AV '23 CONFERENCE ASPHALT PAVEMENTS 2023

Innovative Chemistry for sustainable asphalt pavement

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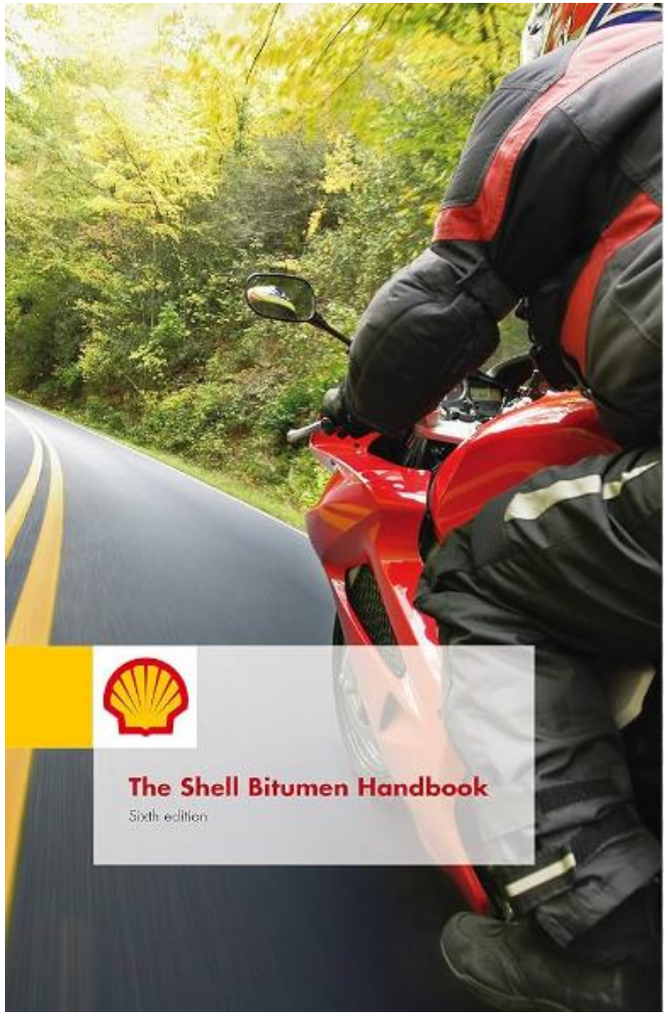
28 – 29 November 2023, České Budějovice

Motto: Let´s asphalt out of the crisis

Introduction

Modification of bitumen by reactive chemistry



8.2.5 *The modification of bitumen by reactive chemistry*

In addition to physical blends of bitumens and polymers, another way to improve the binder properties is through chemical modification: reactive ethylene terpolymers, comprising ethylene, ester groups of methyl, ethyl or butyl acrylate and glycidyl methacrylate groups (also known as reactive epoxy functions), can chemically react with bitumen species (carboxylic groups present in asphaltenes) and can be used to enhance asphalt performance and increase the compatibility between the polymer backbone and the bitumen, keeping the product stable during storage and transportation (Dupont, 2014; Kanabar, 2010; Keyf *et al.*, 2007). There are many other reactive polymeric materials described in the literature or in patent publications that can be used to enhance the properties of bitumen, examples being grafted maleic anhydride styrene block copolymers, polymers with high vinyl content, and hydroxyl, carboxylic or silane-grafted polyolefins (Chaverot *et al.*, 2012; Cong *et al.*, 2011; Crews and Kalinowski, 1954). As this involves various chemical reactions between the reactive functions of the polymer and bitumen species, in certain instances some catalysts such as phosphoric acid (PA) can be used. However, in such circumstances, processing conditions (mixing time, temperature, polymer content) should be carefully defined to avoid uncontrolled kinetic reactions and gelling of the reacted product. In the case of reactive ethylene terpolymers, PA can be used to catalyse the reactivity of glycidyl methacrylate (epoxy) groups with bitumens that have carboxylic reactive functions.

Source: The Shell Bitumen Handbook, 6th edition. p165

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Introduction

Modification of bitumen by reactive chemistry

- Use of reactive chemicals is not new and has been extensively described in the scientific literature (excluding BASF activities)
- BASF is the first to have marketed a suitable reactive isocyanate polymers based on scientific evidences

- J Zhu, B Birgisson, N Kringos, *Polymer modification of bitumen: Advantages and challenges*, European Polymer Journal, 54 (2014) 18-38, https://doi.org/10.1016/j.eurpolymj.2014.02.005
- FJ Navarro, P Partal, M García-Morales, FJ Martinez-Boza, C Gallegos. *Bitumen modification with a low-molecular-weight reactive isocyanate-terminated polymer*. Fuel 86(15) (2007), 2291–9, https://doi.org/10.1016/j.fuel.2007.01.023
- MJ Martín-Alfonso, P Partal P, FJ Navarro, M García-Morales, C Gallegos. *Use of a MDI-functionalized reactive polymer for the manufacture of modified bitumen with enhanced properties for roofing applications*. European Polymer Journal, 44(5) (2008), 1451–61, https://doi.org/10.1016/j.eurpolymj.2008.02.026
- MJ Martín-Alfonso, P Partal P, FJ Navarro, M García-Morales, C Gallegos. *Role of water in the development of new isocyanate-based bituminous products*. Industrial & Engineering Chemistry Research, 47(18) (2008), 6933–40, https://doi.org/10.1021/ie800243w
- FJ Navarro, P Partal, M García-Morales, MJ Martín-Alfonso, F Martínez-Boza, C Gallegos, *Bitumen modification with reactive and non-reactive (virgin and recycled) polymers: a comparative analysis*. Journal of Industrial and Engineering Chemistry, 15(4) (2009), 458–64, https://doi.org/10.1016/j.jiec.2009.01.003
- MJ Martín-Alfonso, P Partal, FJ Navarro, M García-Morales, JCM Bordado, AC Diogo. *Effect of processing temperature on the bitumen/ MDI–PEG reactivity*. Fuel Processing Technology, 90(4) (2009), 525–30, https://doi.org/10.1016/j.fuproc.2009.01.007
- V Carrera, P Partal, M García-Morales, C Gallegos, A Páez. *Influence of bitumen colloidal nature on the design of isocyanate-based bituminous products with enhanced rheological properties*. Industrial & Engineering Chemistry Research, 48(18) (2009), 8464–70, https://doi.org/10.1021/ie9004404
- V Carrera, M Garcia-Morales, P Partal, C Gallegos. *Novel bitumen/ isocyanate-based reactive polymer formulations for the paving industry*. Rheologica Acta, 49(6) (2010), 563–72, https://doi.org/10.1007/s00397-009-0399

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Co-creation with our global external partner network is essential to link chemistry to road performance

- B2Last® is based on isocyanate chemistry
- Mainly a polymeric part (REACh exempted) but has some monomeric fractions (mandatory ISOPA training)
- Low viscous (~250 mPas) black liquid at 25°C
- Solvent free
- No polycyclic aromatic hydrocarbons
- Classified as hazardous substance but not as dangerous goods
- Water hazard class 1
- Isocyanate chemistry is broadly used in the polyurethane industry

A safe-to-handle liquid reactive modifier that is stable and does not separate

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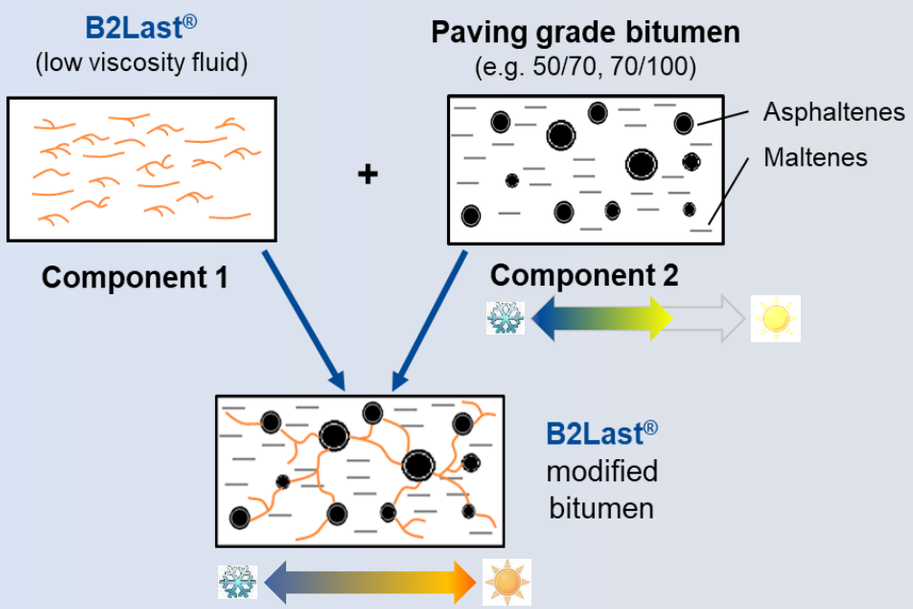
How does B2Last® work?



		160/220		70/100		50/70	
		Original	+ 2,0% B2Last®	Original	+ 2,5% B2Last®	Original	+ 2,0% B2Last®
SP (R&B)	T [°C]	41,0	50,0	47,6	64,4	49,6	63,4
BTSV (G* = 15kPa)	T [°C]	40,8	48,0	47,9	61,9	50,2	63,4
	δ [°]	83,3	74,5	81,3	69,1	82,3	73,0
BBR (after PAV)	T [°C]	-31,7	-31,2	-19,7	-20,7	-21,9	-19,0
UTI	T [°C]	72,5	79,2	67,6	82,6	72,1	82,4

- B2Last® reacts with bitumen constituents and forms a strong elastic polymer network. The high temperature performance improves and doesn´t affect the low temperature behavior of the base bitumen
- Use temperature interval (**UTI = Difference of BTSV + BBR**) increase

B2Last® becomes part of the polymeric network and is fully consumed during the crosslinking reaction

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A product with a wide range of possibilities

- Anti-stripping agent
- H_2S scavenger
- Plastomer / Stiffner
- Compatibilizer for Reclaimed Asphalt
- Workability aid
- WMA additive
- Correction of out of spec. PmB

A product that offers

- Easy modification of bitumen
- Potentially lower CO_2 footprint
- Better cost in use

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B2Last offers solutions along the process chain to address global challenges in the Pavement Industry

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Dosage vs applications

	0,2 to 0,5%	0,5 to 1,5 %	1,5 to 3 %
Bitumen producers			
Bitumen modification		▪ Partial replacement of SBS ▪ Or correction of grade specifications	
Asphalt mixing plants			
WMA			▪ Antistripping agents ▪ Replacement of plastomers ▪ Workability aid ▪ RA up to 50%
HMA	▪ Antistripping agents ▪ Workability aid	▪ Antistripping agents ▪ Stiffening of the bitumen binder ▪ Workability aid	▪ Antistripping agents ▪ Replacement of plastomers ▪ Workability aid ▪ RA up to 60% ▪ Possibility to produce HiMA

- **In-Line blending with static mixer**
- **Modification of a full bitumen tank**
- **Addition in the scale**
- **New: addition in the pug mill (Cooperation with Uni. Braunschweig)**

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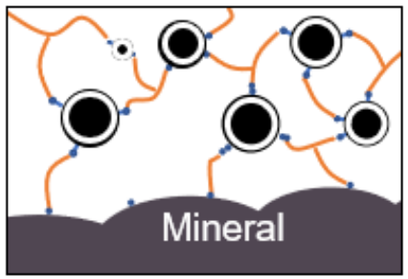
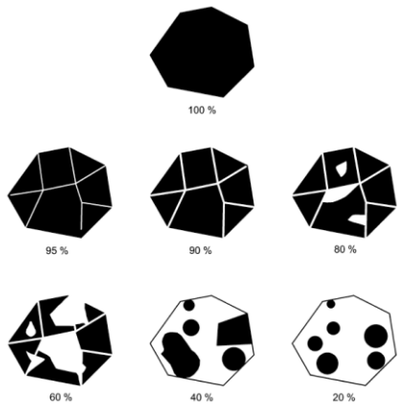
Affinity

Rolling Bottle Test

- Adhesion Test (TP Asphalt part 11)
  - Rotational speed: 60 min-1
  - Temperature: 25°C
  - Mineral class: 8/11 mm
  - 24h Test





Mineral	Pen. Grade bitumen	+ 2% B2Last
Basalt	5 %	52 %
Grauwacke	30 %	65 %
Diabas	52 %	63 %
Andesit	41 %	60 %
Granit	10 %	45 %
Quarzit	10 %	50 %
Gabbro	50 %	80 %

Mineral	Pen. Grade bitumen	+ 1,5% B2Last	+0,3% Wetfix
Red granit	10 %	60 %	65 %

B2Last® works like an adhesion promoter
Lower dosage at 0,3-0,5% is possible

Institute of Highway Engineering | RWTH AACHEN UNIVERSITY

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3 years of paving trials
and soon 5 years of proven performance…

Germany
Globally

2019

Airport Oberpfaffenhofen 150 t

L50 Setterich 500 t

PWC Gilching 300 t

A96 München 1.000 t

2020

USA – Kentucky 13.000 t

B270 Waldfischbach Warm mix 4.000 t

NCAT test track USA – Alabama 300 t

2021

A99 München 2.300 t

Ukraine 400 t

Ukraine 2.000 t

Russia 200 t

A63 Kaiserslautern 500 t

A60 Heidesheim 800 t

A63 Kaiserslautern 500 t

2022

BASF site – Salpeter Str. 1.200 t

Zhanjiang (CN)

Kunchu Express (China) 2.000 t

Latvia 2000 t

Turkey – Chip seal

B51 Trier 3.000 t

Turkey 400 t

BASF site – Paraffin Str. 1200 t

2023

Konstantin place HIMA - Trier 300 t

YTD >800 kt of asphalt mix produced based on B2Last® modification

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B270 Waldfischbach

- **2700 t Asphalt mix**, AC 16 BS, **50% RAP*** content
- **1300 t Asphalt mix**, AC 11 DS, **30% RAP*** content
- Bitumen pen **50/70** and **2,5% B2Last®** (calculated on total binder amount)
- Asphalt mix produced at ~145 °C, and paved at **~135 °C**
  - Due of traffic jam and delayed delivery 5h old asphalt paved at 120°C
  - Monitoring of the degree of compaction with a Troxler probe always higher than 98%
- **Reference asphalt mix (<u>same neat bitumen</u>)**:
  - AC 16 BS, PmB 25/55-55, 50% RAP,
    Asphalt mix produced at 160 °C, paved at ~153 °C
  - AC 11 DS, PmB 25/55-55, 30% AG,
    Asphalt mix produced at 165 °C, paved at ~158 °C

*RAP = reclaimed asphalt pavement

Thanks to better workability and compaction behavior, paving operations are not disrupted

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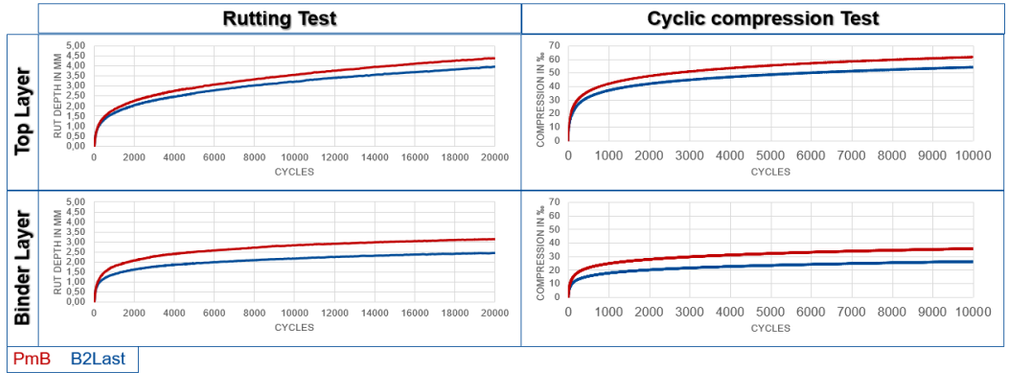
B270 Waldfischbach – Bitumen results

Bitumen key parameters		AC16 B S		AC11 D S	
		PmB 25/55-55	B2Last®	PmB 25/55-55	B2Last®
Softening Point	Temperature / °C	67,0	67,2	65,8	62,8
BTSV	Temperature (G* = 15 kPa) / °C	62,6	64,3	60,4	58,9
	Phase angle (G* = 15 kPa) / °	68,9	69,6	69,2	72,6
MSCR	Recovery at 3,2 kPa / %	46,0	32,8	43,6	14,0
	J_{nr} at 3,2 kPa / 1/kPa	0,204	0,195	0,287	0,606
BBR after PAV	Temperature at *m* = 0.300 / °C	-23,5	-22,1	-21,7	-22,2
UTI	Temperature (BTSV – BBR) / °C	86,1	86,4	82,1	81,1

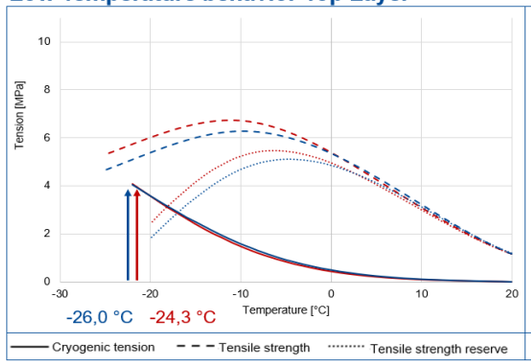
After extraction both binders show similar results

B270 Waldfischbach – Asphalt mix performance

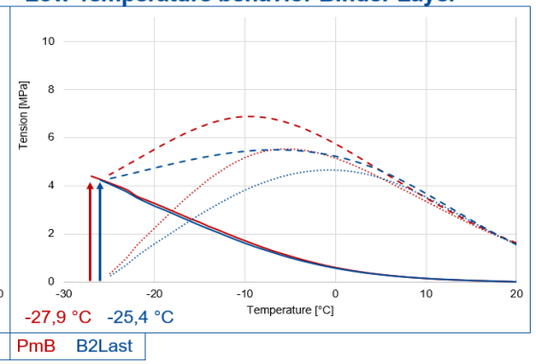
Deformation stability – Rutting Test and cyclic compression Test



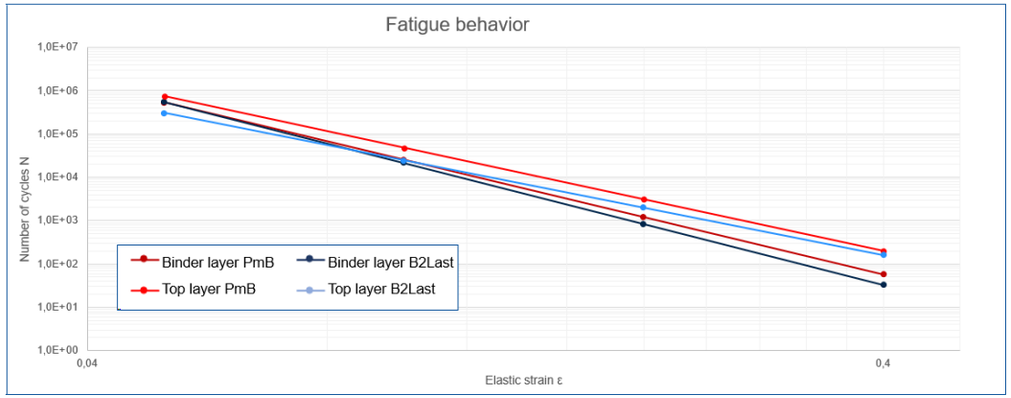
Low Temperature behavior Top Layer



Low Temperature behavior Binder Layer



Cyclic indirect tensile strength (CITS)



Control test		AC16 B S			AC11 D S		
Asphalt mix samples		**PmB 25/55-55**	**B2Last®**	**Requirement**	**PmB 25/55-55**	**B2Last®**	**Requirement**
Binder content	%	5,4	5,1	4,5 - 5,3	6,5	6,6	6,1 - 6,9
Air void content	%	2,7	3,3	3,5 - 6,5 ± 2	1,1	1,4	2,5 - 3,5 ± 1
Softening point	°C	65,1	64,5	≤ 71	65,3	62,8	≤ 71
Drilling samples (Average of 5 samples)							
Degree of compaction	%	102,0	101,6	≥ 98	99,4	99,5	≥ 98
Air void content	%	-	-	-	1,5	1,9	≤ 5,5
Layer composite	kN	38,4	37,2	≥ 12	33,9	31,2	≥ 15

Comparable asphalt mix performance

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3 years of paving trials
and soon 5 years of proven performance…

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Globally

2019

Airport Oberpfaffenhofen
150 t

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A96 München
1.000 t

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USA – Kentucky
13.000 t

B270 Waldfischbach Warm mix
4.000 t

NCAT test track USA – Alabama
300 t

A99 München
2.300 t

2021

Ukraine
400 t

Ukraine
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2023

Konstantin place HIMA - Trier
300 t

YTD >800 kt of asphalt mix produced based on B2Last® modification

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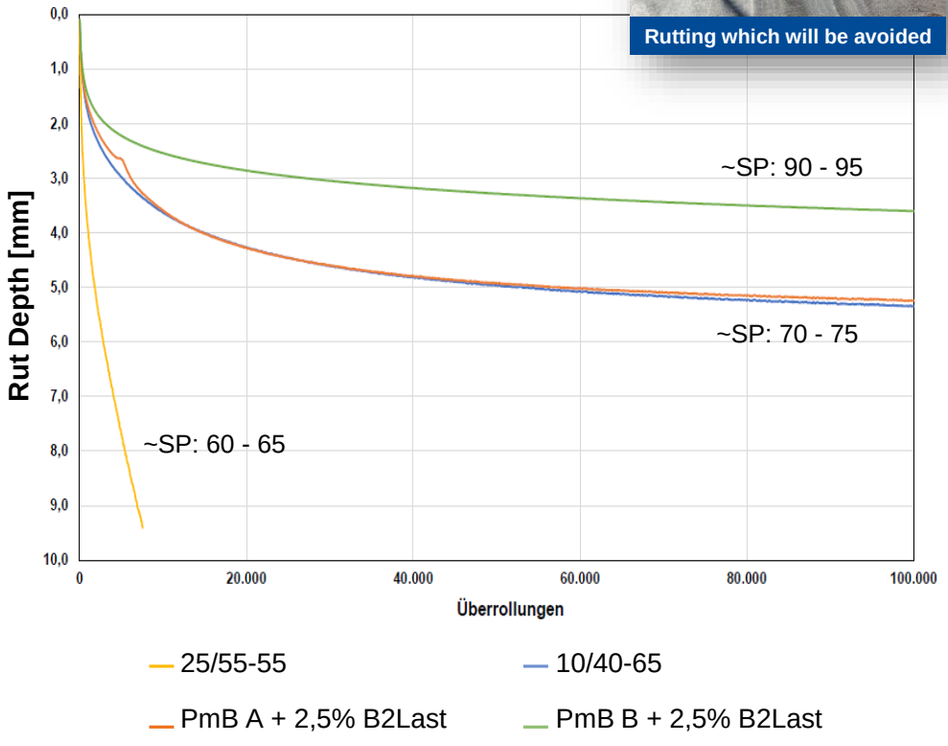
Combination of SBS and B2Last® - HiMA

Parameters		PmB A 25/55-55	+ 2,5% B2Last	PmB 10/40-65	PmB B 25/55-55	+ 2,5% B2Last	PmB 10/40-65
Softening point	T [°C]	60,4	74,6	72,2	61,8	91,0	75,0
BTSV (G* = 15kPa)	T [°C]	58,0	69,3	67,6	56,3	73,5	62,5
	δ [°]	72,7	62,8	65,4	67,9	55,7	64,1
Rutting depth after 100.000 passes at 70 °C	[mm]	-	5,2	5,3	9,4 (~10.000)	3,6	-

Rutting test
at 70°C instead of 60°C
100.000 instead of 20.000 passes



The combination of PmB 25/55-55A and B2Last at the asphalt mixing plant is an easier process towards Highly Modified Asphalt (HiMA) bitumen binder

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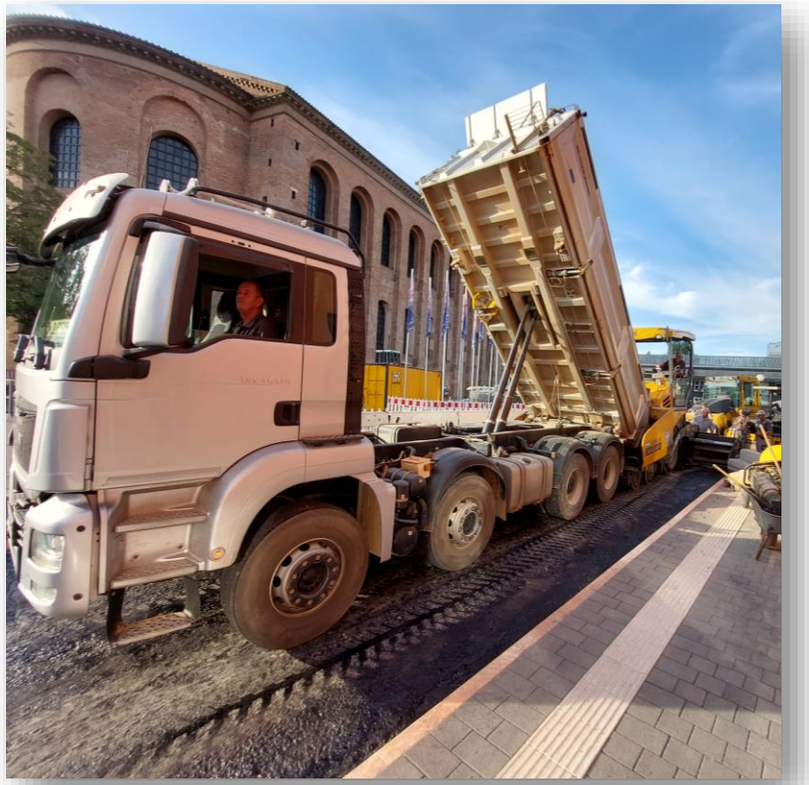
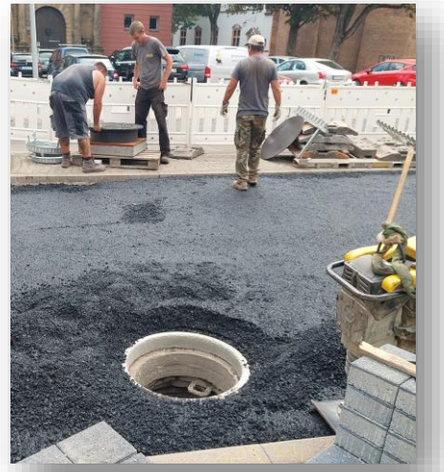
HIMA trial in Trier (GE) – Konstantin place



Parameters		PmB 25/55-55	PmB 25/55-55 + 2,5% B2Last	PmB 25/55-55 + 3,0% B2Last
Softening point	T [°C]	62,0	75,5	79,0
BTSV (G* = 15kPa)	T [°C]	57,1	67,4	72,3
	δ [°]	67,1	60,7	59,3
MSCRT (at 3,2 kPa)	Recovery [%]	34,3	74,9	81,8
	J_{nr} [1/kPa]	0,61	0,05	0,021



Better workability of the asphalt mix out of B2Last modification

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Key take aways

1 The B2Last modification extends the durability and increases the road lifetime.

2 Less energy needed for heating bitumen, aggregates and reclaimed asphalt, resulting in lower CO_2 emissions.

3 Reduces harmful emissions along the value chain, esp. during pavement.

4 Enables used asphalt to be recycled into new road pavements.

5 Implementation of a fundamentally new additive in road construction needs co-creation with partners along the whole value chain.

B2Last®

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Comparing statements refer to industry applications with standard bitumen mixtures

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Global Rollout:
Launched in **North America** and **Europe**, **China** ongoing, **South America** and **India** under evaluation.

B2Last® is also in use at our sites in **Ludwigshafen, Southfield** and **Zhanjiang.**

Thanks for your attention!

- More infos on: www.b2last.com / https://www.porta.cz
- E-mails: b2last@basf.com or jscharff@porta.cz

BASF-Site Ludwigshafen, Salpeterstraße

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