Gas Barrier Coatings
For Flexible Packaging

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working for you.

AIMCAL EUROPE WEB COATING CONFERENCE 2012
12th June Prague
Outline

- Gas barrier Coatings
  - Definition & Background
  - Market Information

- Nanocomposite Gas Barrier Coatings
  - Exfoliated Clay Composites
  - Analysis of Clay Composite Coatings

- Performance in Packaging Applications
  - Environmentally Friendlier Packaging
  - Coating Applications

- Conclusions
Barrier Coatings: Definition

Prevent the penetration (or loss) of specific gases, light or aroma/odour which could compromise the integrity of the packaged product.

Typical Barrier Coatings:
- **Oxygen Barrier**
- Moisture Vapour Barrier
- CO$_2$ Barrier
- UV Barrier
- Aroma Barrier
History/Evolution Of Gas Barriers in Packaging

Glass & Tin
Al Foil

Plastics

First coatings on plastics

Extrusion
Lamination

SiOx & AlOx
Ceramics

Emerging
Technologies

Excellent barriers but heavy

Poor barriers, but light weight

Reasonable barriers
Especially PVdC and Al metallisation also lightweight

EVOH- Excellent O2 Barrier at medium %RH Thick laminates

Excellent moisture vapour and O2 barriers, transparent but brittle

Organic polymer structures and nanocomposites

All of these materials are in present use today

There is no one barrier technology that meets all requirements
Printable Oxygen Barrier Coatings will offer an alternative to existing High Barrier Options

Oxygen Transmission Rates of Typical Flexible Packaging Materials

- Al Foil
- PET-Al
- PET-SiOx/AlOx
- PET-PVDC
- PET-EVOH
- Nylon
- PET
- PP/PE

OTR (cm³/m²/day, @ 23°C & 50% RH)

(Sun Chemical Measurements)
Gas Barrier Coatings:
Market information
Market Overview - Barrier Materials for Food Packaging

Global Addressable (Printable) Market for Barrier Coatings potential – 2,074,000 tonnes 2008

Conversion from current barrier technology/film is a multi $ million coating opportunity

Source: ADC/Kline
Coating Applications

Packaging market overview (barriers)

Market / Applications
- Chilled Food
- Dry Food
- Liquid Packaging

Barrier technology
- PVdC
- EVOH
- Nylon
- Speciality Oxides
- Metallised
- Co-extrusions

Package structure
- Bags
- Lidding
- Stand Up Pouches
- Forming Webs
- Wraps

Temperature & Relative Humidity are Important Considerations
Printable Oxygen Barrier Coatings

A gap exists in the market for transparent barrier coatings; free from halogenated compounds, converter applied, which afford high barrier performance.
Nanocomposite Gas Barrier Coatings
Description, Preparation, Function & Analysis
Emerging Technologies

- **Nanocomposites**
  - Highly dispersed/exfoliated silicates/clays

- **Sol-Gel Coatings**
  - Inorganic/Organic composites formed in-situ
  - e.g. $\text{Si(\text{EtOH})}_4 \xrightarrow{\text{Condensation}} \text{Si(OH)}_4 \xrightarrow{\text{Hydrolysis}} ‘\text{SiOx}’$
  - Organically modified ceramic lacquers.
  - vapor and barrier layer strategy

- **Epoxy Based Coatings**

- **PAA & PGA-based coatings**
Sun Chemical’s Nanocomposite Barrier Coatings

- Finely dispersed nanoparticulate (intercalated/ exfoliated) silicate mineral in a polymer solution/ dispersion
- The dispersion is applied using traditional printing and drying techniques
- The dried polymer coating on a film enhances the oxygen barrier performance of the substrate

Functional oxygen barrier of less than 1.0 cm$^3$/m$^2$/24h at 23°C & 75%RH
The generally accepted theory for barrier improvement is that dispersed/exfoliated ‘platy’ minerals increase the diffusion path length through a coating; ‘TORTUOUS PATH’.

\[ d_2 > d_1 \]
X-Ray Diffraction shows the increase in d-spacing (001) when the clay is successfully exfoliated.

\[ d_{001} = 12.1 \text{ Å} \]
Analysis of Nanocomposites: XRD

Nanocomposites with Higher Clay Loadings

**Nanocomposite; c.25% (w/w) Clay**

35 Å

**Nanocomposite; c.40% (w/w) Clay**

26 Å

Intercalated composites or highly ordered exfoliated composites?
Analysis of Nanocomposites; Electron Microscopy

SEM: Agglomerated Clay

TEM: Nanocomposite Coating

Cast of Dilute Coating on Cu Grid (Sun Chemical)
TEM of Cross Sectioned Coating on PET Film

Clay Particles
The Effect of Exfoliation on the Visual Appearance of NanoComposites

Unfilled Polymer

Non-Exfoliated Clay (Tactoid)

Exfoliated Clay Nanocomposite
The Effect of Clay Exfoliation on the Oxygen Barrier

Oxygen Transmission Rates were measured with an Oxtran 2/21 at 23°C&75%RH.
Nanocomposite Coatings - Influence of Aspect Ratio

Oxygen barrier vs Aspect Ratio

Aspect Ratio = \( \frac{l}{d} \)

Concentration of Mineral in the Coating (% (w/w))

Oxygen Transmission Rate at 23°C & 50%RH (cm³/m²/24h)

Lamination Bond Strengths vs Aspect Ratio

Asphaltolysis vs Aspect Ratio

Concentration of Mineral in the Coating (% (w/w))
Understanding the Role of Clay on Oxygen Barrier Performance; a Mechanistic Study

Arrhenius Plots used to determine the effect of changing clay concentration on Oxygen Permeability

- Slope $\alpha - E_a$ (Activation Energy)
- Therefore; no change in $E_a$
- Polymer Matrix character does not change
- Increase in diffusion path length the likely mechanism

(% Clay = wt. % in the dry coating applied to PET)
Using Arrhenius Plots; Log OTR v. 1/T to Extrapolate Performance

Mocon Oxtran 2/21 Min Temp =11°C
Performance Clay Composite Coatings in Packaging Applications
Comparison of Functional Barriers on PET

Untreated polyester film OTR 100-110 cm\(^3\) / cm\(^2\)

- PVDC major disadvantage – contains chlorine & higher OTR
- AlOx / SiOx major disadvantage – brittle & higher OTR
- EVOH deteriorates over time in humid storage conditions

Oxygen transmission rate measured using a MOCON OX-TRAN® 221 within 24 hours of coating.

Varies with grade and cost

PET: 50\(\mu\) PE:EVOH:PE Extrusion

0.3\(\mu\) dry coating weight
The clay composite coatings provide excellent barrier performance on both PET and OPP with dry film weights as low as 0.2 g/sm (dry).
Influence of Relative Humidity & Coat Weight

Clay Composite coating 12μm PET, tested at 50%RH and 75% RH, at 23°C

Higher Coat Weights are Generally needed at Elevated %RH
Performance Benchmark – Effect of Humidity

Oxygen Transmission Rate (cm$^3$/m$^2$/day @ 23°C)

Relative Humidity

- Clay-Composite
- PET-PE/EVOH/PE
- PET-PVDC
Clay-composite coating improved performance at elevated temperature
Oxide-coated films have poor flex resistance
(Performance improves when laminated and coated)
Clay composite coatings perform as well as EVOH Structures
Key Packaging Trends

1. Rigid to flexible
2. Visible product contents
3. Light weighting
4. Single piece packs
Coating Applications

Trend #2: Visible product contents

Longer shelf life. Visible content packs with high oxygen barrier.
Coating Applications

Trend #4: Single piece packs

Excellent oxygen and aroma / odor barrier for base substrates.
Coating Applications

Light weighting

Commercial 3-Ply Laminate

- Removal of barrier film or foil and one layer of adhesive
- Lighter weight packaging (up to 30% reduction)
- Improved laminate integrity (post flexing $O_2$ barrier improvement)
- Lower material and / or operational costs
- Improved recycling
- Improved shelf life

2-Ply Laminate plus printable barrier coating
Conclusions

- **SunBar™** Clay composite oxygen barrier coatings
  - enable (transparent) barrier packaging having exceptional barrier properties.
  - Oxygen Barrier Performance equivalent/superior to existing technologies
  - Can be applied by conventional printing methods
  - can reduce the environmental impact of plastic packaging. (lightweighting, improved recycling, Cl free, replace metal, more flexible)

- Increasing the mineral aspect ratio provides improved barrier performance.
- Improvements in oxygen barrier shown to result from an increase in diffusional path length (‘Tortuousity’).
Acknowledgements

- Thank you for your attention
- The Functional Coatings Research team at St. Mary Cray (UK)
  - Derek Illsley, Asad Khan, Robert Lines, Safray Khan, Farid Azizian, Peter Brownrigg
- Analytical Departments at St. Mary Cray and Colours Group (USA)
  - Jayne Barnes, Hetal Patel, Lisa Clapp, Costas Nicolaou

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