

Agenda



- Introduction
- 2. PVC (**P**oly**v**inyl **C**hloride)
- 3. PE (**P**oly**e**thylene)
- Bitumen Complex Mix of Hydrocarbons
 Polymer Modified Bitumen (PMB)
- 5. Butyl-Rubber
- 6. Conclusions





1. Introduction

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Objective of this Presentation



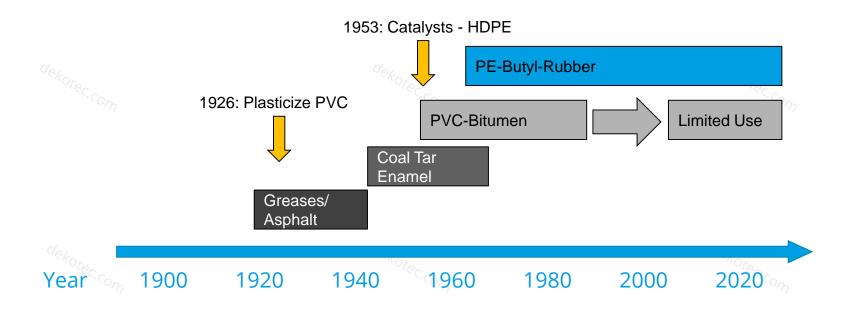
- To understand and to compare the chemistry and the basic properties of each material:
 - PVC (Polyvinyl Chloride)
 - PE (Polyethylene)
 - Bitumen-Complex Mix of Hydrocarbons/
 Polymer Modified Bitumen (PMB)
 - Butyl-Rubber
- Special focus:

Suitability for use in Corrosion Prevention Tapes



History







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Structure of Tapes



Cold-applied Polymeric Tapes: ISO 21809-3 – Coating Type 12

Carrier Film + Compound

- Carrier Film: PVC or Mesh or PE
- Compound: Bitumen or Butyl-Rubber



<u>2-Ply</u>

PVC – Bitumen

Mesh - Bitumen

PE - Butyl-Rubber







2. PVC (Polyvinyl Chloride)





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PVC - History



- 1835 (France): *Henri Victor Regnault* accidentally synthesized Vinyl Chloride. With the exposure to UV, a white solid (powder) developed: Polyvinyl Chloride. (Regnault was not aware of his discovery).
- 1912 (Germany): Fritz Klatte synthesized Vinyl Chloride from Ethine and Hydrogen Chloride and laid the foundation for the production of PVC. (No products were successfully market at that time).
- Due to lack of raw materials as a result of World War I, production of PVC started in the USA and Germany.
- 1926 (USA): Plasticize PVC by blending it with various additives **Essential for application of tapes!**



PVC - Chemical Structure



Vinyl Chloride Monomer

Acetylene + Hydrogen Chloride (gas)
Using Mercuric Chloride as catalyst (toxic to humans)

$$C_2H_2+HCI$$
 CH2=CHCI

Polymerization of Vinyl Chloride Monomer

Chemical reaction of monomer molecules to form a Polymer chain (=PVC)



PVC - Additives



Various processing aids are needed:

- Impact modifiers Thermal modifiers
- Fillers
- Biocides
- Pigments
- Plasticizers
- Heat Stabilizers UV stabilizers



PVC - Plasticizers Issue



Plasticizers (up to 40%) make PVC flexible, but only at -18°C and higher

Exudation - "Sweating Effect":

<u>Plasticizers are not stable and migrate to:</u>

- Environment: Groundwater Pollution
- Adhesive (Bitumen)
 - Backing stiffness embrittlement: Cracking's
 - Adhesive plasticizing: Gummy with poor Lap Shear

Plasticizers are suspected to cause **Cancer**









PVC + Heat (from +70°C) Dehydrochlorination

Dehydrochlorination: Allylic Chloride Structure + HCl

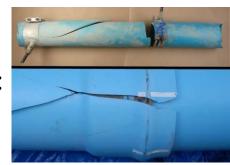
Allylic Chloride Structure: Thermally unstable in Polymer & Toxic

HCl + H₂O (vapor)
 Hydrochloric Acid: Corrosive & Toxic

Stabilizers: to reduce loss of HCl

But: Dehydrochlorination is autocatalytic ("self-dissolution"):

Reaction products are catalysts for the same reaction – **Snowball Effect**







3. PE (Polyethylene)





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PE - History



- 1898 (Germany): White waxy substance was accidentally synthesized by Hans von Pechmann. (no practical use at that time)
- 1933 (UK): Eric Fawcett & Reginald Gibson "accidentally" synthesized in industrial manner a white, waxy material. Later Michael Wilcox Perrin produced in a high-pressure synthesis Polyethylene.
- 1944 (USA): Bakelite Corp. & DuPont started commercial production.
- 1951 (USA) and 1953 (Germany):
 Milestone success: catalysts + mild temperature & pressure + Ethylene
 - LDPE (Low Density PE) &
 - HDPE (High Density PE).







Chemical Reaction: Catalyst + monomer molecules to form Polyethylene chains

Monomer molecules: Ethylene (simplest Alkene)
Similar chemical composition as **Candles or Chewing-Gum**







Rigidity/Flexibility



Flexible from -40°C without Plasticizers

High ductility



Plastic deformations before rupture

High impact strength



Absorbs energy and deform without fracture







No Dehydrochlorination



No heat stabilizers



Good Thermal stability

Melting Point (HDPE)



120°C – 180°C

Melting Point (PVC)



77°C – 88°C



PE - Electrical Resistance & Water Absorption



Electrical Resistance (EN 12068)

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 10^{16} Ω cm 10^{11} Ω cm

Water Absorption (ASTM D570)

PE PVC Plasticized



0.02% - 0.06%



0.20% - 1.00%



PE - Basic Properties (NACE CIP Level II)



- Temperature resistant close to +100°C.
- Good low temperature flexibility.
- Excellent resistance to chemicals.
- Resistant to creep.
- High impact resistance.
- Excellent tensile strength.



PE - Basic Properties (NACE CIP Level II)



- High electrical resistivity.
- Insoluble in organic solvents.
- Does not crack under stress.

Perfect for Corrosion Prevention Tapes

Note: There is no PVC property mentioned by NACE





4. Bitumen

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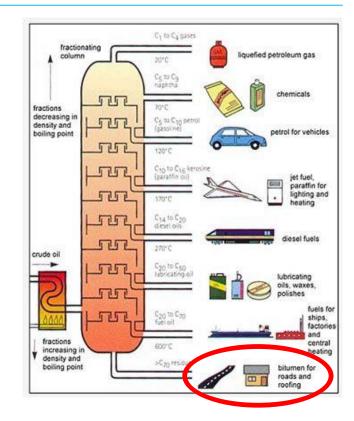
Bitumen - Asphalt



- Complex Hydrocarbons (C_nH_m) Mixture
- Natural:



- Refined: Crude Oil Distillation
 - 1500 Crude Oil types, but:
 - only 7% are suitable for qualitative Bitumen
 - Quality issue No defined composition



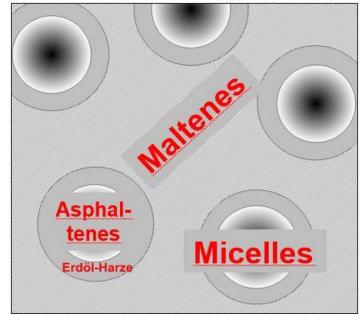


Bitumen - Colloidal Model



This model explains the aging behavior of Bitumen

- Non-soluble Solid Asphaltenes radius in nm (10-9 m)
- Asphaltenes are coated by soluble Resins
- Asphaltenes + Resins= Solid Micelles
- Oily Liquid matrix: Maltenes
 Temperature sensitive
- Sol Type Bitumen
 Asphaltenes Micelles are fully dispersed & non-interactive





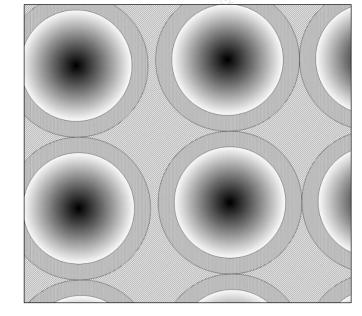
Bitumen - Colloidal Model (Structural Ageing)



When Bitumen ages:

- Asphaltenes are growing (Oxidation) Micelles are growing
- Maltenes evaporate
- Micelles are clumping & forming chains structures

Gel Type Bitumen Ratio: Asphaltenes/Maltenes increases Bitumen becomes hard, brittle & porous!







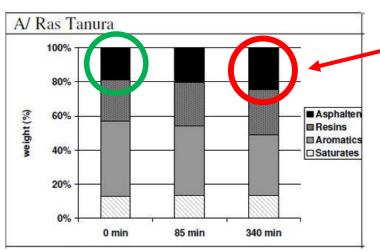


Rolling Thin Film Oven Test (RTFOT) – ASTM-D1754 & EN 12607

<u>Asphaltene expansion rate</u>:

- Depends on Crude Oil origin & temperature
- Is linear with time





The proportion of Asphaltenes is considerably growing after only 340 min.



Bitumen - Colloidal Model (Structural Ageing)



Structural Ageing is the weak point of Bitumen!

- Oxidation is the most influential factor.
- Ageing is a process that can not be interrupted.

Ageing speed depends on:

- Crude Oil Origins & temperature
- Bitumen mixture (**Polymers** can only reduce ageing speed).

Ageing Result: Bitumen becomes hard, brittle & porous!







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Bitumen becomes hard, brittle & porous







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Polymer Modified Bitumen (PMB)

Polymers (ex: SBS, SBE, EVA, EBA) are added:

- ...to make the mixture sticky (adhesion).
- ...to increase plasticity window temperatures (breaking-softening).

BUT:

- Cheap Polymers don't reduce ageing speed.
- Non-homogeneous mixture (Polymer chains are not broken during mixing).
- Ex: Problems with storage conditions!



Bitumen - Pipeline Coatings (Storage Issues)



Storage at Room Temperature (+23°C) for 5 months:

PVC-Bitumen:



Can no longer be used

PE-Butyl Rubber (3-ply coextruded):



Still in perfect condition



Bitumen - Pipeline Coatings (Ageing Testing)



100 days (T_{max}+20°C) aging tests – EN 12068 & ISO 21809-3:

Requirement Peel Strength to steel surface: $A_{100}/A_o \ge 0.75$

- Mesh-Bitumen Tape (2-ply laminated): $A_{100}/A_o \pm 0.60$
- PE-Butyl-Rubber Tape (3-ply coextruded): $A_{100}/A_o \ge 0.90$



Bitumen - Pipeline Coatings (Ageing Testing)



Hot Water Immersion (HWI) Tests – ISO 21809-3:

Requirement Peel Strength to steel surface: ≥ 1N_{/mm}

Requirement Peel Strength to steel surface after 28 days HWI: $\geq 0.4N_{/mm}$

<u>Initial</u> <u>After HWI</u>

- Mesh-Bitumen Tape (2-ply laminated): $> 1.0 N_{/mm} 0.2 0.4 N_{/mm}$
- PE-Butyl-Rubber Tape (3-ply coextruded): $> 3.0 N_{/mm} > 3.0 N_{/mm}$







High Porosity = high Cathodic Protection (CP) current demand

ISO 15589-1:2015 – Cathodic Protection onshore Pipelines.
 § 8.4. Cathodic Protection Current Demand

§ 8.4.2 - Coating Breakdown Factors (f_f)

 $I_{tot} = \pi D \times L \times k \times j \times f_f$

I_{tot}: total current demand

k: contingency factor - non uniform distribution (≥ 1.25)

j: design current density (100mA/m² - 1A/m²)

f_f: High Coating Breakdown Factor = High CP current demand



Bitumen - Pipeline Coatings (Porosity Issue)



$$f_f = \mathbf{f_i} + (\Delta \mathbf{f} \times \mathbf{t_{dl}})$$

 $\mathbf{f_i}$: initial $\mathbf{f_f}$

 Δf : Avg yearly increase of f_f

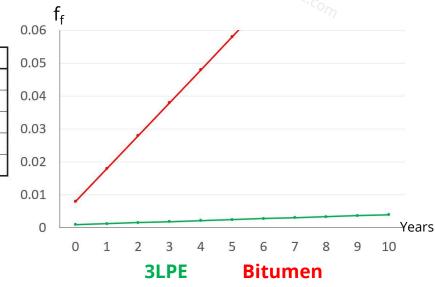
t_{dl}: design life (years)

Table 2 — Typical design coating breakdown factors

Pipeline coating	$f_{\rm i}$	Δf
FBE	0,005	0,003
3LPE	0,001	0,000 3
3LPP	0,001	0,000 3
Liquid epoxy	0.008	0,01
Coal tar urethane	0,008	0,01

Coal Tar and Bitumen are very similar materials with comparable properties

Coating Breakdown Factors after 10 years





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§ 8.4.3 – Current density

 $I_{tot} = \pi D \times L \times k \times j \times J_c$

k: contingency factor - non uniform distribution (≥ 1.25)

j_c: design current density (Table 3)

Table 3 — Typical design current density values for coated pipeline

Type of coating	Current density for optimized design mA/m2	Current density for conservative design
3LPE or 3LPP	0,001 to 0,02	0,05 to 0,2
FBE	0,02 to 0,2	0,4 to 0,7
Coal tar or bitumi- nous coating	0,2 to 0,3	0,3 to 0,8

NOTE These values are given for pipelines built with respect to standards mentioned in 7.5.2 and 7.5.3.



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5. Butyl-Rubber





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Butyl-Rubber - History



- 1825 (UK): *Michael Faraday* (better known for discovery of electromagnetic induction, diamagnetism and electrolysis) discovered Isobutylene.
- 1931 (Germany): BASF developed Polyisobutylene (PIB), which was sold under the trade name Oppanol B.
- 1937 (USA): Development into Butyl-Rubber by Standard Oil laboratory.
- Today, the majority of the global supply of Butyl-Rubber is produced by:
 - **ExxonMobil** (USA), one of the descendant of Standard Oil (USA).
 - LANXESS AG (Germany), Bayer AG bought Polysar Rubber (Canada) in 1990.



Butyl-Rubber



Isobutylene Isoprene Rubber (IIR) is polymerization of:

- 98% Poly-Isobutylene (PIB)
- 2% Isoprene

Chemical structure close to PE

$$\begin{pmatrix}
H & H \\
C - C \\
H & H
\end{pmatrix}_{n}$$







Basic Properties

- Low permeability to air, gases & moisture (tire profile and tubes).
- Glass transition temperature: -67°C.
- Maximum temperature: +100°C (+150°C if vulcanized with sulfur).
- Resistant to ageing & weathering (stable).
- Hardness & tensile strength properties.
- Low filler content.
- Safe (chewing-gum effect).



Perfect for Corrosion Prevention Tapes



Butyl-Rubber (NACE CIP Level II)



- Temperatures resistant close to +100°C.
- Pliable and moldable material.
- Typical use: mastics, adhesives, sealants.
- Excellent resistance to acids.



Note: No Bitumen property is mentioned by NACE







PE-Butyl-Rubber Tape after 40 years of operation exceeds current requirements







6. Conclusions

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Properties	PVC	Bitumen	PE	Butyl-Rubber
Low Temperature	-18°C	-50°C	-40°C	-67°C
Melting Point Temp.	+77°C	+80°C	+120°C	+100°C
Electrical Resistance	$10^{11}\Omega$ cm		$10^{16} \Omega \text{cm}$	
Water absorption	0.2% - 1.0%		0.02% - 0.06%	
Ageing	Poor	Poor	Stable	Stable
	Cracks	Porous	HWI & Ageing tests	











PVC-Bitumen

From their intrinsic material properties, PVC & Bitumen are **unsuitable** as base material for Polymeric Tapes.

- PVC needs Plasticizers and Stabilizers which evaporate with ageing.
- Bitumen shows Structural Ageing: it becomes hard, brittle and porous.



PVC-Bitumen Tapes show poor performance on long terms









PE-Butyl-Rubber

According to their material properties, Polyethylene (PE) & Butyl-Rubber are **well suited** for Polymeric Tapes

- Polyethylene doesn´t need Plasticizers or Stabilizers: excellent thermal stability.
- Butyl-Rrubber: stable & strong sealing compound.



PE-Butyl-Rubber Tapes show excellent performance on long terms



Best as 3-ply real-coextruded tapes

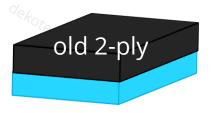






PVC-Bitumen: old fashioned technology with some storage issues and

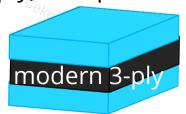
significant long-term risks







PE-Butyl-Rubber: modern technology allowing modern product design (3-ply) with proven outstanding performance and unique track record.











Thank you for your attention!

If you have any further questions please contact us!



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PVC-Bitumen vs. PE-Butyl-Rubber (Ageing)







ours @ 75°C 36 hours @ 75°C

PVC-Bitumen Tape





100 days @ 70°C° ¬

PE-Butyl-Rubber Tape

Peel strength ≥ 2.75N/mm



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