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SELENIZZA

Contribution of natural asphalts to the implementation of HMA mix for cold climate

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Selenice Bitumi

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Contents

1. ***Modification of petroleum road bitumen by the addition of natural asphalts***

2. ***Characteristics and low temperature behaviour of Selenizza SLN and natural asphalt modified binders***

2. ***Mix design examples used in countries with vast temperature fluctuations. Selection criteria***

4. **Natural bitumen: An environmentally friendly product**

5. ***Conclusions***

Characterisation of different natural asphalts

- A study was carried out by the University of Rome ***''LA SAPIENZA"*** *to characterize* ***natural bitumen*** *and evaluate their* ***contribution*** *to the modification of* ***straight-run bitumen***
- *The aim of this research work was* ***to characterize*** *some of the natural asphalts, most diffused commercially and to evaluate their* ***efficiency as modifiers***

➢ **Three natural asphalts** were selected:

Natural asphalt	Bitumen content (%)	Asphaltènes content(%)	Penetration (à 25°C,1/10 mm)	R&B (°C)
Gilsonite	> 99	70	0	160–170
Selenizza	85-90	42*	0	115
Trinidad	53-55	33-37	1 - 4	93–98

➢ An Iranian ***Straight Run bitumen*** (Gach Saran) with penetration **80-100,** was **added with each** of the three types of natural asphalts :

- by the percentage of **10%**
- at a minimum temperature of **150 – 180 °C**

➢ *Two techniques have been used:*

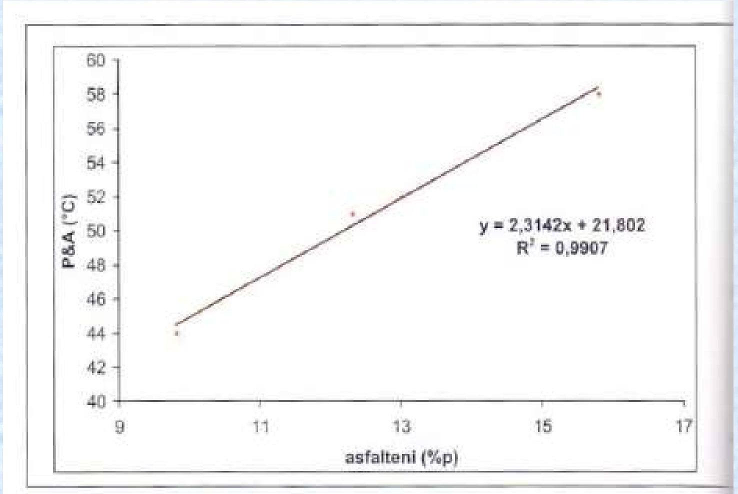
- ***Dynamic rheological analysis & Modulated Differential Scanning Calorimetry*** **(MDSC)**

Characterisation of different natural asphalts

Effect on Penetration and Softening Point

As **expected,** for the three cases, the resulting modified bitumen was characterized by **higher softening point** (R&B temperatures) and **lower penetration values**, compared to the original standard bitumen, due to the presence of **high percentages of asphaltenes** content in the natural asphalts

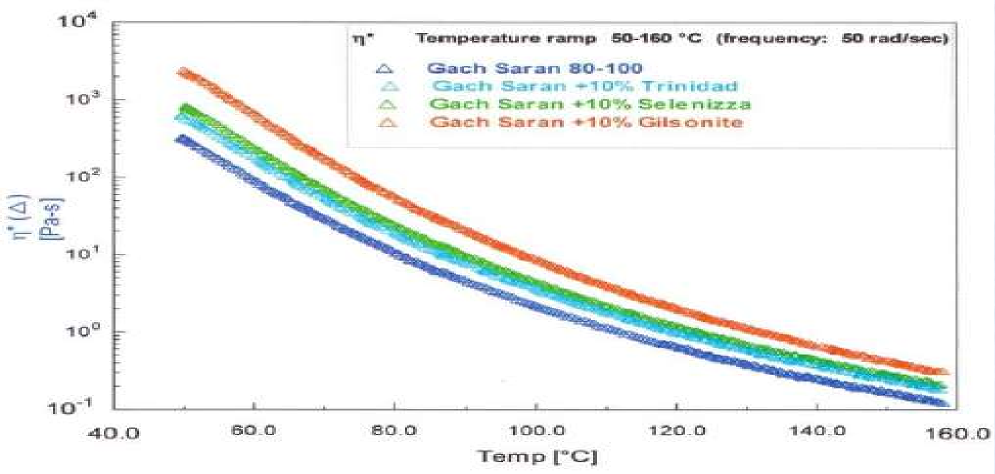
Type of bitumen	Penetration at 25° (1/10 mm)	R&B Temperature °C	Asphaltenes content (%)
Original bitumen	96	44	9,8
+10% Gilsonite	38	58	15,8
+10% Selenizza	67	52	13,0
+10% Trinidad	78	51	12,3



Relationship between aspaltene content and R&B

Effect on viscoelastic properties at high temperatures

For **medium and high temperatures** (50 – 160°C), the **rheological behavior** whose softening point represent the lower limit, is not a function of the modifier quality and **depends exclusively on the asphaltenes content**



The **viscosity values increase,** the viscosity curves **shift upwards**, their shape and the slope remain unchanged and parallel for all sample types. The **modifiers don't affect the** internal **interactions** between the **asphaltene components** in the modified bitumen, which is a typical phenomenon for the **compatible additives**

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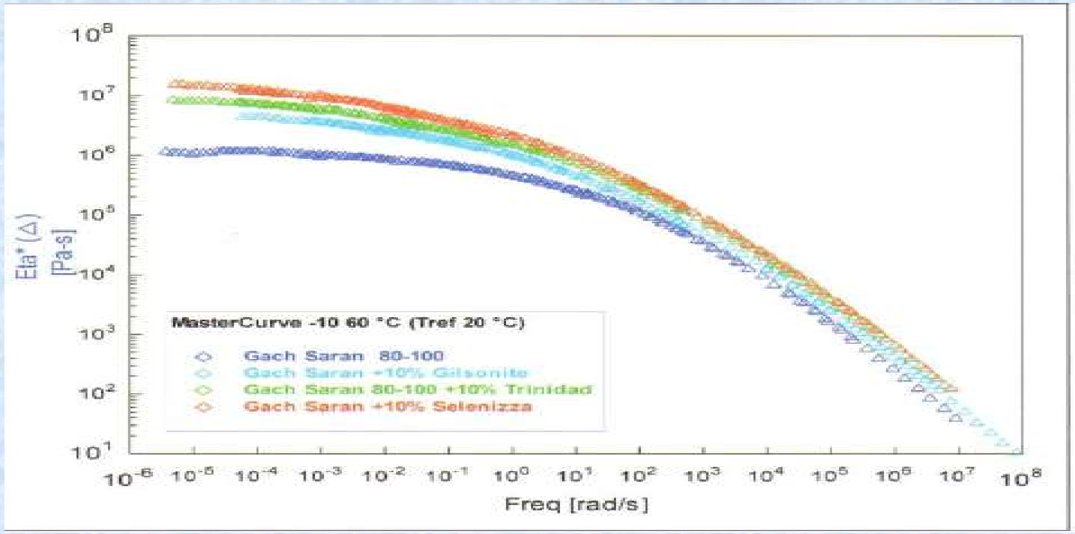
Effect on viscoelastic properties at low temperatures

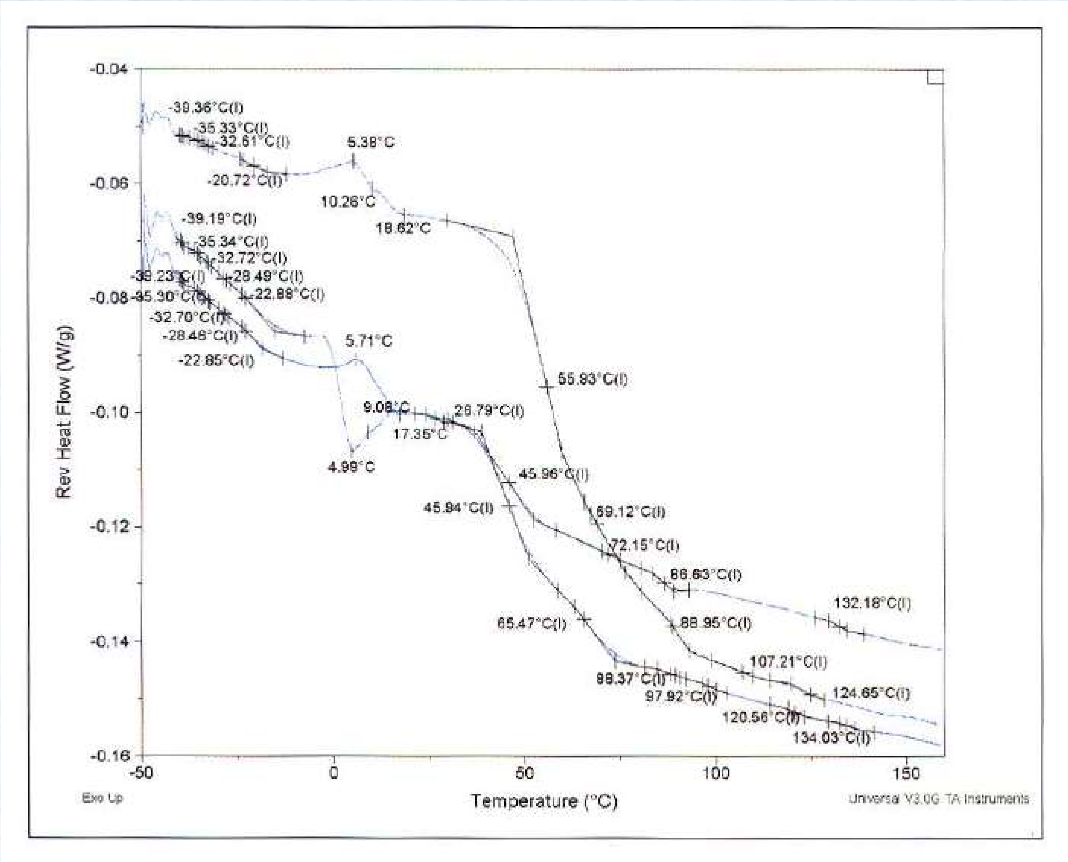
- For the **low temperatures (10 - 60°C**), the rheological **modifications** seem complex and are **differentiated**



- **Master curves** η*, G',G'' = f(ω) drawn under **reference temperature 20°C & temperature interval [-10 ÷ 60 °C]**. The **viscoelastic** behavior and the **ductility** of the modified samples are **impacted by the quality of the natural bitumen** (bituminous+i**norganic** component). At **T=20°, inversion** of the zero shear **viscosity** η_0 (GS) < η_0 (Gil) < η_0 (Trid < η_0 (Sln)

Characterisation of different natural asphalts

Modulated Differential Scanning calorimetry MDSC



The **samples** (7 – 10 mg), were **subjected to a modulated heating ramp** resulting from a sinusoidal temperature ripple overlaid on a linear temperature ramp:

$dQ/dt = C_p \beta + f(T, t)$ Temperature range: [-50 °C, + 160 °C]

For the bitumen, the **reversing curve** ≈ 1/ C_p , is **more indicative: vitreous transitions , fusions**

Trinidad & Selenizza : affect the **lower limit** of the softening range of the straight run bitumen (+55,8 °C ➔ 45,9°C) **due to the presence** of **different maltenic phases** (of lower molar mass), which **soften at lower temperatures**. The **asphaltenic phases**, result to **behave independently**. A dilution effect of the original bitumen is obtained

Gilsonite, does not act as a diluent, but **expands the softening** range to **higher temperatures**

The **modifications** operate in such a way as to **increase** the **consistency**, **the viscosity** and the **stability** of the original bitumen

Characterisation of natural bitumen Selenizza®SLN

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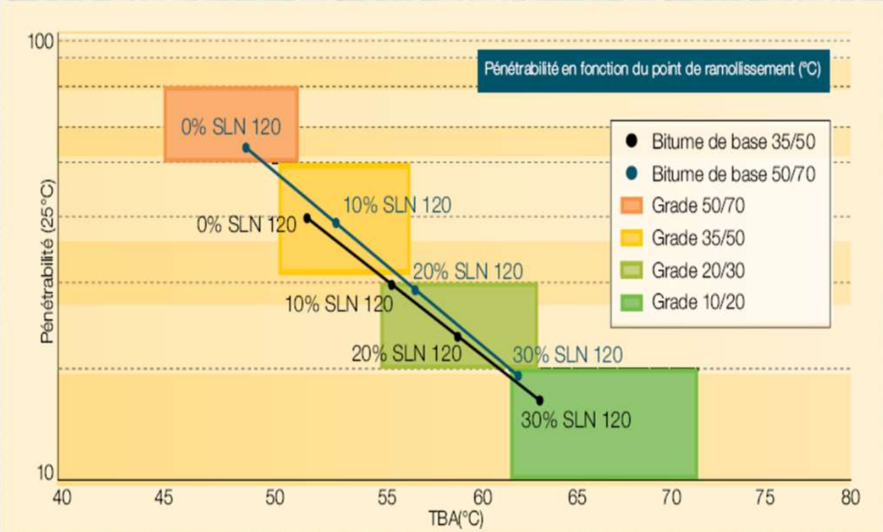
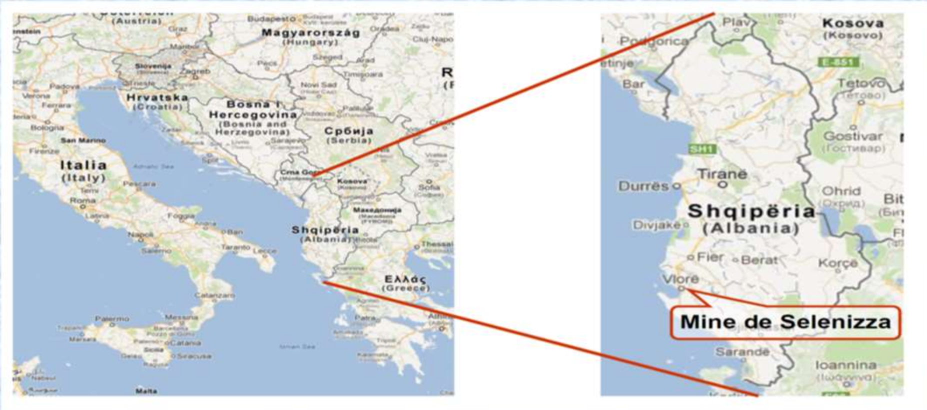
Description	Penetration [dmm]	TR&B[°C]	Penetration Index	Grade obtained
Petroleum bitumen 50/70	54	49,0	-1,28	-
Mixed with 5% natural bitumen	38	52,6	-1,18	35/50
Mixed with 10% natural bitumen	28	56,2	-1,01	20/30
Mixed with 15% natural bitumen	20	-61,6	-0,60	10/20
Natural Bitumen	0	120,0	-0,18	-

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





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Characterization of natural bitumen Selenizza®SLN

- A **PhD thesis** was recently presented at the University of Strasbourg in France, on the **potential of using** natural bitumen in the production of **hard penetration grade binders** and **high modulus asphalt mixes** that lead to implementation **of cost effective** pavements (thin and long lasting pavement layers)

- **The study,** in line with the strategy of **sustainable industrial development**, **proposes an alternative method** using natural bitumen to produce HMA **aging resistant** and relatively **efficient at low temperatures**.

- These researches are **very topical at this time,** considering the **problems encountered** while using **hard petroleum bitumen** such **as the risk of cold cracking, rapid aging, supply difficulties,** as well as the **inability to produce hard bitumen** from certain crude oils…

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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]	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	
	I E* I [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**

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Selenizza®SLN- Aging Inhibitor

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

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

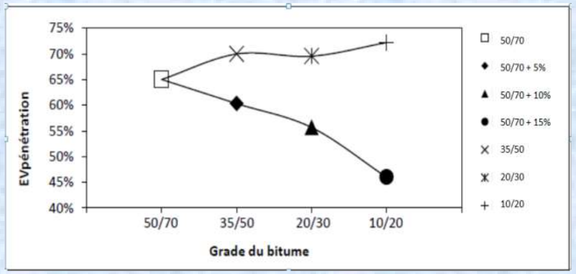
where EV_x – The evolution of the mechanical property x

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

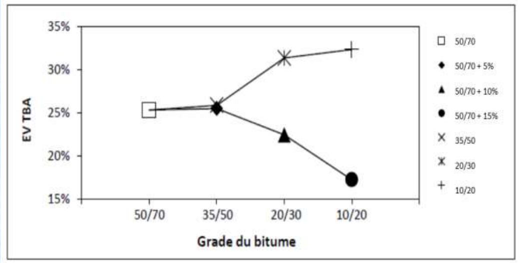
From the **ageing point of view**, the binders modified with Selenizza can **advantageously replace** hard petroleum bitumen for the production of HMAC

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



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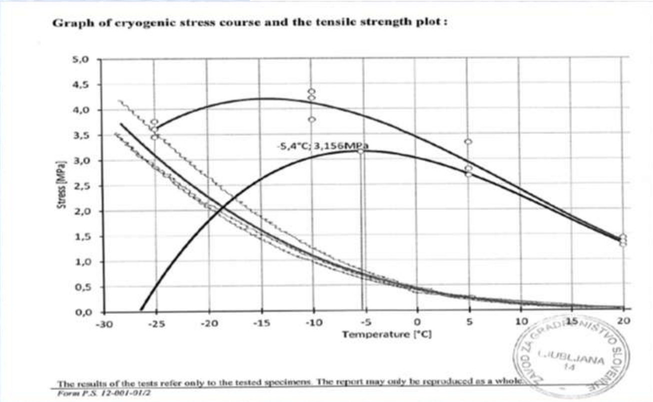
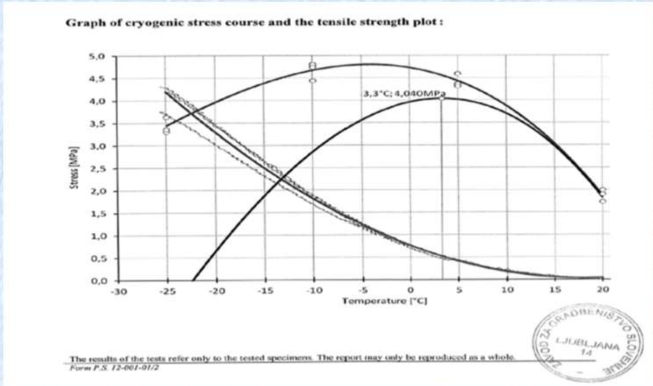
Low-temperature fracture

The Laboratory **TSRST comparative tests** from Slovenian National Building Institute (**ZAG), conducted on base course asphalt mixture specimen AC 22 with 50/70 pen bitumen,** and **same mix design** with 50/70 **modified with SelenizzaSLN** showed that Selenizza **has little influence on the** low temperature fracture resistance **.** SLN brings **some rigidity** (curves are shifted to the right, toward positive temperatures). At **T= 3,3 °C**, the asphalt mixture with Selenizza is subjected to a higher tensile strength **4,04 MPa**, as compared with the tensile strength **3,156 MPa at T= - 5,4 °C**, for the classical asphalt mixture

Graph of cryogenic stress course and the tensile strength plot



Binder 50/70



Binder 50/70 + SLN

Test results summary :

Failure temperature at TSRST	$T_{failure}$	-28,4°C
Maximum tensile strength reserve	$\Delta\beta_{t,max}$	3,156MPa
Temperature at $\Delta\beta_{t,max}$	$T(\Delta\beta_{t,max})$	-5,4°C

Test results summary :

Failure temperature at TSRST	$T_{failure}$	-25,3°C
Maximum tensile strength reserve	$\Delta\beta_{t,max}$	4,040MPa
Temperature at $\Delta\beta_{t,max}$	$T(\Delta\beta_{t,max})$	3,3°C

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High performing EME (Switzerland)

In order to respond to the **technical challenges** imposed by:

1. very **severe stresses** and strains that bituminous pavements are subject to due to the **large increase** in the number **of trucks** crossing the Swiss Alps every year

2. **very harsh climatic** conditions of the country (temperatures fluctuate between -20°C and +40°C)

Switzerland has integrated in its national standard for bituminous mixtures, the **concept of** High Modulus Asphalt Mixes **(EME)**

SELENIZZA® NATURAL BITUMEN

High performing EME (Switzerland)

- **The performance class 1** is recommended to improve the **resistance to permanent deformation** (rutting)
- **The class 2**, to improve the **fatigue resistance** of the asphalt mix layer. More difficult to reach, it includes **tough requirements** on **stiffness modulus** and **fatigue resistance** (more severe than the French one) :

Specifications of Swiss standard on EME

	Méthode d'essai	AC EME 22 C1	AC EME 22 C2
Teneur en vides des éprouvettes Marshall (%)	EN 12697-8	≤ 3.0 - 5.0	≤ 1.0 - 3.0
Sensibilité à l'eau, résistance à la traction par fendage ITSR (%)	EN 12697-12	≥ 70	≥ 70
Teneur en liant en pourcentage de la masse d'enrobé (%)		≥ 4.6	≥ 5.4
Résistance à l'orniérage à 30 000 cyles et 60 °C	EN 12697-22		
Profondeur d'ornière sur une plaque de 10 cm d'épaisseur (%)		≤ 5.0	≤ 7.5
Module complexe à 15 °C/10 Hz (MPa)	EN 12697-26	≥ 11 000	≥ 14 000
Résistance à la fatigue à 10 °C/25 Hz (microdéformations)	EN 12697-24	≥ 100	≥ 135

Tableau 1

High performing EME (Switzerland)

To respond to this constraints, **CO.MI.BIT, an asphalt mix manufacturing cooperative,** located in Taverne (Canton Ticino), has developed a new mix design of type **AC EME 22 C2** that improves the **fatigue performance** by using **a polymer modified bitumen** all while maintaining a **high stiffness modulus** using **Selenizza®SLN** as hardening additive. The binder was composed of a Shell **Cariphalte 25 RC** PmB and natural bitumen Selenizza SLN. Two alternatives of mix design **same grading curve**, have been tested a final binder with penetration ranging between **10 to 20 dmm**

3.9% Shell Cariphalte 25 RC**+ 1.4% SLN = 5.3%** (Selenizza **26%** of the total binder):

3.9% Shell Cariphalte 25 RC**+ 1.6% SLN = 5.5%** (Selenizza **29%** of the total binder):

Composition du liant	Unité	Formule 1	Formule 2
Shell Cariphalte 25 RC	%	3,9	3,9
SLN 120	%	1,4	1,6
Teneur en liant théorique (en % de la masse d'enrobé)	%	5,3	5,5
Module complexe à 15 °C/10 Hz (EN 12697-26)	MPa	19 441	18 336
Pourcentage de vides hydrostatique	%		
Résistance à la fatigue à 10 °C/25 Hz (EN 12697-24)	Microdef	139	145
Pourcentage de vides hydrostatique	%		

Tableau 4
Résultats des essais de module et de fatigue obtenus par Shell Global Solutions

High performing EME (Switzerland)

- The obtained **modulus** and **fatigue** tests results **clearly exceed** the Swiss standard specification for the asphalt mixes AC EME 22 C2.To prevent the **cracking risk** at low temperatures, **a new job** mix formula was envisioned and then verified by **LAVOC Laboratory** at the Swiss Federal Institute of Technology Lausanne.
- The mix design was modified with a **less strong value** of the **stiffness modulus** by introducing a lower percentage of Selenizza (**22%**), while maintaining a **high level of fatigue resistance** :

4.7% Shell Cariphalte 25 RC**+ 1.4% SLN = 6.1%** Richness modulus **K= 3.74**

Test results conducted by LAVOC, was the following (**void content**= **2.4%):**

- ε_6 (extrapoled) ≈ **150 µdef** **(Swiss standard ≥135 µdef)**
- **Modulus** (15°C/10 Hz) **= 15 100 MPa** **(Swiss standard ≥ 14 000 MPa)**

High performing EME (Switzerland)

- Other mix design of type **AC EME 22 C1** were developed and validated in cooperation with **LAVOC Laboratory** at the Swiss Federal Institute of Technology Lausanne, with very good results in terms of fatigue performance and with low susceptibility to rutting

3.9 % PmB Shell Cariphalte 25 RC + **1,4%** SLN = **5.3%**

Test results:

- **Richness modulus K=3.30** (standard ≥2.7)
- **Rutting (at 30 000 cycles) = 1.9 %** (standard ≤5%)
- ε_6 (extrapoled) ≈ **134 microdéformations** (standard ≥100 µdef)
- **Modulus** (15°C/10 Hz) **= 18 016 MPa** (standard ≥ 11 000 MPa)

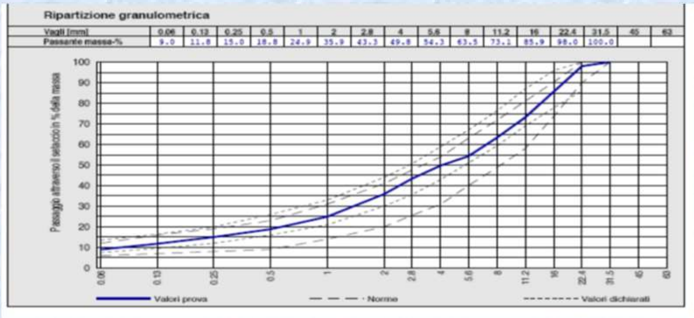
- The **high value of richness modulus** generates good **fatigue performances** and the asphalt mix has **low rutting susceptibility**

High performing EME (Switzerland)

- **It should also be noted the use of Selenizza with the recycled aggregates**

  Example: **AC EME 22 C2** with binder Shell B **15/20** + **10%** RA + **0.3%** SLN

  Binder content = **5.34%** (4.4% Shell 15/20 + 0.64%RA + 0.3% SLN)



- **Rutting** (at 30 000 cycles) = **3.8 %** (standard ≤7.5%)
- **ε_6** (extrapoled) ≈ **153** microdéformations (standard ≥130 µdef)
- **Modulus** (15°C/10 Hz) **= 14 800 MPa** (standard ≥ 14 000 Mpa)

- The mixture has low rutting susceptibility **and is effective in terms of fatigue resistance.** The good behavior that was observed was also due to the addition of Selenizza

High performing EME (Switzerland)

- In Switzerland, after 10 years' **service with harsh winters,** in the various road construction projects where Selenizza was used for the manufacture of high performing EME , **no thermal cracks were found** confirming the relevance of these EME mix designs that have led to **high mechanical performances**

- These results **confirm the potential** for successfully **combining** the benefits of **polymer modified bitumen** and of natural bitumen **Selenizza SLN**

Construction sites with Selenizza®SLN

2011 : Bridge Val Verzaska, Ticino - Switzerland

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Construction sites with Selenizza®SLN

Lugano - Switzerland

Construction sites with Selenizza®SLN

Mastic asphalt Switzerland

Construction sites with Selenizza®SLN

Highway Ticino - Switzerland

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Construction sites with Selenizza®SLN

2011 : Highway Bypass Bern -Switzerland

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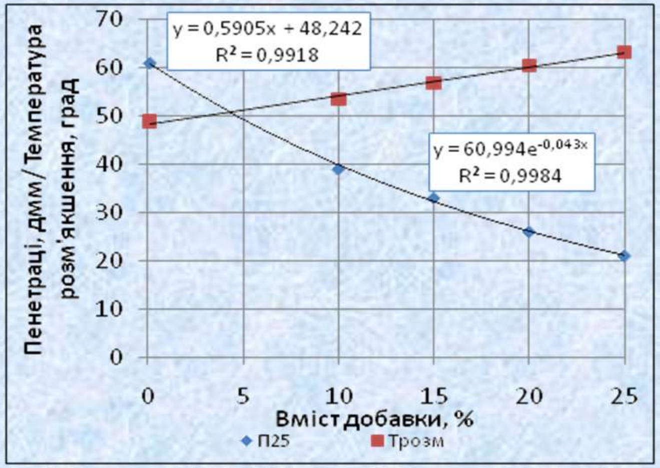
High performing asphalt mixes in Ukraine

In Ukraine, SelenizzaSLN was is recognized as **construction material and has** been classified as a Bitumen modifier for asphalt mixes that should be inserted to a proportion of **4-12% by mass of the base Bitumen** (mainly **5%** and **8%**) **.**

The National Technical University of Ukraine has analyzed the properties of Selenizza aiming to determine its compatibility with the Ukrainian bitumen (**60/90 grade bitumen)** and with those of **bordering foreign countries.**



TR&B and Penetration** Modification **of BND 60/90** bitumen with **the % of Selenizza

High performing asphalt mixes in Ukraine

- Highway **Kiev – Kovel,** in the **western part of Ukraine**, surface paving SMA -20, 8cm base course & 8cm binder course, on 3 segments with a total length of approximately **5 km**

with Selenizza

with polymers

After 3 years' service, the road is still in a very good condition !!!

In the middle of the highway constructed using Selenizza, on a small section, **for comparision purposes,** was used a **polymer modified binder**. The asphalt roadway surface with Selenizza is **smoother** and is more **black in color** compared to the segment where Kraton modified binder was used

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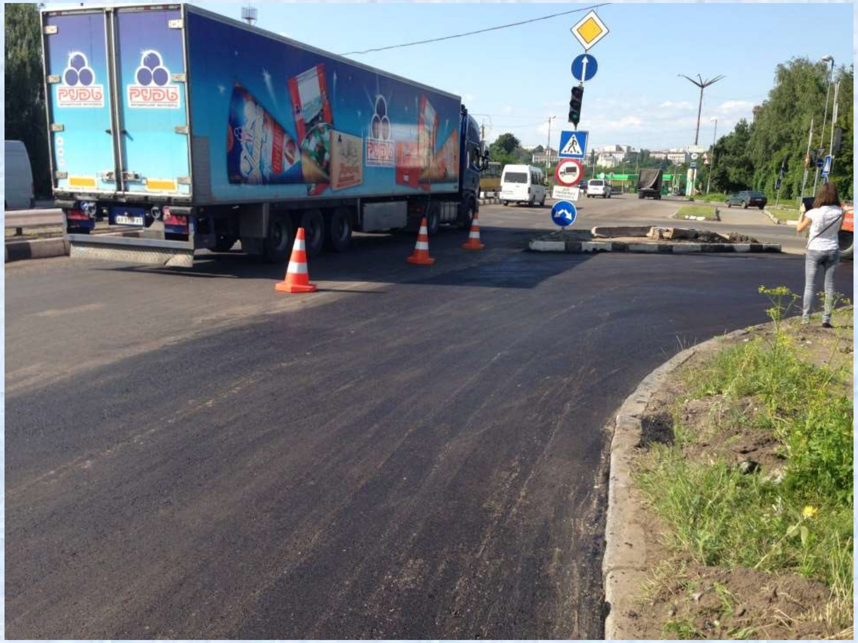
High performing asphalt mixes in Ukraine

Zhitomir, 70 Km west of **Kiev**

Before



After

High performing asphalt mixes in Ukraine

National highway Mykolaiv (Ukraine)

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High performing asphalt mixes in Ukraine
Kiev

SMA with 6 % Selenizza

Heavy traffic highway interchange entering Kiev

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SELENIZZA SLN *an additive whose amount of* ***percentage*** *incorporated is* ***deduced*** *from the* ***total quantity*** *of the base bitumen*

EXAMPLE	AGGREGATES	BINDER		
		Normal bitumen	SLN	Replaces
BASIC JMF	**95 %**	**5%**		⇩
ALTERNATIVE JMF	**95 %**	**4%**	**1%**	**1 % Normal bitumen**

LIFE CYCLE ASSESSMENT

SELENIZZA compared to petroleum bitumen

Consumers and Goverments are **increasingly demanding** information about the **sustainability of products** and **interested in comparing potential solutions. Life-cycle Assessment** (**LCA**) focuses on the sustainability of different pavements and materials, seeking to measure the **environmental impacts** of all stages of a product's life, from cradle to grave

University of Rome in cooperation with the company **Selenice Bitumi,** carried out e **research project,** whose aim was to **analyze and compare** for the first time, in terms of **energy consumption** and **CO_2 emission** between:

1. the various steps necessary to produce the **conventional bitumen from crude oil**
2. the production process of the **Albanian natural asphalt** (Selenizza)

LIFE CYCLE ASSESSMENT
SELENIZZA compared to petroleum bitumen

Deposit of natural bitumen Selenizza

LIFE CYCLE ASSESSMENT

SELENIZZA compared to petroleum bitumen

Comparing the results

Bitumes routiers de distillation

Total	*Consommation d'énergie*	MJ/t					**4,71**
CO_2	*Emissions dans l'air*	g	144563	37422	7831		**226167**

L'asphalte naturel Selenizza

Total	*Consommation d'énergie*	MJ/t					**2,376**
CO_2	*Emissions dans l'air*	g	59300	4500	59145		**127298**

- **Selenizza's** production cycle has an **environmental impact** approximately **44% less** than the distillation bitumen

- **Energy consumption** is also reduced by **around 50%** compared to bitumen produced from crude oil

Main outcomes

The **aging effect** and **thermal fatigue** are **coupled**. Low temperature fatigue cracking and ageing, **are cumulative** in effect **by amplifying** the **thermal stress** generated during **cooling.** Consequently, it is reasonable to assume that the use of binders **modified with Selenizza**, offers **an advantage** in terms of **behavior** of asphalt mixes **at low temperatures** compared with equivalent petroleum paving grade bitumen

The **combination** of **natural bitumen** with **polymers** offers an **attractive solution** on a **technical** and on an **economic level**. **A part of SBS** may **be replaced** by natural bitumen in order to **reduce the cost** of asphalt mixture production. Also, according to some authors, the replacement of SBS by natural asphalt, **increases the workability,** which could allow the reduction of the **compaction energy.**

The addition of natural bitumen in polymer modified bitumen, leads to an increase of the **magnitude** of the **complex modulus and of the phase angle.** This interesting result**,** shows that the **combination** of natural bitumen with polymers, **simultaneously improves** the binder **rigidity,** which is responsible for the good performance at **high temperatures**, with its **viscous dissipation**, that is responsible for low temperature performance.

Conclusions

- **100% compatible** with bitumen from refinery (and polymer modified bitumen)
- High performance **in modulus** & **permanent deformation**
- Better **bitumen-aggregates adhesion**
- Pavement **thickness reduction**
- Better **workability**
- **Aging retarder &** Higher **lifetime** of the pavements
- Minor **environmental impact**

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