



AGORA 4
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Natural bitumen, an answer to the challenges of future asphalt mixes

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SELENIZZA®
NATURAL BITUMEN



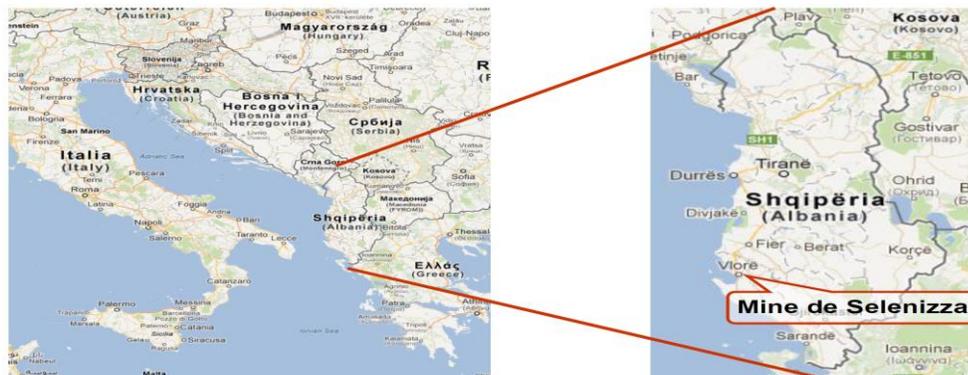
- Characteristics of natural bitumen Selenizza[®]SLN
- Antiaging properties and hardening effect of Selenizza[®]SLN
- Potential use of waste vegetable oils-modified natural bitumen for developing a new type of binder
- Example of innovative asphalt mix design for surface layers reusing 100% RAP and a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



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CHARACTERISTICS OF NATURAL BITUMEN Selenizza®SLN

- The mine of Selenice is **located** in southwest Albania.
- It has been mentioned since **ancient times** by Aristotle & actively exploited by **the Romans**.
- in **1868**, The French **geologist Coquand** published a **geological description**
- The **ottoman** government **transferred rights** to the French (1871), Italians (1919-1943).
- After the **World War II** exploited by **the Albanian** government.
- Since 2001, the mine is **managed** by the French company KLP Industries





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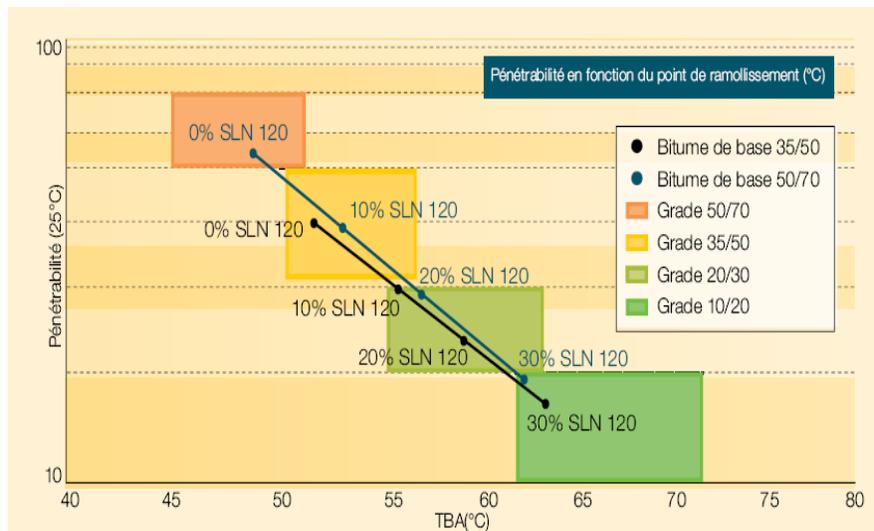
Description	Penetration [dmm]	TR&B[°C]	Penetration Index	Grade obtained
Petroleum bitumen 50/70	54	49,0	-1,28	-
Mixed with 5% natural bitumen	38	52,6	-1,18	35/50
Mixed with 10% natural bitumen	28	56,2	-1,01	20/30
Mixed with 15% natural bitumen	20	-61,6	-0,60	10/20
Natural Bitumen	0	120,0	-0,18	-

- 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
- Depending on % of Selenizza added and on the base bitumen, it is possible to obtain **precise penetration** and/or R&B **softening point** value of the **resulting binder**
- The **evolution** of log P and R&B temperature, is in **linear proportion** to the % of Selenizza:

$$\log P_m = \log P_n + x * (\log P_a - \log P_b)$$

$$T_m = T_b + x * (T_a - T_b)$$

which helps to calculate the right dosage of Selenizza





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Physico-chemical properties

Selenizza's organic phase is similar to that of petroleum bitumen with the specificity of high content of polar fractions (resin + asphaltene) resulting in a:

- vitreous transition at higher temperatures
- enhanced adhesion between the bitumen and mineral aggregates
- colloidal instability index I_c values, indicate sol or sol-gel character
- addition of natural bitumen does not affect the glass transition of bitumen
- 35/50 compared to modified alternative $\rightarrow T_g = -23.1^\circ\text{C}$ versus $T_g = -19.3^\circ\text{C}$
- better resistance of natural bitumen to brittle fracture

Complex modulus

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

IATROSCAN fractions

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

Evolution of glass transition temperatures

	Total heat flux				
	T_{g1} [°C]	T_g [°C]	T_{g2} [°C]	ΔT_g [°C]	$\Delta\Phi$ [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



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Ageing Inhibitor

RTFOT test (to simulate oxidation of bitumen during mixture manufacturing)

PAV (to simulate in-service ageing)

Ageing effect was quantified using the following mathematical expression:

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

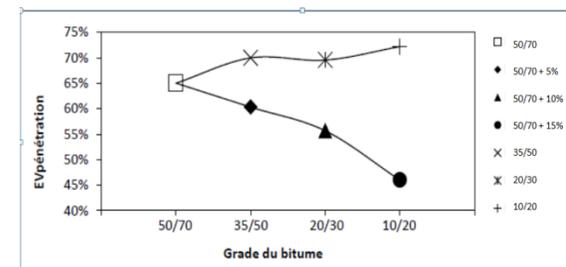
EV_x: the evolution of mechanical property X

Changes of modified specimens were lower than those of 50/70

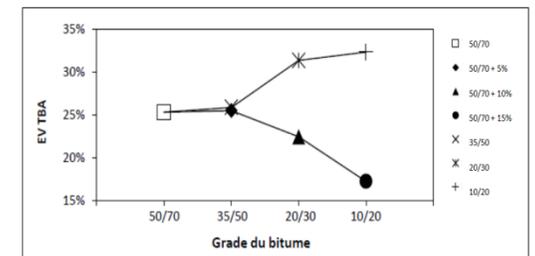
Changes are attenuated with the increase of % SLN

Modified bitumen are characterized by minor changes compared to petroleum bitumen of equivalent grades

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



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POTENTIAL USE OF WASTE VEGETABLE OILS-MODIFIED NATURAL BITUMEN FOR DEVELOPING A NEW TYPE OF BINDER

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 quarry of natural bitumen (Albania)



c) Example of blend with waste sunflower oil

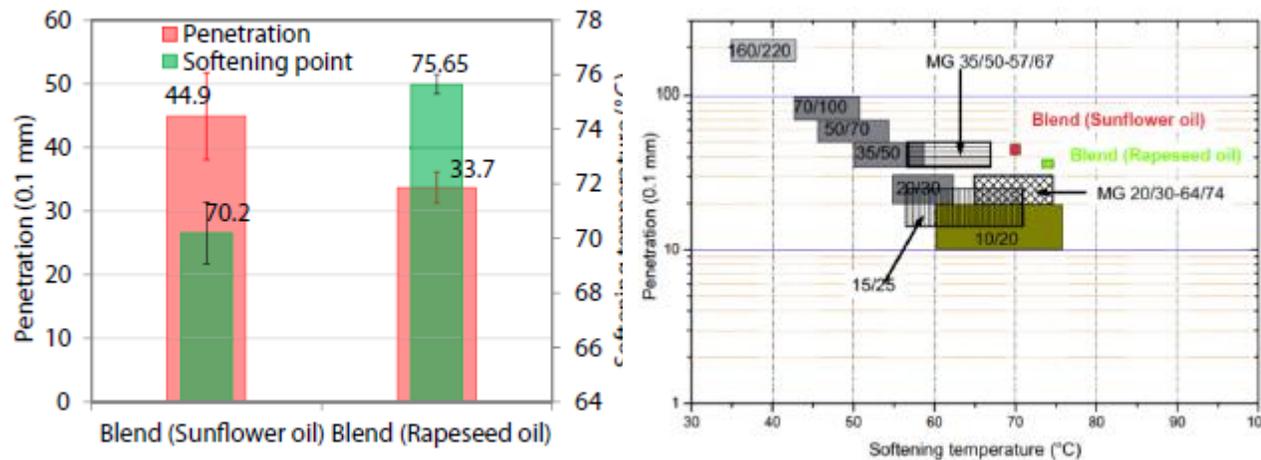
Fig. 1. Main constituents of binders.



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BINDER CHARACTERIZATION

Engineering properties



Complex Modulus

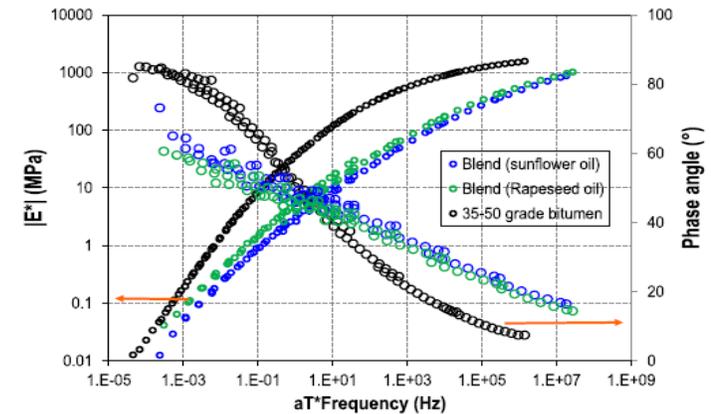


Fig. 6. Binders complex modulus and phase angle master curves at 15 °C.

- Both close to the **P35/50 petroleum bitumen**. Reference bitumen is **stiffer** than the produced binders in the temperature range between 20 °C and 60 °C.
- The **rapeseed oil binder is harder** than the sunflower oil binder; **Softening** temperatures **exceed** those of **conventional** petroleum bitumen.
- Blended binders have **lower phase angles** than reference bitumen for the **reduced frequency** $a_T \times f \leq 2.5$ Hz (e.g. $T \geq 20$ °C) and **higher phase angle** for the reduced frequency $a_T \times f \geq 2.5$ Hz (e.g. $T \leq 20$ °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** due to the waste **vegetable oil's** T_g that are **lower** than those of **bitumen**.



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ASPHALT MIX CHARACTERIZATION

A **Semi Coarse Asphalt Concrete** (BBSG 3, 0/10) has been **manufactured** according to the mix composition described in Table 4.

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%

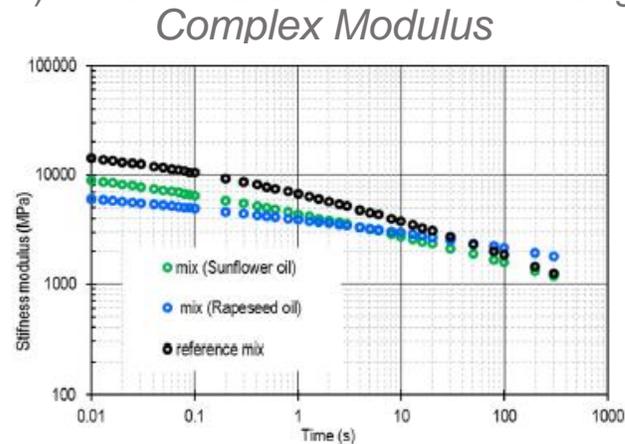


Fig. 8. master curves of the stiffness modulus of the mixes at 15 °C.

Evolution of the rut depth

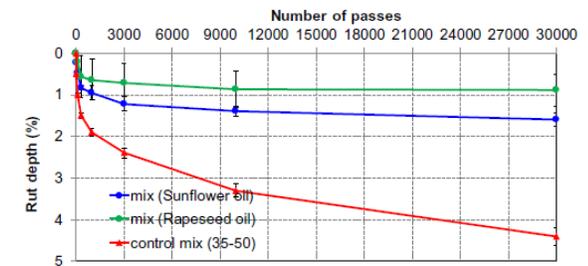


Fig. 7. Evolution of the rut depth.

- **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 $\leq 5\%$** 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 $a_T \times f$ 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 occur is not known yet.



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EXAMPLE OF INNOVATIVE ASPHALT MIX DESIGN FOR SURFACE LAYERS USING 100% RAP AND A BINDER COMPOSED OF Selenizza®SLN AND VEGETABLE OIL

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.

In order to be able to **complement** and **verify the** results of **asphalt ageing**, the **binder** was aged **in parallel** with the **asphalt mixture**.

To **simulate** the **accelerated ageing** of bitumen and asphalt mixtures the **following methods** were used in laboratory:

- Rolling Thin Film Oven Test (**RTFOT**) according to DIN EN 12607-1:2013
- Pressure Ageing Vessel (**PAV**) according to DIN EN 14769:2012
- **AASHTO R 30** Short term mixture conditioning (a laboratory procedure used to simulate the effects of HMA aging and binder absorption that occurs during the pre compaction phase of the construction process Standard Practice for mixture conditioning of hot mix asphalts)
- **BSA ageing** (Braunschweiger Alterung) - practical method of asphalt mix ageing developed at the Technical University Braunschweig



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EXAMPLE OF INNOVATIVE ASPHALT MIX DESIGN FOR SURFACE LAYERS USING 100% RAP AND A BINDER COMPOSED OF Selenizza[®]SLN AND VEGETABLE OIL

JA = Reference Asphalt Mixture

JB = Aged Asphalt Mixture

JC = Asphalt Mixture with Rejuvenator

12 different variants of Asphalt Concrete AC DN 11



Variants JA, JB & JC of Asphalt Concrete AC DN 11

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



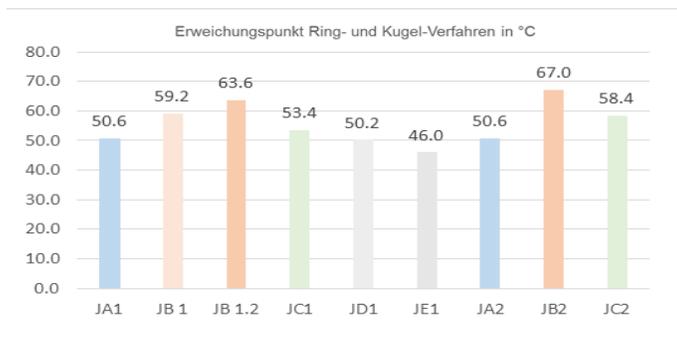
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Binder Investigation

It can be seen that due to ageing, the softening temperature of aged binders (JB1, JB1.2 and JB2) increased in comparison with (JA1, JA2) reference variants 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.

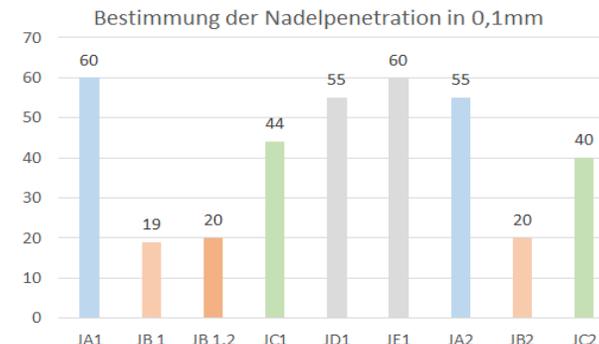
Softening point R&B

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		



Penetration

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		





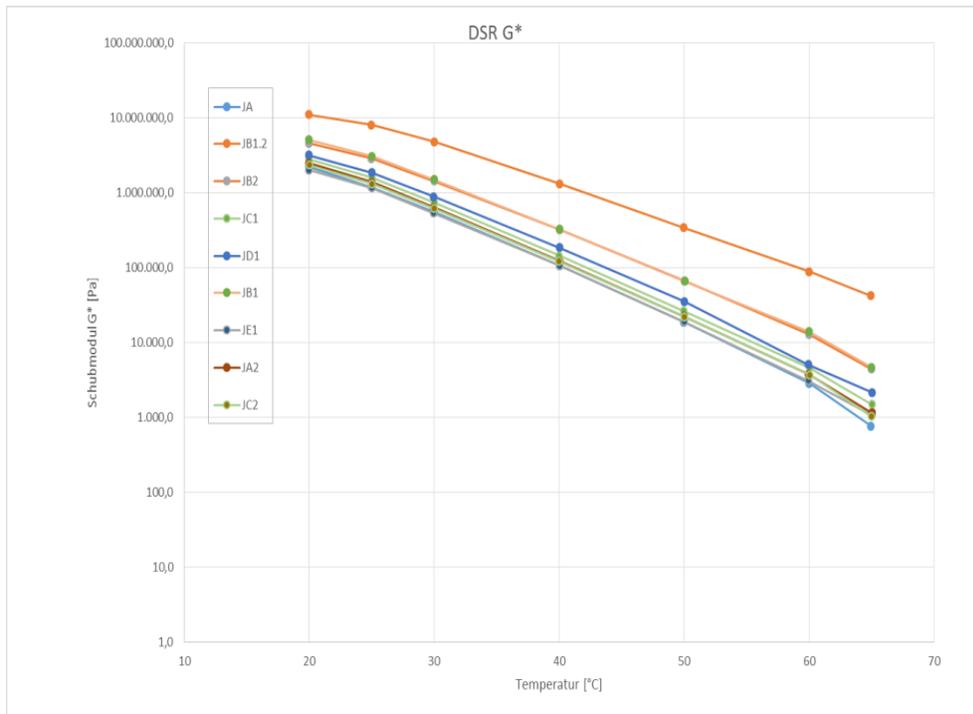
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Binder Investigation

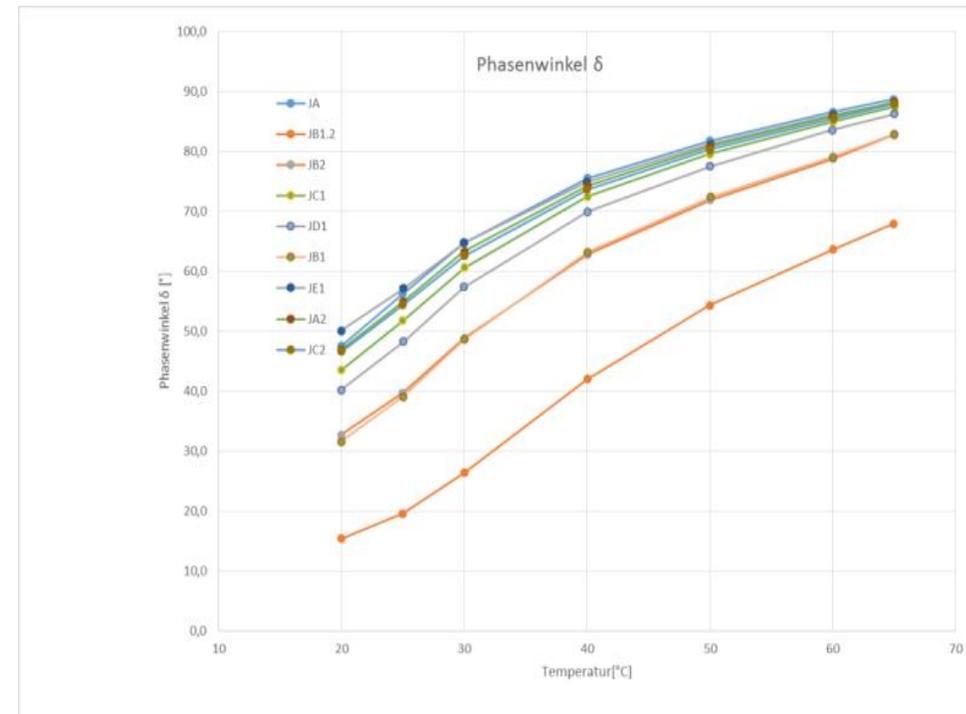
The results of **Dynamic Shear Rheometer analysis** at a load frequency of 1.59 HZ and temperature range of 20°C to 65 °C showed that aged variants (**JB**) have a **greater rigidity** compared to reference variant (**JA**) over the entire temperature range. The **rejuvenated variants (JC)** are **again in the range** of the **initial values**.

It can be seen that the **phase angle** results for temperature sweeps at the range of 20 °C - 65 °C, for **the aged variants (JB)**, in particular compared to the reference variant (**JA**), have a **lower phase angle** over the entire temperature range. The rejuvenated variants (**JC**) are **again in the range** of the **initial values**.

Temperature sweep G^* test



Temperature sweep phase angle test





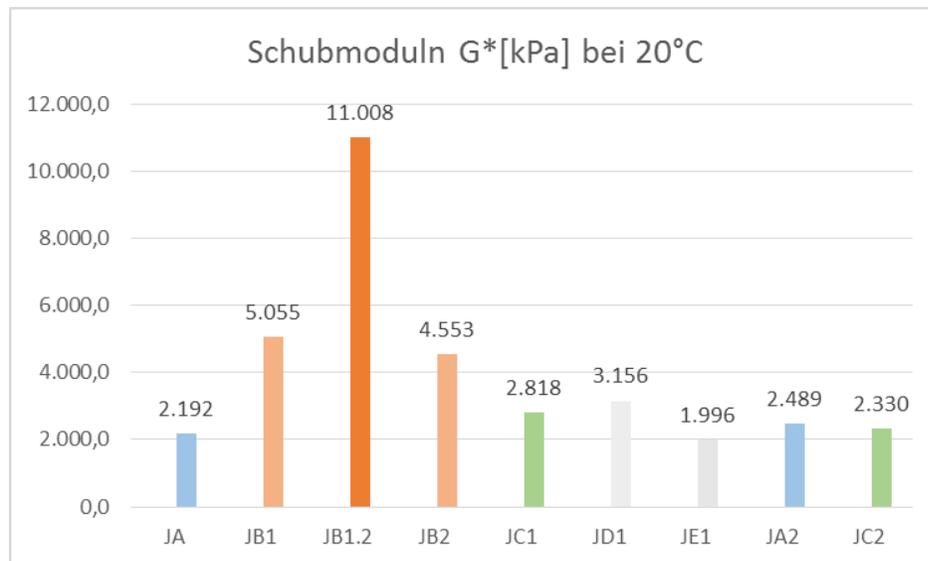
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Binder Investigation

It can be seen that the **shear modulus** at 20 °C of the **aged variants**, have **increased** 100% to 500% with respect to the **reference variant**. It can also be seen that the **values of the rejuvenated variants (JC)**, are **again in the range** of the initial values.

It was observed that the **addition of the additive leads to a difference in the percentage distribution** of the main SARA groups. 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**.

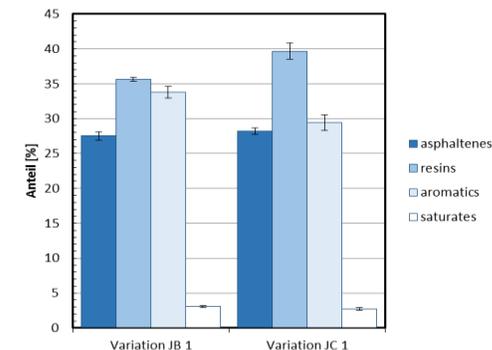
Shear Modulus 20°C



Comparison with SARA Analysis of JB1 and JC1

Variation JB 1	average [%]	standard deviation
asphaltenes	27,548	0,233
resins	35,635	1,205
aromatics	33,763	0,801
saturates	3,056	0,635

Variation JC 1	average [%]	standard deviation
asphaltenes	28,179	0,240
resins	39,675	0,111
aromatics	29,423	0,972
saturates	2,723	0,621





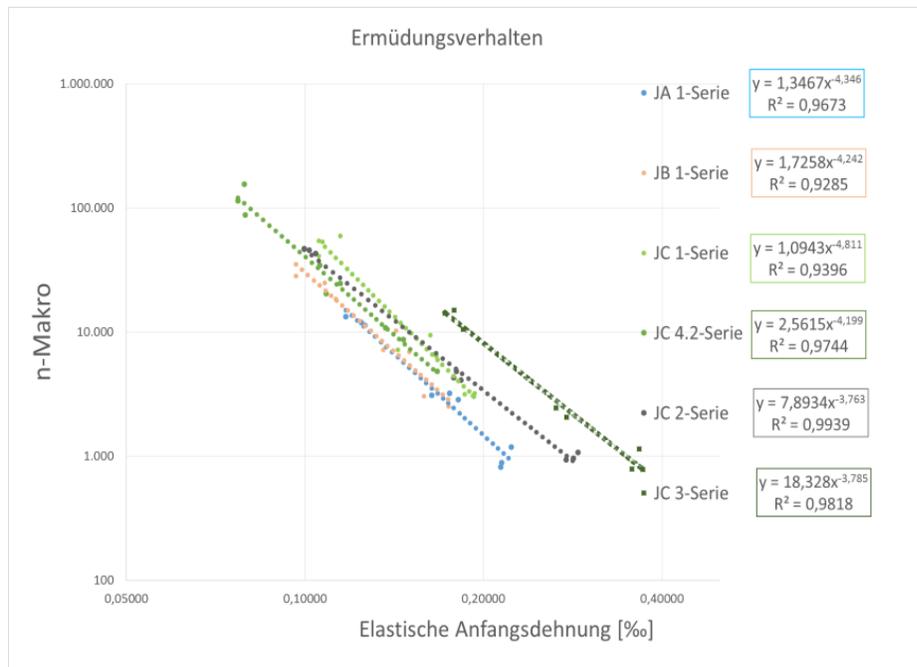
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Asphalt Mix Investigation

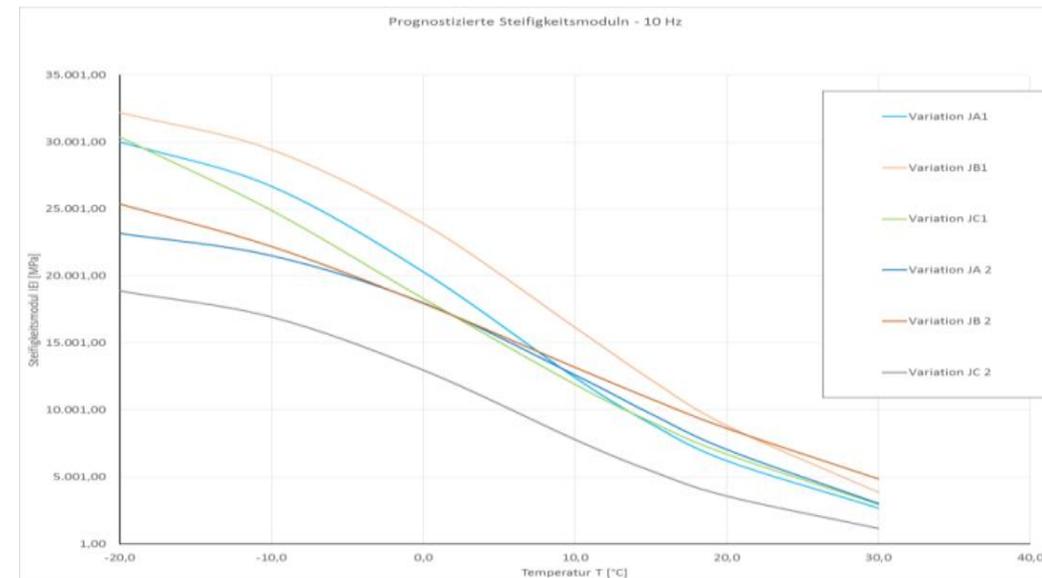
The fatigue functions of dynamic indirect tensile testing at 20 °C (on the ordinate axis, are plotted the number of load cycles to the occurrence of macro cracks N_{Makro} , and on the abscissa axis, is shown the initial elastic strain), show that the rejuvenated variants (JC variants) in relation to 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 rejuvenated variant to the reference variant (JC-JA), it was observed that the values after rejuvenation, are in the range of the reference variants or below.

Fatigue behaviour



Stiffness modulus-temperature function





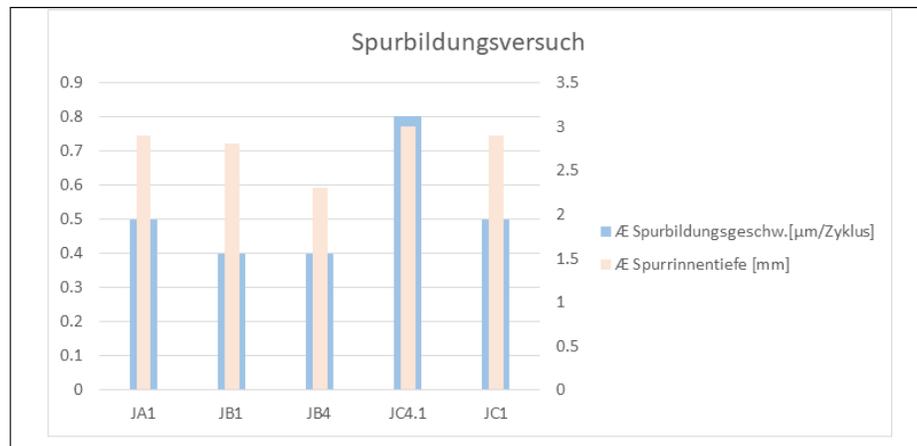
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Asphalt Mix Investigation

From the **wheel track test** after 10,000 cycles, it was observed that no variant reached the **8cm rut depth failure criteria**. All variants were in **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



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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 **test 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