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CHEMO MECHANICAL CHARACTERIZATION OF BITUMINOUS MATERIALS

New binders using natural bitumen Selenizza

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SELENICE BITUMI SHA

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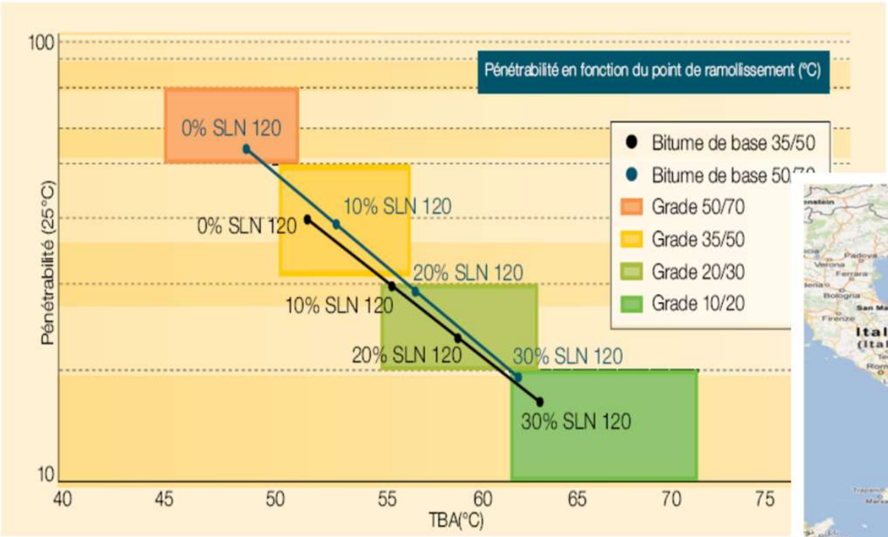
Contents

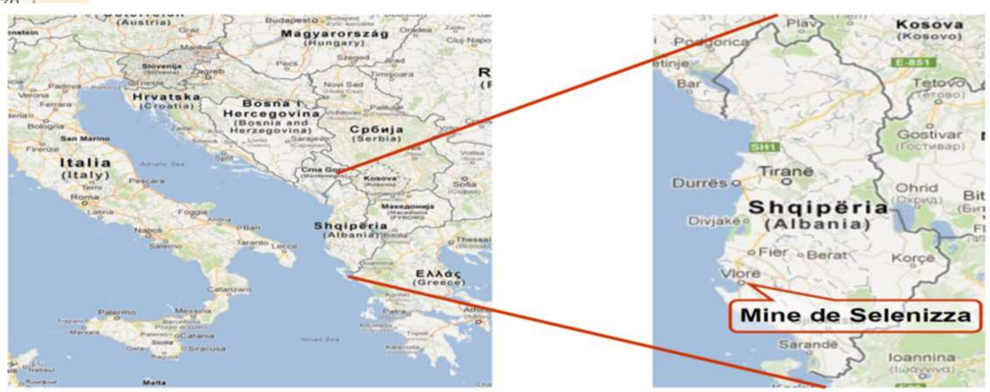
- Antiaging properties and hardening effect of Selenizza®SLN
- Potential use of waste vegetable oils-modified natural bitumen for developing a new type of binder
- Example of innovative asphalt mix design for surface layers reusing 100% RAP and a binder composed of Selenizza®SLN and vegetable oil
- Conclusions

Hardening effect of Selenizza®SLN

Description	Penetration [dmm]	TR&B[°C]	Penetration Index	Grade obtained
Petroleum bitumen 50/70	54	49,0	-1,28	-
Mixed with 5% natural bitumen	38	52,6	-1,18	35/50
Mixed with 10% natural bitumen	28	56,2	-1,01	20/30
Mixed with 15% natural bitumen	20	-61,6	-0,60	10/20
Natural Bitumen	0	120,0	-0,18	-

Structurally, the **organic phase** of Selenizza can be **compared** to **crude oil bitumen**, but with different **proportions** of maltenic and asphaltenic **fractions,** making it **100% compatible** with any type of road bitumen





Hardening effect of Selenizza®SLN

IATROSCAN fractions

SARA IATROSCAN method		Saturated [%]	Aromatic [%]	Resin [%]	Asphaltene-i [%]	I_c
Purified sample-depth	Average Standard deviation	1,7 0,35	24,8 2,29	35,1 1,35	38,4 1,88	0,67
Purified sample-surface	Average Standard deviation	1,5 0,14	22,7 1,37	37,2 1,90	38,6 1,58	0,67
Raw sample-depth	Average Standard deviation	1,6 0,29	23,8 1,40	34,6 1,16	40,01 1,99	0,71
Raw sample-surface	Average Standard deviation	1,6 0,24	19,7 2,02	37,9 1,60	40,8 2,74	0,73

Evolution of glass transition temperatures

	Total heat flux				
	T_g1 [°C]	T_g [°C]	T_g2 [°C]	ΔT_g [°C]	ΔΦ [W/g]
Petroleum bitumen 50/70	-31,9	-22,9	-13,2	18,6	0,022
Mixed with 5% SLN	-30,9	**-23,1**	-13,8	17,1	0,019
Mixed with 10% SLN	-30,3	-23,1	-13,3	17,0	0,018
Mixed with 15% SLN	-32,1	-23,3	-13,4	18,8	0,019
Natural asphaltite SLN	-12,6	-1,1	16,2	28,8	0,021

Complex modulus	Measures at 100°C, 5 Hz	
	| E* | [GPa]	δ [°C]
Albanian Natural Bitumen	0,95 - 1,27	48,3 - 51,7

SARA (IATROSCAN) fractions analysis, with **colloidal instability** index I_c values indicating a **sol** or **sol-gel** character.

Reach in resins and asphaltenes responsible for its elevated hardness, high R&BT, high |E*|, zero penetration

Compared to petroleum bitumen, Selenizza's **organic phase has higher content** of **polar** fractions (resin + aspahltene) resulting in a:

- **vitreous transition** at **higher temperatures**
- **enhanced adhesion** between the bitumen and mineral aggregates
- addition of natural bitumen **does not affect the glass transition temperature** of bitumen
- 35/50 compared to modified alternative ➔ T_g = -23.1°C versus T_g = -19.3°C
- better resistance of natural bitumen to **brittle fracture**

Selenizza®SLN - Ageing Inhibitor

RTFOT test (to simulate oxidation of bitumen during mixture manufacturing) & **PAV** (to simulate in-service ageing)
Aggeing effect was quantified using the following mathematical expression:

$$EV_x = \frac{|x^{RTFOT+PAV} - x^{New}|}{x^{New}} \cdot 100$$

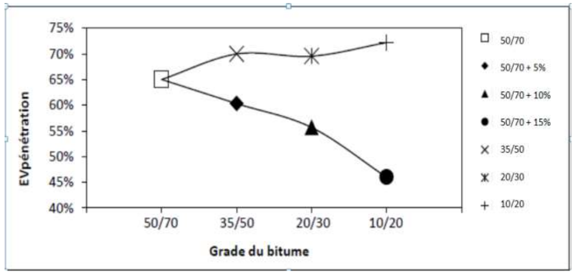
where EV_x – The evolution of the mechanical property x

1. **Changes** of modified specimens **were lower** than those of **50/70** 2. Changes are **attenuated** with the increase **of % SLN** 3.Modified bitumen are characterized by **minor changes** compared to petroleum bitumen of equivalent grades

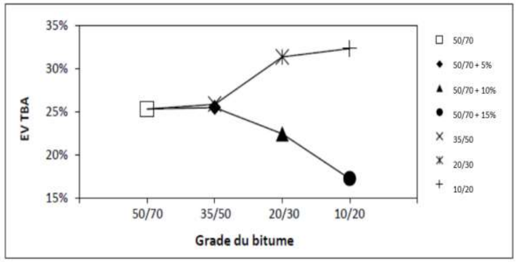
From the **ageing point of view**, the binders modified with Selenizza can **advantageously replace** hard petroleum bitumen for the production of HMAC

Description	Penetration (dmm)					TR&B (°C)				
	New binder	After RTFOT	Δ_1 (%)	After PAV	Δ_2 (%)	New binder	After RTFOT	Δ_1 (%)	After PAV	Δ_2 (%)
Petroleum 50/70	54	37	31.5	19	64.8	49	53.4	8.9	61.4	25.3
Mixed with 5%	38	27	28.9	15	60.5	52.6	57.2	8.7	66.0	25.4
Mixed with 10%	28	21	25	13	53.5	56.2	60.8	8.1	68.8	22.4
Mixed with 15%	20	14	30	11	45	61.6	65.4	6.1	72.2	17.2
Petroleum 35/50	40	27	32.5	12	70	52.6	56.8	7.9	66.2	25.8
Petroleum 20/30	23	12	47.8	7	69.5	60.0	67.0	11.6	78.8	31.3
Petroleum 10/20	18	9	50	5	72.2	65.0	72.6	11.7	86.0	32.3

Evolution of penetration after RTFOT and PAV ageing



Evolution of R&B after RTFOT and PAV ageing



New binder with natural bitumen & vegetable oil

A recent study, conducted by the French Centre for Studies and Expertise **CEREMA** and the French Institute for Science and Technology **IFSTTAR,** focused for the first time on the use of waste **rapeseed or sunflower vegetable oils** and **natural bitumen** to produce asphalt **binders** for mixes

Table 1
Composition of binders.

Constituent materials	Natural bitumen		Waste vegetable oil	Hard bitumen
	Hydrocarbon	Mineral fraction		
Percentage	60.7%	10.7%	17.9%	10.7%

a) Overview of the wastes oils

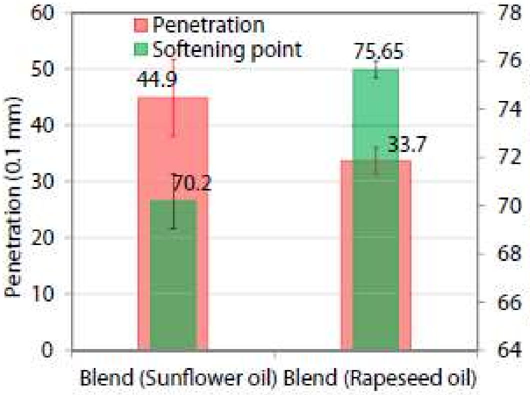
b) Selenizza's quary of natural bitumen (Albania)

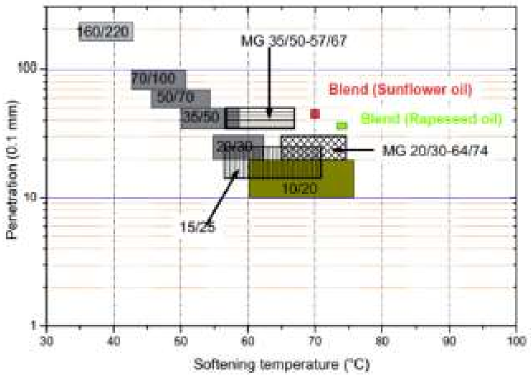
c) Example of blend with waste sunflower oil

Fig. 1. Main constituents of binders.

New binder with natural bitumen & vegetable oil

Binder characterization





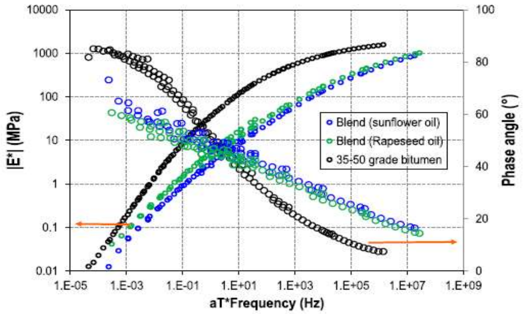


Fig. 6. Binders complex modulus and phase angle master curves at 15 °C.

- Both close to the **P35/50 petroleum bitumen.** The **rapeseed oil binder is harder** than the sunflower oil binder. **Softening** temperatures **exceed those** of **conventional** petroleum bitumen.
- Reference bitumen **is stiffer than** the produced binders in the temperature range **between 20 °C and 60 °C.**
- Blended binders have **lower phase angles** than reference bitumen for the **reduced frequency** a_T x f ≤ 2.5 Hz (e.g. **T ≥ 20 °C**) and **higher phase angle** for the reduced frequency a_T x f ≥ 2.5 Hz (e.g. **T ≤ 20 °C**).
- Produced binders' phase **angles are not equal zero,** this means that the **viscous effects are not negligible** compared to reference bitumen. An **advantage for low temperature stress relaxation**
- The **differential scanning calorimeter** analysis **highlighted the fact** that the **new produced binders** were characterized by the **increase of low temperature performance d**ue to the waste **vegetable oil's T_g** that are **lower** than those of **bitume**n.

New binder with natural bitumen & vegetable oil

Asphalt mix characterization

A **Semi Coarse Asphalt Concrete** (BBSG 3, 0/10) has been **manufactured** according to the mix composition described in the table below

Composition of Mixes

Table 4
Composition of mixes.

BBSG3, 0/10 according to the EN 13108-1 (2007)	
Granular fractions	Percentage by mass
0/2	26.1%
2/6	23.7%
6/10	42%
Filler (limestone)	1.9%
Binder (asphaltite + waste oil + P15/25 bitumen)	6.3%

Complex Modulus

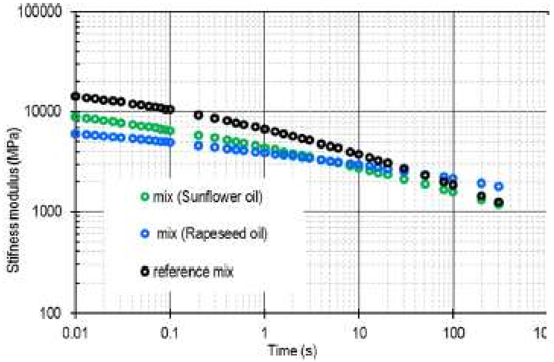


Fig. 8. master curves of the stiffness modulus of the mixes at 15 °C.

Evolution of Rut Depth

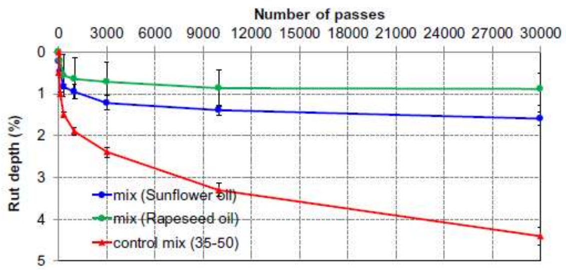


Fig. 7. Evolution of the rut depth.

- **Reference mix** obtained with the P35/50 bitumen **is stiffer** than the two others which is **consistent** with the evolution of the complex modulus of the binders.
- The percentage of **rut depth** ≤ 5% at 60 °C for 30,000 loading cycles. Therefore, the results obtained with the produced binders, **comply with the standard** EN 13108-1 (2007).The evolution of rut depth seems to be **inconsistent** with the evolution of the **stiffness modulus**. At **60 °C** (which corresponds to a_T x f between 10^{-5} and 10^{-3} Hz, the reference binder stiffness is close to the produced binders' stiffness. The **better resistances** to the permanent deformation obtained with produced binders are probably **due to the asphaltite** even if the real **mechanism** that occurs is **not known yet**

Innovative asphalt mix design for surface layers reusing 100% RAP and the new binder

One of the factors **limiting the use** of **high percentages of RAP** is the **hardening of bitumen** in the RAP because of **ageing.** In a recent study conducted by the University **of Erfurt,** was evaluated the use **of 100% RAP** with the addition of a **new rejuvenator**, based on natural bitumen **Selenizza®SLN** and **vegetable oil,** rich **in unsaturated acids,** aiming to restore the original characteristics of the bitumen and its effectiveness

12 Variants of Asphalt mixtures without a rejuvenator and the same aged mixtures with **3, 4 and 8 % rejuvenator content** by mass of the bitumen in the asphalt, were investigated.

JA = Reference Asphalt Mixture
JB= Aged Asphalt Mixture
JC = Asphalt Mixture with Rejuvenator

Variant	Asphalt mix	Binder	binder content [M-%]	Additive content [M-%]
JA 1	AC 11 DN	Shell B 50/70	6,2	-
JA 2	AC 11 DN	BP3 B 50/70	6,2	-
JA 3	AC 11 DN	Olexobit PmB 25/55-55	6,2	-
JB 1	AC 11 DN	Shell B 50/70 - BSA	6,2	-
JB 2	AC 11 DN	BP3 B 50/70 - AASHTO R30	6,2	-
JB 3	AC 11 DN	Olexobit PmB 25/55-55 - AASHTO R30	6,2	-
JB 4	AC 11 DN	RC -Elxleben	6,2	-
JC 1	AC 11 DN	Shell B 50/70 - BSA	6,2	4,0
JC 2	AC 11 DN	BP3 B 50/70 - AASHTO R30	6,2	8,0
JC 3	AC 11 DN	Olexobit PmB 25/55-55 - AASHTO R30	6,2	8,0
JC 4.1	AC 11 DN	RC -Elxleben	6,2	3,0
JC 4.2	AC 11 DN	RC -Elxleben - BSA	6,2	3,0

12 different variants *of Asphalt Concrete AC DN 11*

Innovative asphalt mix design for surface layers reusing 100% RAP and the new binder

Binder Investigation

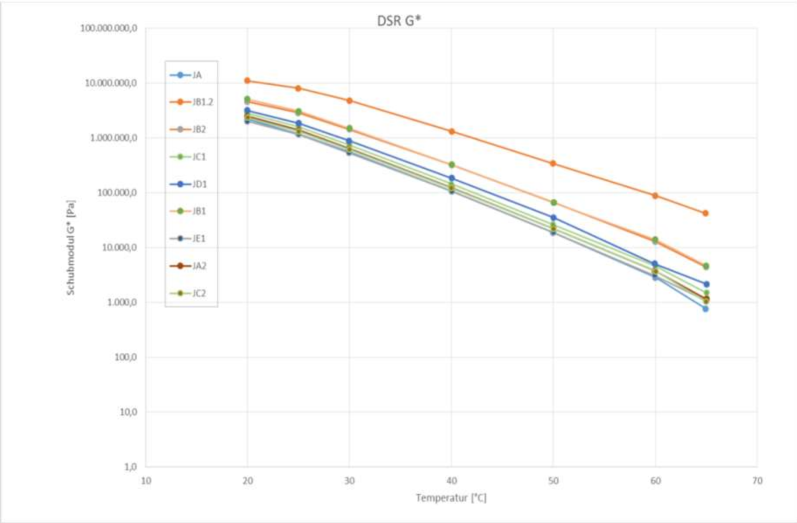
Due **to ageing,** the **softening temperature** of aged binders (JB1, JB1.2 and JB2) increased and the **penetration decreased**. The addition of the **additive leads** to a **significant reduction** of softening point (JC1, JC2) as well as a **significant increase** of the penetration.

The results of **Dynamic Shear Rheometer analysis** at a load frequency of **1.59 HZ** and temperature range of **20°C to 65 °C** showed that aged variants **(JB) have a greater rigidity** compared to reference variant (JA) over the entire temperature range. The **rejuvenated variants** (JC) are **again in the range** of the **initial values.**
SARA analysis show that rejuvenation leads to an **increase of** the **polarizable fractions** resins and asphaltenes and at the same time, it can be seen a **reduction** of the **aromatics and saturates**.

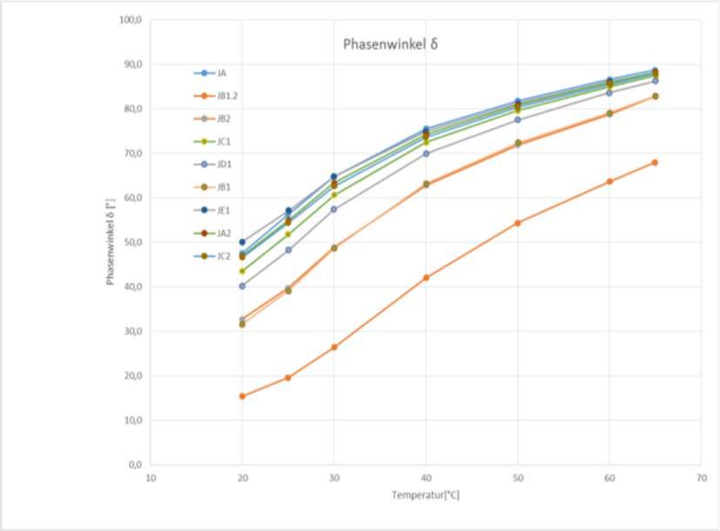
Bitumensorte	***20/30***	***30/45***	***50/70***	***70/100***
Softening Point [°C]	*63 - 55*	*60 - 52*	*54 - 46*	*51 - 43*
JA1			50,6	
JB 1	59,2			
JB 1.2	63,6			
JC1		53,4		
JD1			50,2	
JE1			46,0	
JA2			50,6	
JB2	67,0			
JC2	58,4			

Bitumensorte	*20/30*	*30/45*	*50/70*	*70/100*
Penetration [0,1 mm]	*20 - 30*	*30 - 45*	*50 - 70*	*70 - 100*
JA1			60	
JB 1	19			
JB 1.2	20			
JC1		44		
JD1			55	
JE1			60	
JA2			55	
JB2	20			
JC2		40		

Temperature sweep G* test



Temperature sweep phase angle test

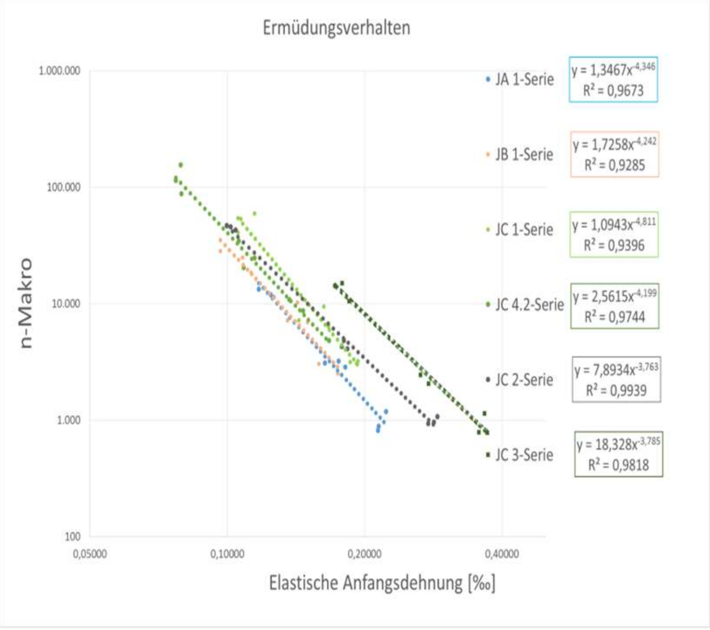


Innovative asphalt mix design for surface layers reusing 100% RAP and the new binder

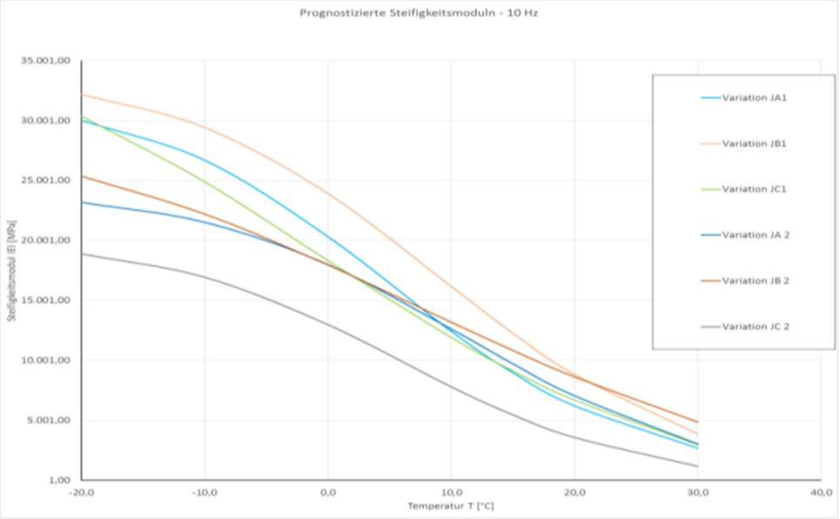
Asphalt Mix Investigation

The fatigue functions of dynamic indirect tensile testing at 20 °C (on the ordinate axis, are plotted the number of load cycles to the occurrence of macro cracks N_{Makro}, and on the abscissa axis, is shown the initial elastic strain), **show that the rejuvenated variants (**JC variants) **in relation to the aged** variant (JB) and **reference variant** (JA), with **the same elastic initial strain**, endure more **load charges** up to the **macro cracking**.
From the stiffness-temperature functions for 10 Hz in the temperature range **-20°C to C + 30°C,** it can be seen that **ageing leads** to **an increase** of the **stiffness modulus** (JA to JB) in the temperature range under consideration. At the same time, there **is a reduction** in stiffness modulus **after the addition** of the additive (JB to JC). Comparing the rejuvinated variant to the reference variant (JC-JA), it was observed that tha values after rejuvination, are in the **range of the reference** variants or **below**

Fatigue behavior



Stiffness modulus –temperature function

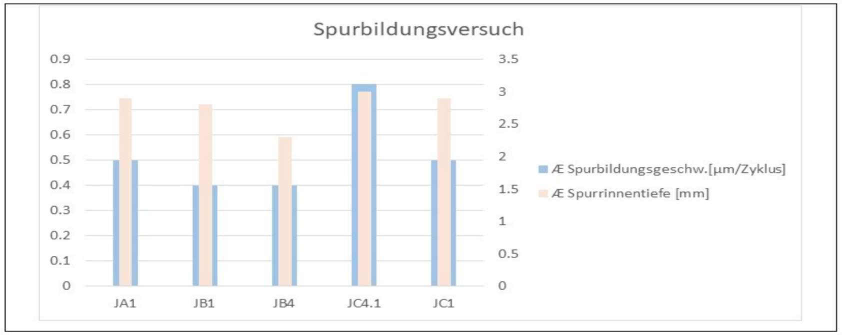


Innovative asphalt mix design for surface layers reusing 100% RAP and the new binder

Asphalt Mix Investigation

From the **wheel track test** after 10,000 cycles, it was observed that no variant reached **the 8 mm rut depth failure criteria.** All variants were **within the authorized standard range**
It can be seen that the **values of** the **degrees of bitumen coverage** of the variants **JA-JC** shown in the table, have only **very small deviations**. Compared to the **reference variant JA,** the variant **JC** (24-72h) has **5% -10% more coating**

Wheel Tracking Test



Degree of bitumen coverage

		Rolling time [h]			
		6	24	48	72
Coverage [%]	Var. JA1	80	55	45	40
	Var. JA2	80	55	45	40
	Var. JB1	80	60	50	45
	Var. JB1.2	75	55	45	40
	Var. JB2	75	55	50	45
	Var. JC1	80	60	55	45
	Var. JC2	80	60	50	45

In conclusion, the series of lab scale experimentations has shown that the use of the developed Rejuvenator additive, **reverses the ageing rheological** binder properties and **restores the original fresh** bitumen values, positively influencing binder and asphalt mix characteristics. It significantly **improves the fatigue** behavior (which could be **explained** by the increase of **polar resins percentage** in the binder composition) and **reduces the risk of cracking**.
A **trial section** with the implementation of an upper layer using **100% RAP** with **vegetable oil and Selenizza®SLN,** has **been laid in Greußen**, near Erfurt.

Test section in D-99718 Greußen.

MAIN OUTCOMES

- The addition of the natural bitumen Selenizza®SLN, **strongly affects** the **mechanical behavior** of road pavement bitumen and **decreases the susceptibility** to **ageing of modified** bitumen as the percentage of natural bitumen content increases
- The **hardening** and **anti-ageing properties** of natural bitumen, may **be used advantageously** to **develop new binders combining** its high performance **mechanical and durability properties** (thanks to its high percentage of asphaltene content), with the **rejuvenating capability** of waste **vegetable oils**, whose Aromatics, Resins and Saturates fractions contents, are relatively close to those of petroleum bitumen.
- The expanded use of reclaimed asphalt (RAP) materials in the production of asphalt mixtures has significant **economic benefits** and **environmental advantages**. 100%RAP mixtures were **successfully implemented** with the addition of a **new developed rejuvenator** based on waste vegetable oil and natural bitumen Selenizza®SLN. The new developed binder, which contains a high proportion of maltenes, re-balanced the composition of the aged binder, conferring to the asphalt mixtures high mechanical properties and optimal performance characteristics

THANK YOU

SELENIZZA®
NATURAL BITUMEN