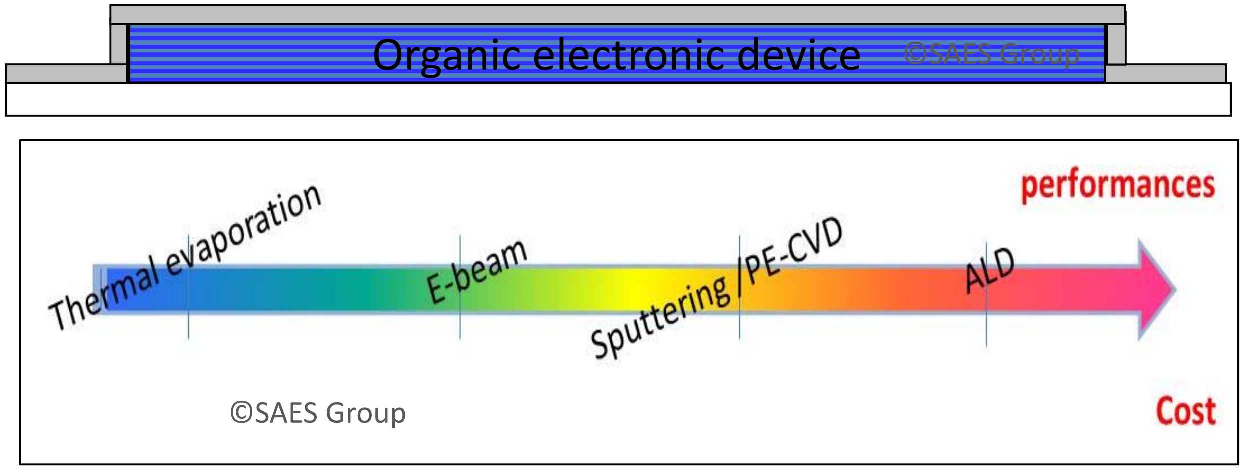
Types of encapsulation

- Different encapsulation approaches may be chosen depending on:
  - the desired lifetime
  - the inherent stability of the system
  - the target market for the organic device

- Encapsulation types:
  - Glass-to-glass encapsulation
  - Thin film encapsulation
  - Lamination of barrier films

Thin film encapsulation

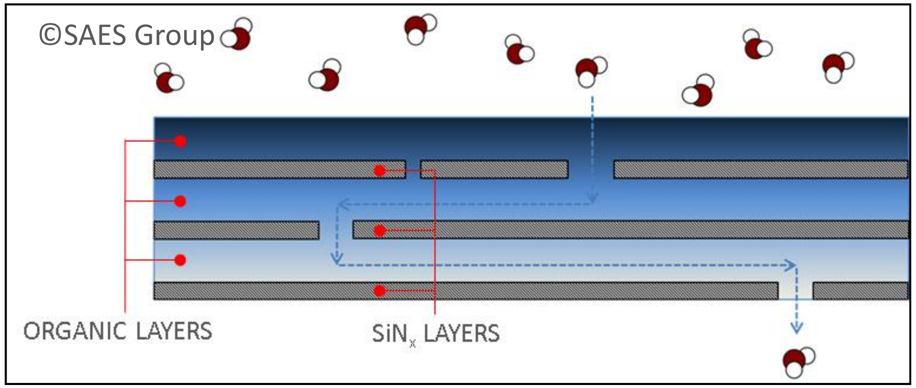
- Thin layers of inorganic materials (e.g SiOx or SiNx) are generally adopted to strongly reduce the diffusion of water and oxygen to acceptable levels.
- Typically the cost structure of multi-stack encapsulation material is strongly affected by the costs of the inorganic barrier layers



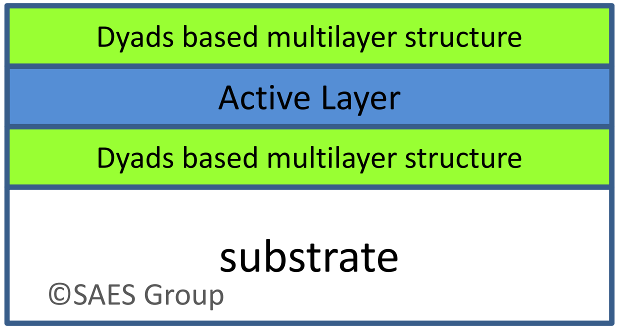
Intrinsic defects

- Inorganic layers have an intrinsic tendency to show columnar growth that is frequently characterized from defects generation providing easy paths for gas penetration

- Multilayer structures are adopted through a dyad approach where alternating layers of organic and inorganic materials (dyads) are applied to create a “tortuous path”



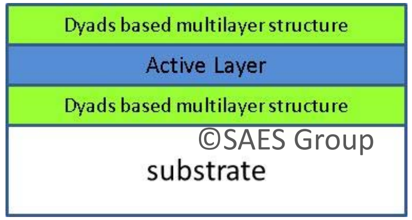
- The integration of an active layer can strongly slow the gar permeation



Polymer-matrix solid solutions of inorganic hydrophilic salts

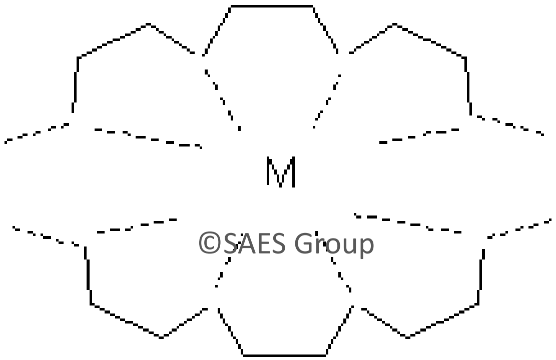
AqvaDry®

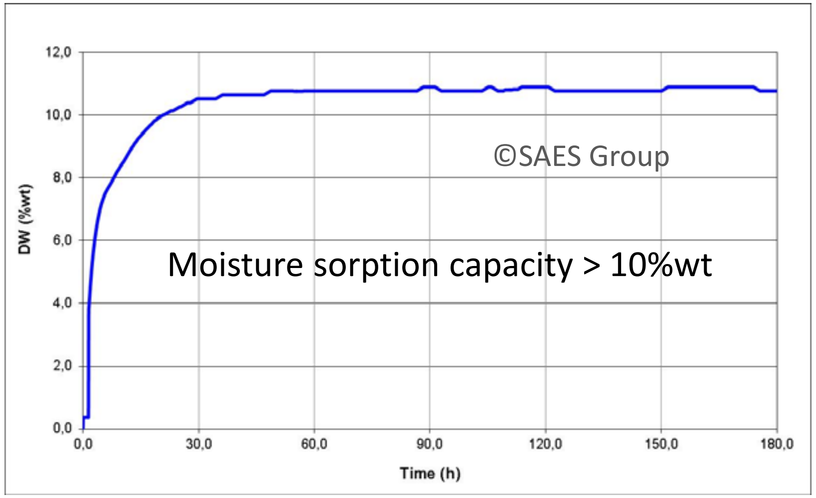
- AqvaDry is a liquid scavenger made of an active specie in a polymer matrix.
- It is designed to work as dryer film or as an active layer
- AqvaDry is a fluid and transparent liquid
- It is a solvent free scavenger
- No mixing or stirring is required
- Deposition must be carried out in glove box (< 10 ppm H_2O)
- Two versions: UV-curable (AqvaDry-U1)
  Thermally curable (AqvaDry-T1)



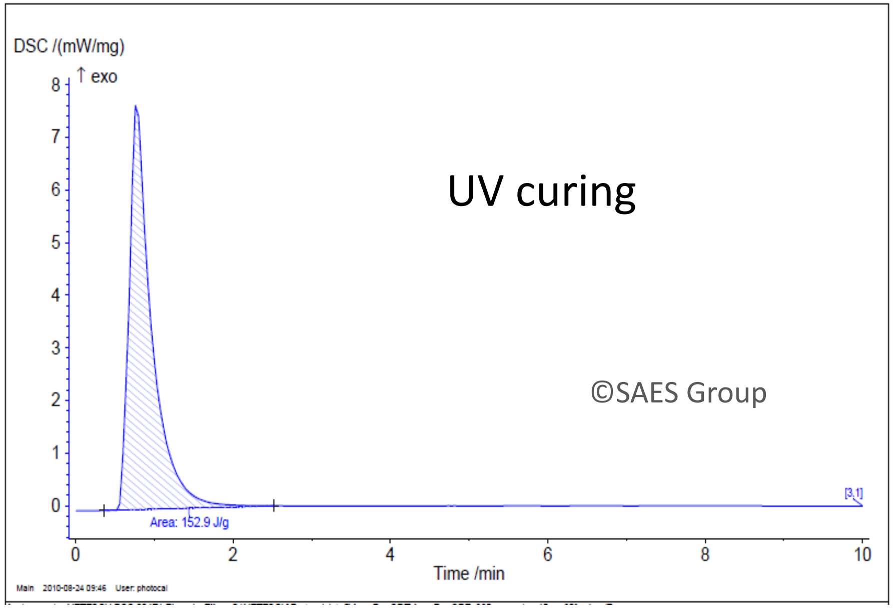
Inorganic salts (solid solution)

- Liquid scavenger made of an active specie in a polymer matrix
- Strong coordination between the getter materials and the polymer matrix





Curing conditions



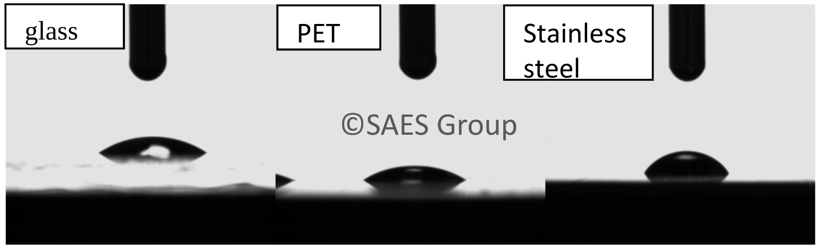
- UV curing conditions for 10-100 um thick layer:

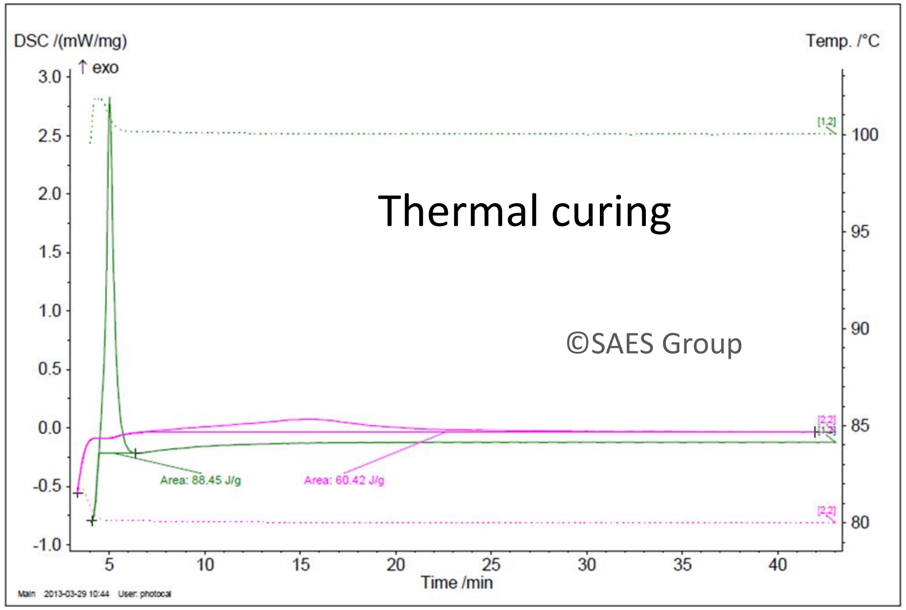
  100mW/cm2 for 15s (@365nm)
- Volume shrinkage ~ 8% (z-axis)
- No Thermal post-curing required

- Thermal curing conditions:

  80°C for 30 minutes

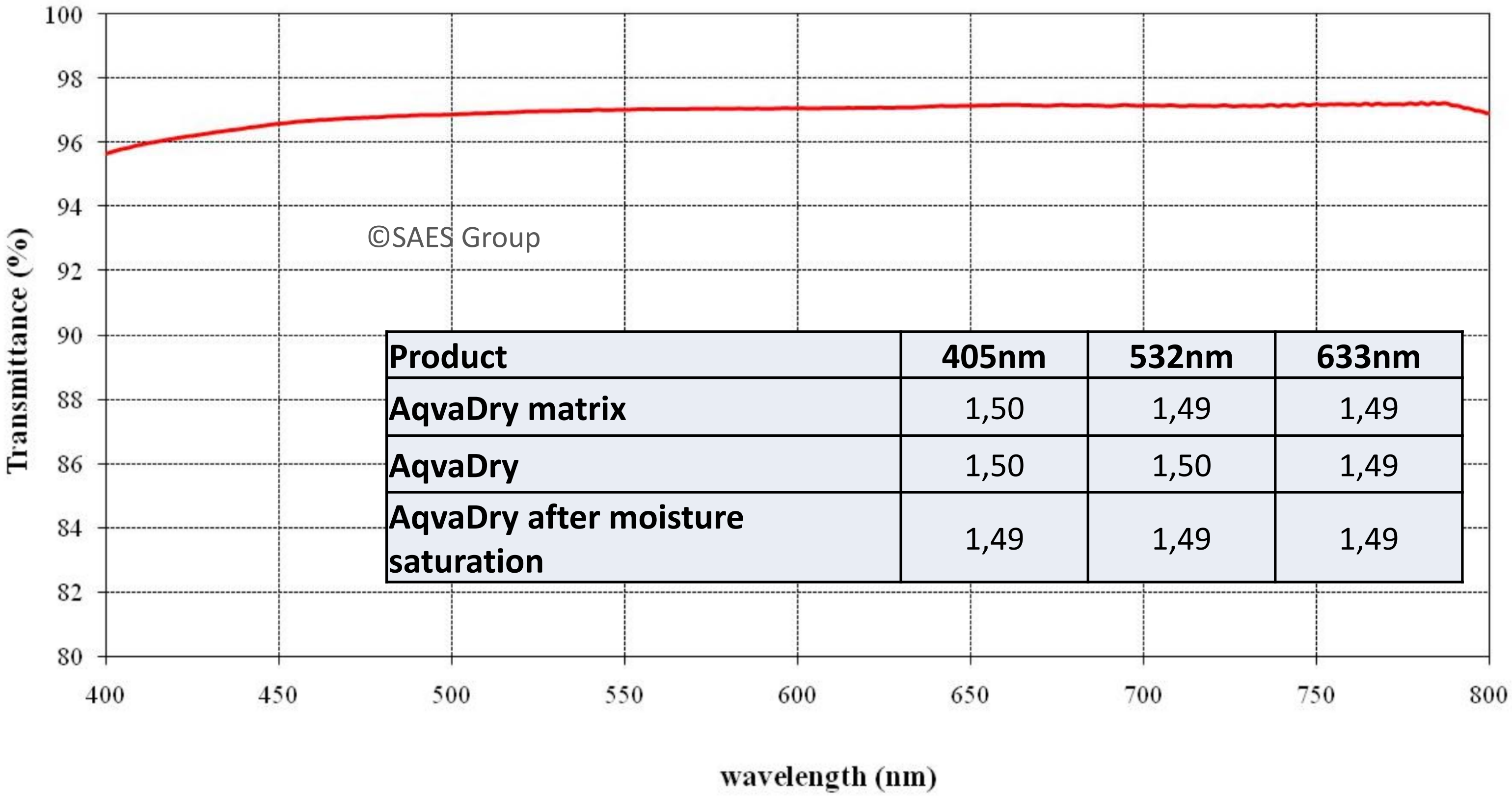
  100°C for 15 minutes





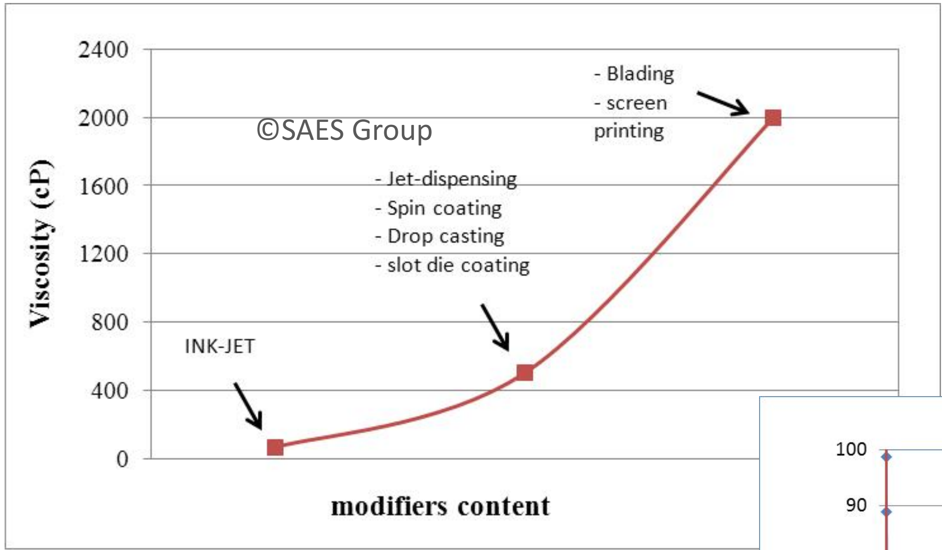
Optical Transmittance

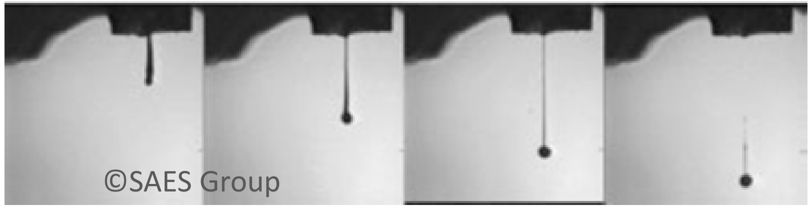
Transmittance > 95% for a film 100um in thickness



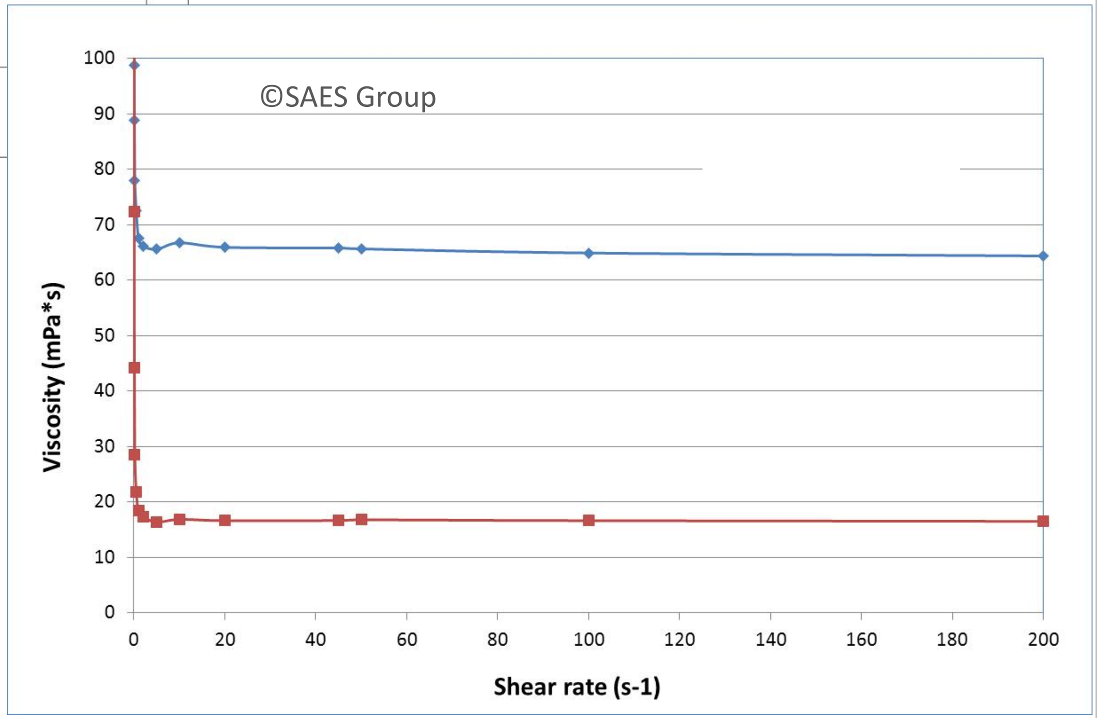
Product	405nm	532nm	633nm
AqvaDry matrix	1,50	1,49	1,49
AqvaDry	1,50	1,50	1,49
AqvaDry after moisture saturation	1,49	1,49	1,49

Getter Ink : rheological properties





Drop break-up is strongly related to the polymer molecular weight.



AqvaDry® datasheet

AqvaDry

Transparent Dispensable Dryer

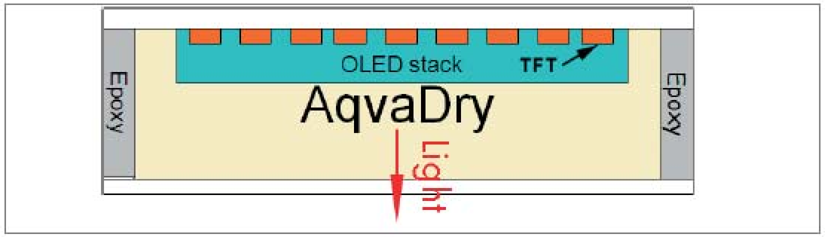
HIGHLIGHTS

General Features

- ☐ High moisture sorption capacity to assure long life to organic devices
- ☐ The material can be used as film and filler
- ☐ Optical transparency in the visible region during and after moisture adsorption
- ☐ Compatibility with standard production process
- ☐ Compatibility with ODF production process
- ☐ Possibility of thermal and UV curing

Product Description

The development of Active Matrix OLED (AMOLED) displays and devices is challenging the traditional dryers technologies both in terms of production process compatibility and optical properties. SAES has succesfully developed a new wave of dryer materials "AqvaDry" that are optically transparent in the visible during moisture adsorption as well as are compatible with traditional display manufacturing production processes, in particular with One Drop Fill (ODF) process. AqvaDry can be used in form of a film, but also in form of a filler between the two glass plates of AM OLED displays.



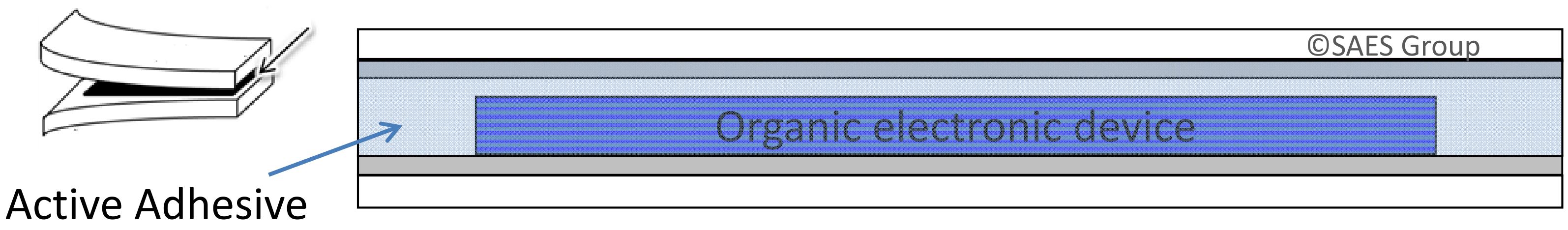
Types of encapsulation

- Different encapsulation approaches may be chosen depending on:
  - the desired lifetime
  - the inherent stability of the system
  - the target market for the organic device

- Encapsulation types:
  - Glass-to-glass encapsulation
  - Thin film encapsulation
  - Lamination of barrier films

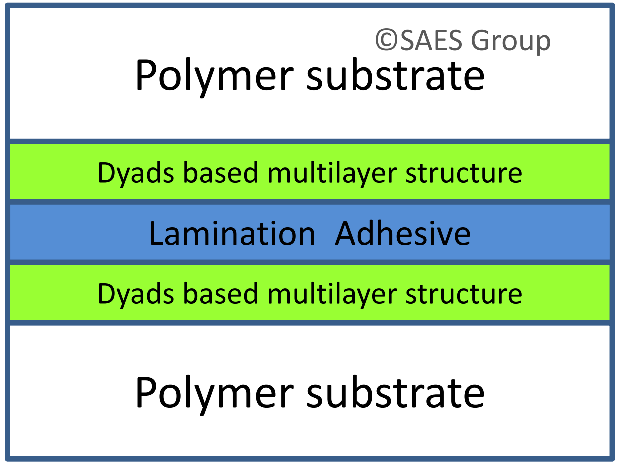
Lamination of barrier films

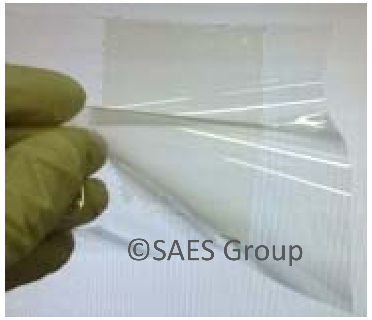
- As polymer substrates do not offer the suitable barrier performance for many applications, the application of thin film barriers layers is required to get sufficient lifetimes
- A huge advantage of multilayer barrier technology is the possibility to manufacture the barrier films in advance, so their production conditions are not limited by the sensible material that will be protected
- Multilayer structures are combined together by using a lamination process where a polymer adhesive is usually applied onto the full area



SAES approach : active lamination adhesive

- UV or thermally curable, solventless, 1-component formulation
- Medium viscosity dispersion of active material in organic matrices
- Formulation designed for multilayer barrier integration
- Good wettability on PET and PET/SiOX





SAES approach : active lamination adhesives

- FlexGloo TM
  - sealant able to combine the superior barrier performances of epoxies with mechanical properties typical of flexible adhesives.
  - Available in UV , visible or thermally curable formulation
- AqvaDry® Adhesive
  - Sealant combines high getter performances of transparent getter with mechanical properties typical of acrylic adhesives.
  - Available in UV or thermally curable formulation

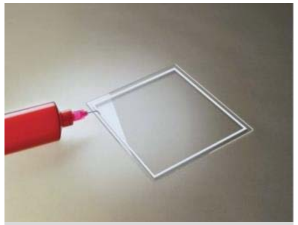
Material Property	FlexGloo	AqvaDry® Adhesive
Appearance	Whitish glue	transparent
Viscosity @ 25 °C (cP) (*)	5800	1500
Density (g/cm³)	1.20	1.10
T_g (glass transition temperature) (°C)	20-30	10
Storage Modulus @ RT (MPa)	10	n.a.
Storage temperature (°C)	+2 - +5	+2 - +5
Shelf life (months) (***)	3	6
Pot life (RT, < 10 ppm H_2O) (days)	> 5	> 5
Storage atmosphere	Dry air or nitrogen	Dry air or nitrogen
Lap Shear Strength(****) (MPa)	0.4	n.a.
WVTR @ 23°C, 65% R.H. (*****)	3.0	n.a.
Water sorption capacity (%wt)	1	10

SAES (FPC) Business Dev.

Main applications

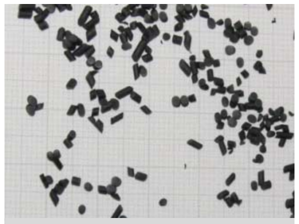
- ✓ OLED Displays
- ✓ OLED Lighting
- ✓ OLET Displays
- ✓ LCOS Displays
- ✓ EPD Displays
- ✓ Gas Barrier films
- ✓ Specialized food packaging
- ✓ Hybrid Getters for special applications

- Dispensable, printable and optically transparent dryers and getters
- Active edge adhesives
- Alkali Metal Dispensers


Dispensable Getters - Glue


Dispensable Getters - Filler


Dispensable Getters - Paste


Hot Melt Getters

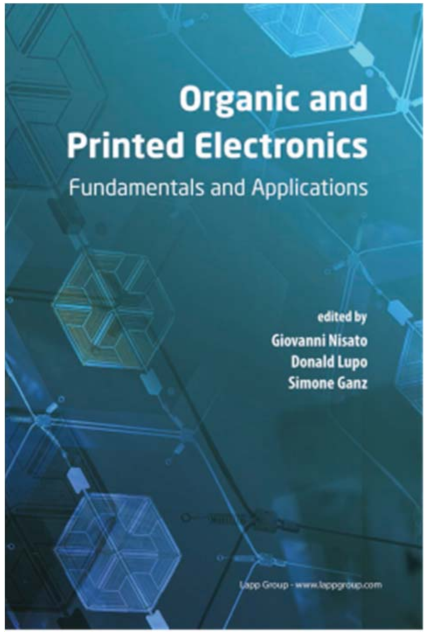
Conclusions

- A new family of Functional Polymer Composites has been described
- Dispensable getter materials properties can be designed by considering the final application requirements
- The integration of novel dispensable SAES Functional Polymer Composites and concepts provide a lifetime insurance for organic electronic devices

New book on Organic Electronics

- Organic and Printed Electronics:
  Fundamentals and Applications

  - Edited by G. Nisato, D. Lupo , S. Ganz
  - Forthcoming by Pan Stanford
  - Chapter: Encapsulation of Organic Electronics
    - John Fahlteich, Andreas Glawe, Paolo Vacca



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  - Elisabetta Bossi, PhD student in Materials Eng.
  - Stefano Zilio, Head of Chemical and Physical Characterization Lab

Thank you for your attention

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