Material Performances Comparison of Cold-applied Polymeric Tapes

PVC - BITUMEN
vs.
PE - BUTYL-RUBBER

Agenda

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

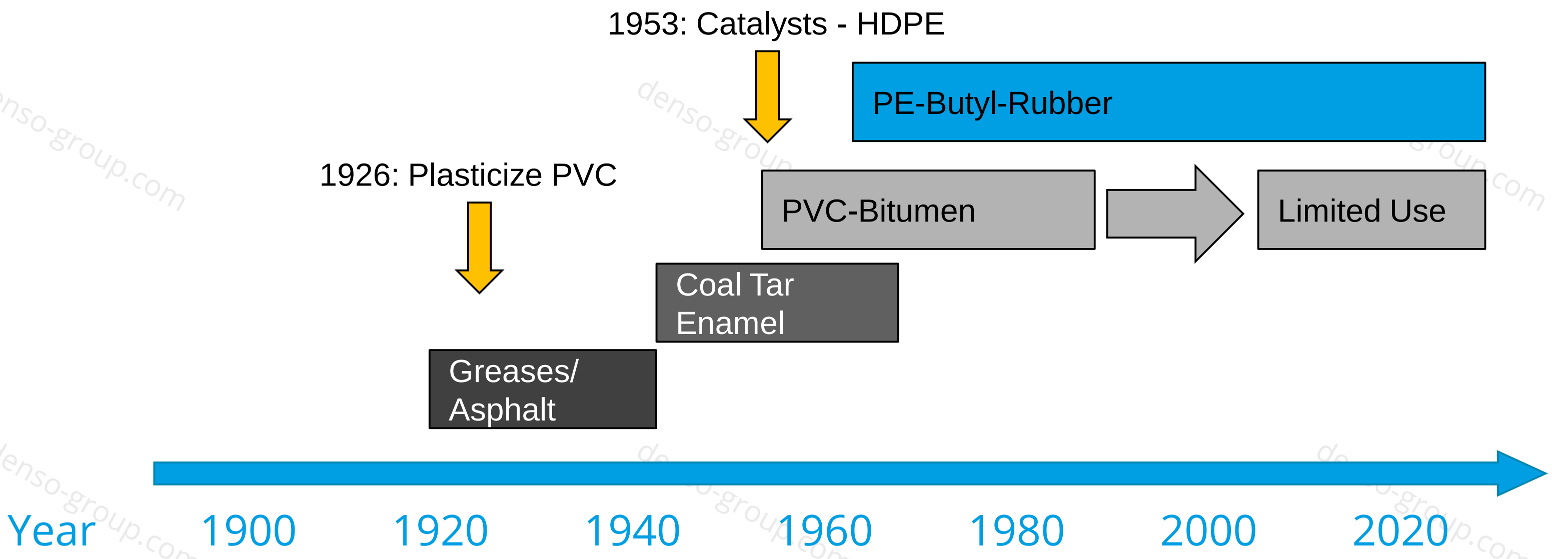
1. Introduction

Objective of this Presentation

- To understand and to compare the **chemistry and the basic properties** of each material:
  - PVC (**P**oly**v**inyl **C**hloride)
  - PE (**P**oly**e**thylene)
  - Bitumen-Complex Mix of Hydrocarbons/ **P**olymer **M**odified **B**itumen (PMB)
  - Butyl-Rubber
- Special focus:

  Suitability for use in Corrosion Prevention Tapes

History

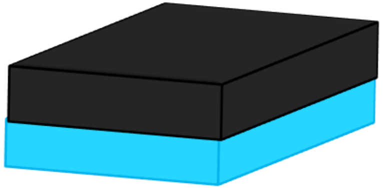

1953: Catalysts - HDPE
PE-Butyl-Rubber
1926: Plasticize PVC
PVC-Bitumen
Limited Use
Coal Tar Enamel
Greases/ Asphalt
Year
1900
1920
1940
1960
1980
2000
2020

Structure of Tapes

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

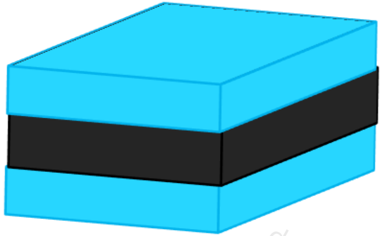
Carrier Film + Compound

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



2-Ply

PVC – Bitumen
Mesh – Bitumen
PE – Butyl-Rubber



3-Ply

PE – Butyl-Rubber

2. PVC (Polyvinyl Chloride)

PVC - History

- 1835 (Germany): *Henri Victor Regnault (F)* 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 (GER)* 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!**

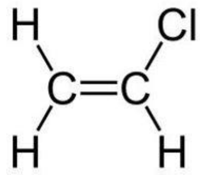
PVC - Chemical Structure

Vinyl Chloride Monomer

$$C_2H_2 + HCl \rightarrow CH_2=CHCl$$

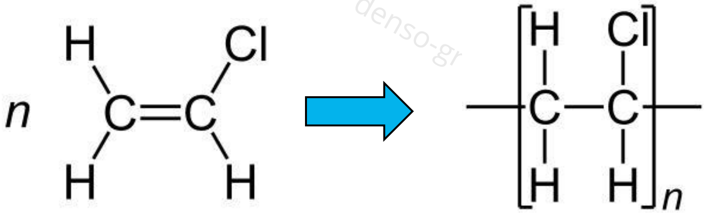
Acetylene + Hydrogen Chloride (gas)

Using Mercuric Chloride as catalyst (toxic to humans)



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":

Plasticizers are not stable and migrate to:

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

Plasticizers are suspected to cause **Cancer**

PVC - Stabilizers Issue (Heat Instability)

PVC + Heat (from +70°C) ➡ Dehydrochlorination

Dehydrochlorination: Allylic Chloride Structure + HCl

- Allylic Chloride Structure: Thermally unstable in Polymer & Toxic
- HCl + H_2O (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)

PE - History

- 1898 (Germany): White waxy substance was accidentally synthesized by *Hans von Pechmann (GER)*. *(no practical use at that time)*

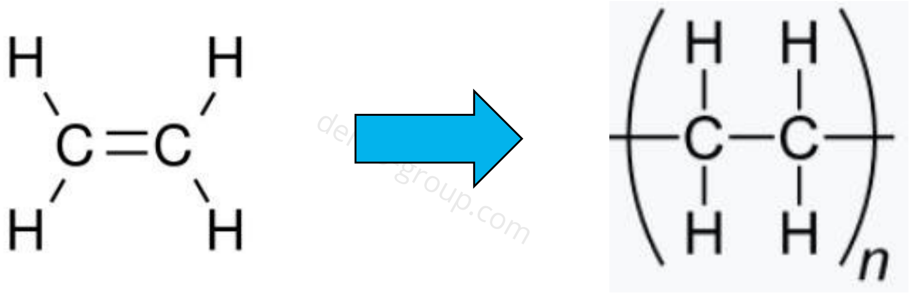
- 1933 (UK): *Eric Fawcett* (UK) & *Reginald Gibson (UK)* "accidentally" synthesized in industrial manner a white, waxy material. Later *Michael Wilcox Perrin (UK)* produced in a high-pressure synthesis Polyethylene. ➡ LDPE

- 1944 (USA): Bakelite Corp. & DuPont started commercial production.

- 1951 (USA) and 1953 (Germany):
  Milestone success: catalysts + <u>mild</u> temperature & pressure + Ethylene
  - LDPE (**L**ow **D**ensity **PE**) &
  - HDPE (**H**igh **D**ensity **PE**).

PE - Polymerization of Ethylene Monomer

Catalyst + *n*



Chemical Reaction: Catalyst + monomer molecules to form Polyethylene chains

Monomer molecules: Ethylene (simplest Alkene)

Similar chemical composition as **Candles or Chewing-Gum**

PE – Basic Mechanical Properties

Rigidity/Flexibility	→	Flexible **from -40°C without Plasticizers**
High ductility	→	Plastic deformations before rupture
High impact strength	→	Absorbs energy and deform without fracture

PE – Basic Mechanical Properties

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)

PE	→	10^{16} Ω cm
PVC	→	*10^{11} Ω cm*

Water Absorption (ASTM D570)

PE	→	0.02% - 0.06%
PVC Plasticized	→	*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**

<u>Note</u>: There is no PVC property mentioned by NACE

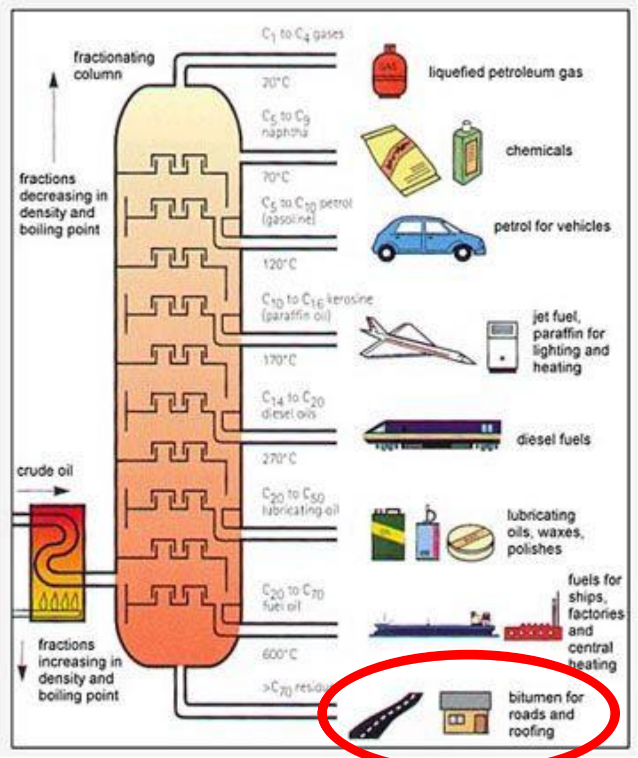
4. Bitumen

Bitumen - Asphalt

- Complex Hydrocarbons (C_nH_m) Mixture
- Natural:

Natural bitumen from the Dead Sea

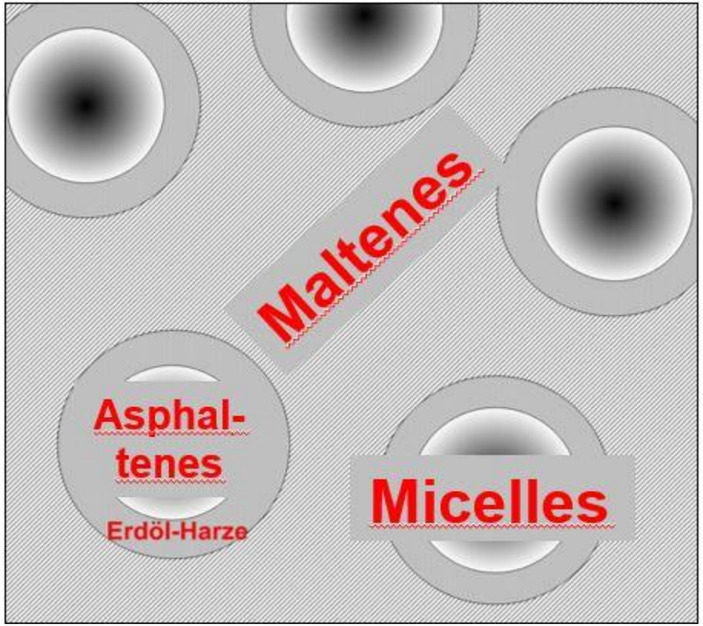
- Refined: Crude Oil Distillation
  - *1500 Crude Oil types, but:*
  - *only 7% are suitable for qualitative Bitumen*
  - Quality issue – No defined composition



Bitumen - Colloidal Model

This model explains the aging behavior of Bitumen

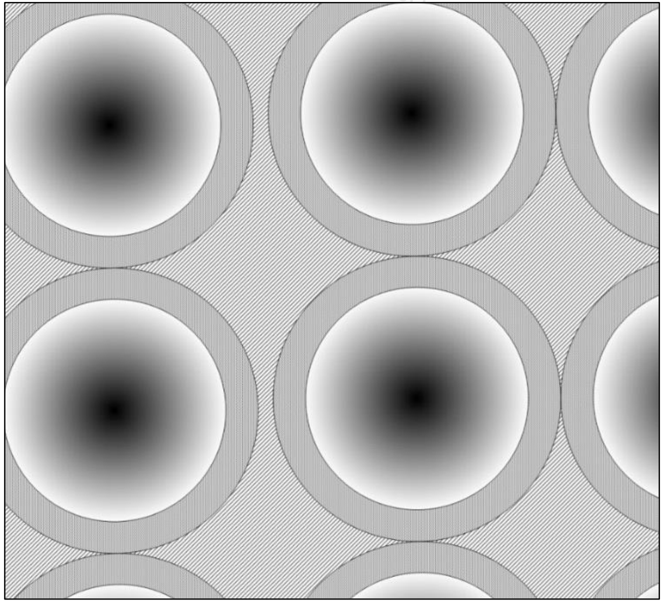
- Non-soluble Solid **Asphaltenes** - radius in nm (10^{-9} m)
- Asphaltenes are coated by soluble Resins
- Asphaltenes + Resins
  = Solid **Micelles**
- Oily Liquid matrix: **Maltenes**
  Temperature sensitive
- **Sol Type Bitumen**
  Asphaltenes Micelles are fully dispersed & non-interactive



Bitumen - Colloidal Model (Structural Ageing)

When Bitumen ages:

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



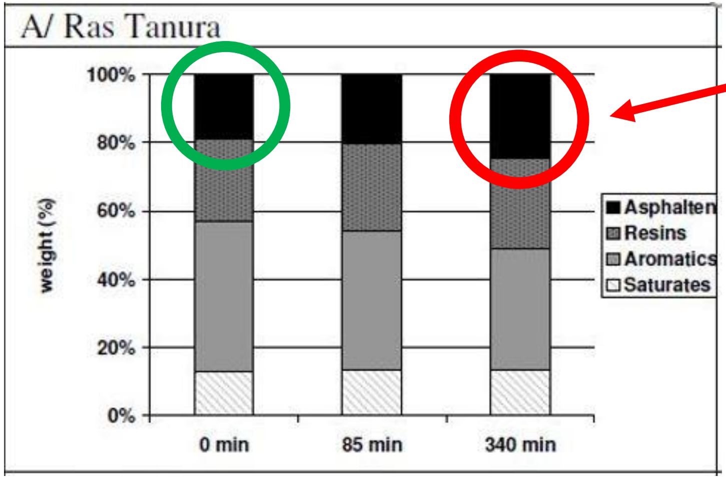
- **Gel Type Bitumen**
  Ratio: Asphaltenes/Maltenes increases
  Bitumen becomes **hard, brittle & porous!**

Bitumen - How to measure ageing?

Rolling **T**hin Film **O**ven **T**est **(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)

DENSO

Structural Ageing is <u>the weak point of Bitumen !</u>

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

<u>Ageing speed depends on</u>:

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

<u>Ageing Result:</u>
Bitumen becomes **hard, brittle & porous!**

Bitumen - Pipeline Coatings (Ageing Issue)

Bitumen becomes

hard, brittle & porous

Bitumen - Pipelines Coatings

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!**

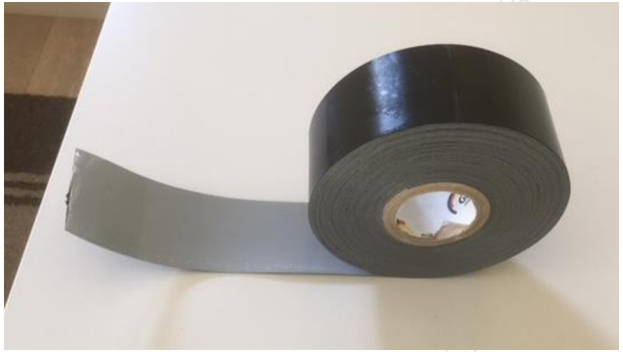
Bitumen - Pipeline Coatings (Storage Issues)

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: $A_{100}/A_o \geq$ **0.75**

- Mesh-Bitumen Tape (2-ply laminated): A_{100}/A_o **± 0.60**
- PE-Butyl-Rubber Tape (3-ply coextruded): A_{100}/A_o **≥ 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:	≥ 0.4N$_{/mm}$

	Initial		After HWI
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$_{/mm}$

Bitumen - Pipeline Coatings (Porosity Issue)

High Porosity = high Cathodic Protection (CP) current demand

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

<u>§ 8.4.2 - Coating Breakdown Factors (**f_f**)</u>

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

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)

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

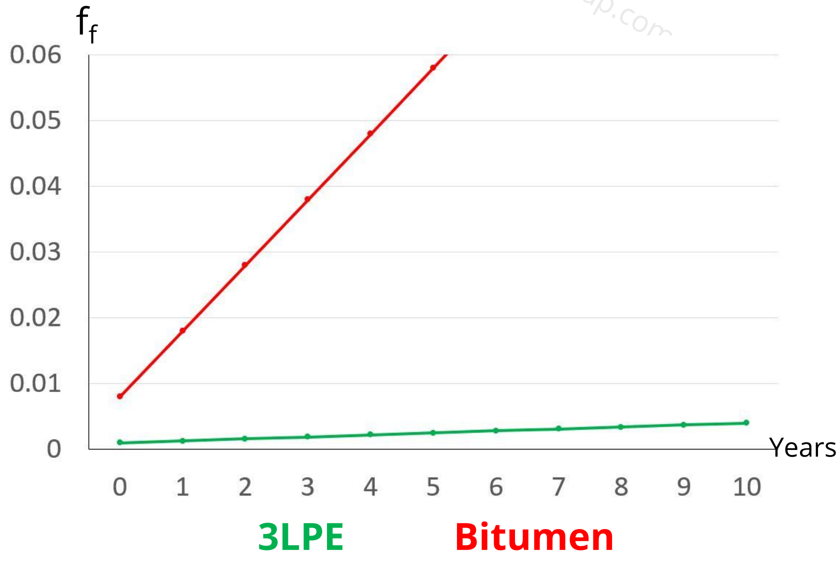
f_i: initial f_f
Δf: Avg yearly increase of f_f
t_{dl}: design life (years)

Table 2 — Typical design coating breakdown factors

Pipeline coating	f_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



Bitumen - Pipeline Coatings (Porosity Issue)

§ 8.4.3 – Current density

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

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 mA/m2
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 bituminous 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.		

5. Butyl-Rubber

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:

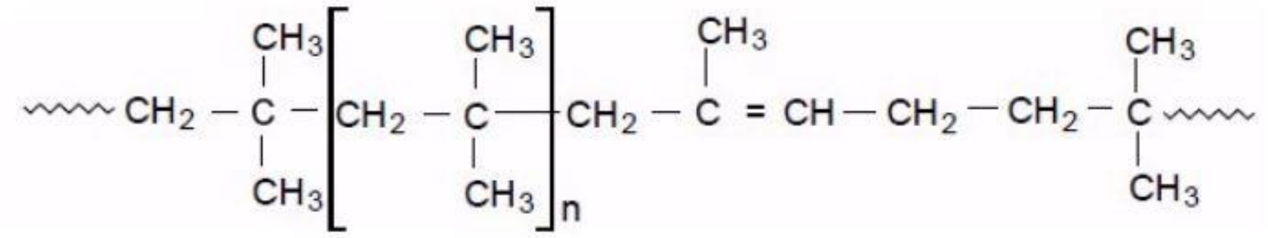
  - **ExxonMobil** (USA), one of the descendant of Standard Oil (USA).

  - **LANXESS AG** (Germany), Bayer AG bought Polysar Rubber (Canada) in 1990.

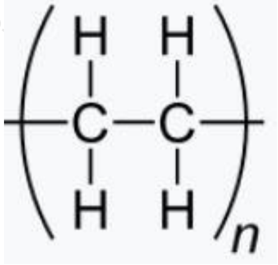
Butyl-Rubber

Isobutylene **I**soprene **R**ubber (IIR) is polymerization of:

- 98% **P**oly-**I**so**b**utylene (PIB)
- 2% Isoprene



Chemical structure close to PE



Isobutylene Isoprene Rubber (IRR)

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.

➡ **Perfect for Corrosion Prevention Tapes**

Note: No Bitumen property is mentioned by NACE

Butyl-Rubber: properties are stable over time

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

6. Conclusions

PVC-Bitumen vs. PE-Butyl-Rubber

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} Ω cm		10^{16} Ω cm	
Water absorption	0.2% - 1.0%		0.02% - 0.06%	
Ageing	Poor	Poor	Stable	Stable
	Cracks	Porous	HWI & Ageing tests	

PVC-Bitumen vs. PE-Butyl-Rubber

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***

PVC-Bitumen vs. PE-Butyl-Rubber

PE-Butyl-Rubber

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

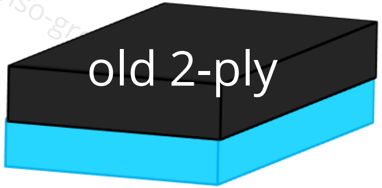
- Polyethylene doesn´t need Plasticizers or Stabilizers: **excellent thermal stability.**
- Butyl-Rrubber: **stable & strong** sealing compound.

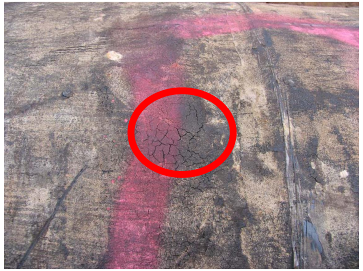
➡ ***PE–Butyl-Rubber Tapes show excellent performance on long terms***

Best as 3-ply real-coextruded tapes

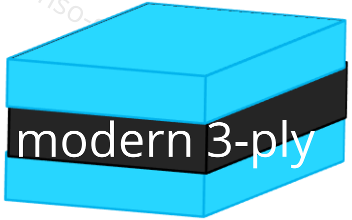
PVC-Bitumen vs. PE-Butyl-Rubber

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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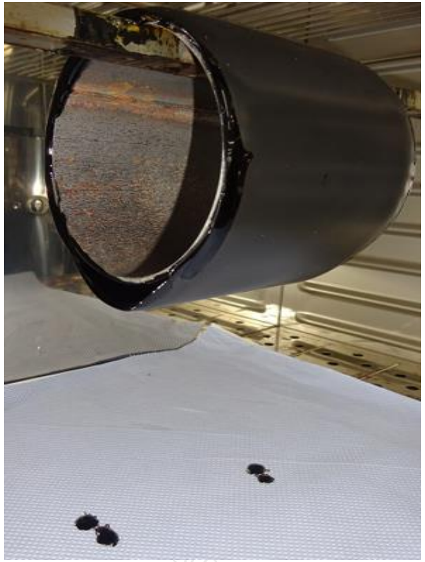
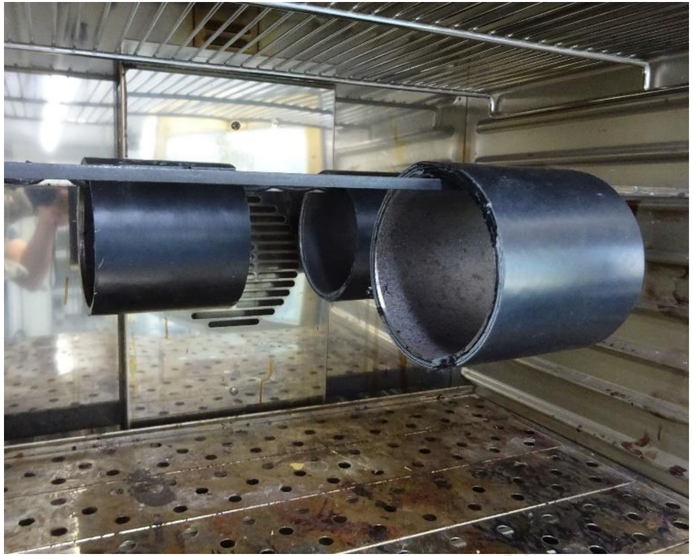
ANNEX

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



24 hours @ 75°C

36 hours @ 75°C



100 days @ 70°C

PVC-Bitumen Tape

PE–Butyl-Rubber Tapes

Peel strength ≥ 2.75N/mm