Version 1.0

December 2015

Final Report:

The Evaluation of Three Different Formulations of Rejuvenator

Submitted by:
CSIR Built Environment
PO Box 395
Pretoria 0001

our future through science

Author:

Name	Organisation	Telephone No.	E-mail Address
Mr. J O'Connell	CSIR BE	+27 (0)12 841 2295	JOConnell@csir.co.za

Submitted to:
TarSpray cc
Suite 418
Private Bag X153
Bryanston
2021

DOCUMENT RETRIEVAL PAGE			**Report No:** CSIR/BE/IE/ER/2015/0067/B
Title: Investigating the Cause of Deformation along the T2 Route between Korogwe and Mkumbara			
Authors: J O'Connell,			
Client: Strabag international	**Client Reference No:**	**Date:** December 2015	**Distribution:** Restricted
Project No: 59E2189	**GWDMS:** 97 876		**ISBN:**

Abstract:

A proposed Interim Guideline document for the evaluation of rejuvenation agents was composed for Agrément SA. Tarspray approached CSIR to evaluate three of their rejuvenation formulations in terms of two of the tests proposed in the Interim Guideline, namely:

- Chemical analysis using thin film chromatography (TLC)
- Rheology determined by the dynamic shear rheometer (DSR)

The fatigue parameter G*.Sinδ shows that the binder fatigue properties improved with all three formulations, only showing slight differences with:

Formulation 3 > Formulation 2 > Original Formulation

Keywords: Rejuvenation

Proposals for implementation: Asphalt Design Protocols

Related documents:

Proposal: Proposal for the Technical Evaluation of Asphalt Rejuvenator (Roadseal Rejuvenator) for Agrement Certification

Project Proposal CSIR/BE/TIE/EP/2015/0012/B

Signatures:				

NOTE: This document may only be distributed in full.

1 INTRODUCTION

A proposed Interim Guideline document for the evaluation of rejuvenation agents was composed for Agrément SA. Tarspray approached CSIR to evaluate three of their rejuvenation formulations in terms of two of the tests proposed in the Interim Guideline, namely:

- Chemical analysis using thin film chromatography (TLC)
- Rheology determined by the dynamic shear rheometer (DSR)

2 EXPERIMENTAL

2.1 Slab Preparation

Medium-continuous asphalt mix, prepared using 50/70 penetration- grade bitumen, was supplied by Tarspray. Five slabs (400 x 300 x 60mm) were compacted to 5.0% voids, without re-heating the mix. The voids were calculated using the maximum theoretical relative density of 2.705, supplied by Tarspray. The design for the mix is shown in Figure 3.1. After compaction, the slabs were artificially aged by placing them in a forced-draft oven at 90°C for 5 days. This was in order to simulate environmental ageing in order to prepare aged substrates where the effect of the rejuvenator samples that were supplied could be demonstrated

2.2 Rejuvenator Application

After ageing, the slabs were cooled to 50°C, and the three rejuvenator samples were applied to three slabs (one sample per slab) at an application rate of 0.3 ℓ/m^2 (Figures 3-2 to 3-5). The slabs were designated "Original Formulation", "Formulation 2" and "Formulation 3" in accordance with the rejuvenator names, respectively. One slab had no rejuvenator applied to it and was designated "Blank". The fifth slab was kept as a back-up.

After application, the slabs were allowed to dry and absorb at room temperature (23 - 27°C) for 5 days, before placing them back in a forced draft oven at 60°C for 5 days for short term ageing.

2.3 Evaluation of Rejuvenator Effects

In order to evaluate the effects of the binder, it was necessary to recover the binder from the slabs. To this end, four 150mm cores were cored from each slab and the top 10 mm sliced off for recovery (Figures 3-6 to 3-10).

The thin film chromatographic (TFC) analysis and dynamic shear rheometer properties was determined for each binder.

Designed by : Asphalt Technical Services Checked by : J Meyer Date : 2015/01/22	ASPHALT MIX DESIGN	Contract: Gauteng Asphalt Route: Section: Layer: Wearing Course Mix: Continuous graded medium	Form D3

Asphalt Technical Services

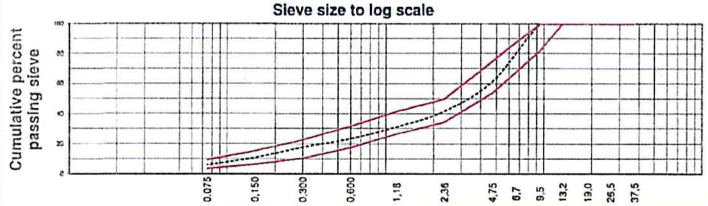
AGGREGATE PROPERTIES

	Sample No	Nom. Size	Type and Source
1	1	6.7mm	Amphibolite - PPC Laezonia
2	2	Crusher Sand	Amphibolite - PPC Laezonia
3	3	Mine Sand	Quartzite - Quarry Services
4			
5			
6			

Sieve Analysis (B 4) - % Passing Sieves

Sample No. No.		1	2	3	4	5	6	COMBINED GRADING Mix	Spec.	
% In Mix		45,0	50,0	5,0						
Sieve Size (mm)	37,5	100	100	100				100	100	100
	26,5	100	100	100				100	100	100
	19,0	100	100	100				100	100	100
	13,2	100	100	100				100	100	100
	9,5	100	100	100				100	82	100
	6,7	89	100	100				95		
	4,75	18	97	100				62	54	75
	2,36	2,0	72	99				42	35	50
	1,18	2,0	51	99				31	27	42
	0,600	1,0	36	97				23	18	32
	0,300	1,0	26	87				18	11	23
	0,150	1,0	16	48				11	7	16
	0,075	0,4	10,1	14,5				6,0	4	10
BRD	[B 14 + 15]	2,968	2,968	2,624				2,951		
Water absorp.	[B 14]	0,3							1.0 max	
Water absorp.	[B 15]		0,6	0,9					1.5 max	
ACV	[B 1]	5,6							25 max	
10 % FACT	[B 2]	572							160 min	
Flak. Index	[B 3]	28,3							30 max	
Sand eqv.	[B 19]		64,0	44,0					30 min	
PSV	[BS 812]								50 min	

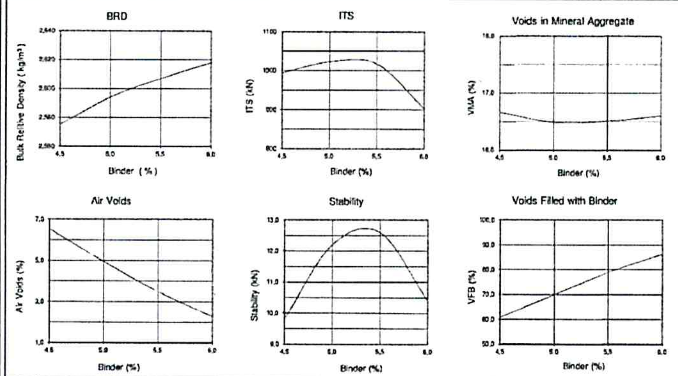
Sieve size to log scale



BINDER PROPERTIES

Type	50/70	Source	Sapref
Pen @ 25°C (0,1 mm)	62	Visc. @ 60 °C (Pa.s)	223
Soft. Pt (°C)	48	Visc. @ 135 °C (Pa.s)	0,35
RD	1,029	Hot Flow (mm)	
Temp. (Mix) (°C)	148 - 158	Temp. (Comp)	142 - 147

DESIGN CURVES



DESIGN CRITERIA		1	2	3	4	5	PROPOSAL	SPECIFICATION MIN.	MAX.
Binder	%	4,5	5,0	5,5	6,0		5,0		
Film thickness	µm	6,2	7,1	8,0	8,8		7,3	5,5	8,0
Absorp. (Binder)	%	0,47	0,44	0,38	0,39		0,44		0,5
Max. TRD (Rice)	kg/m³	2,755	2,729	2,701	2,679				
BRD (Marshall)	kg/m³	2,575	2,594	2,607	2,618				
Voids in Mix	%	6,5	4,9	3,5	2,3		4,9	3	6
VMA	%	16,7	16,5	16,5	16,6		16,5	14	
VFB	%	60,8	70,0	78,9	86,3		70	65	
Immersion Index	%	80,0	92,0	96,0	100,0		92	75	
Dynamic Creep	kN	21,7	22,1	19,8	17,2		22,1	20	
ITS	kPa	994	1022	1017	904		1041	1000	
Stab. (Marshall)	kN	9,8	12,2	12,6	10,4		12,2	8	18
Flow (Marshall)	mm	3,8	4,1	4,4	4,8		4,1	2	6
Stab. / Flow Ratio		2,6	3,0	2,9	2,2		3,0	2,5	
Air Perm.			0,93	0,89			0,93	1 x 10⁻⁸	
Filler / Binder Ratio		1,3	1,2	1,1	1,0		1,2	1,0	1,5

Rices 2015/10/21 = 2,702
2,708

Figure 2-1: Mix Design of Asphalt supplied by Tarspray

Figure 2-2: Slab after application of Original Formulation

Figure 2-3: Slab after application of Formulation 2

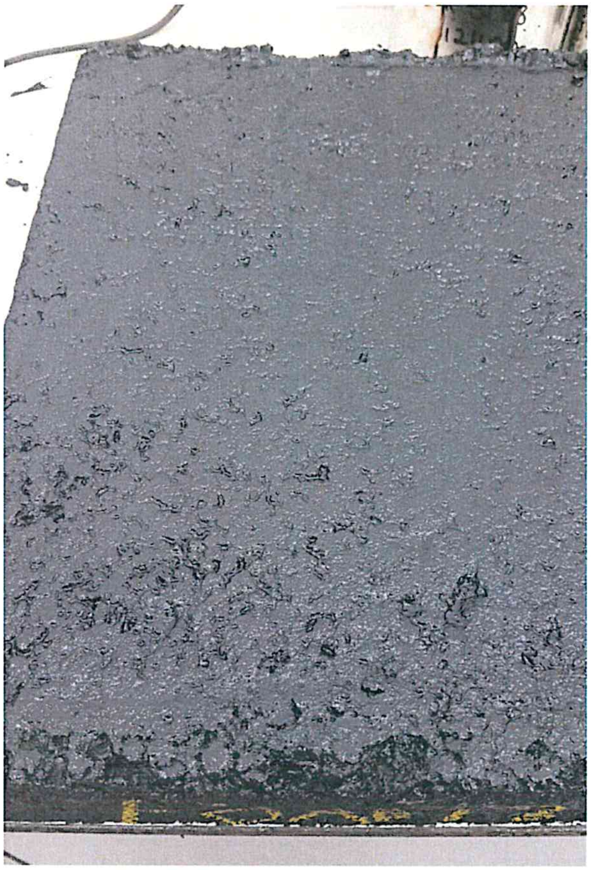


Figure 2-4: Slab after application of Formulation 3

Figure 2-5: Blank Slab

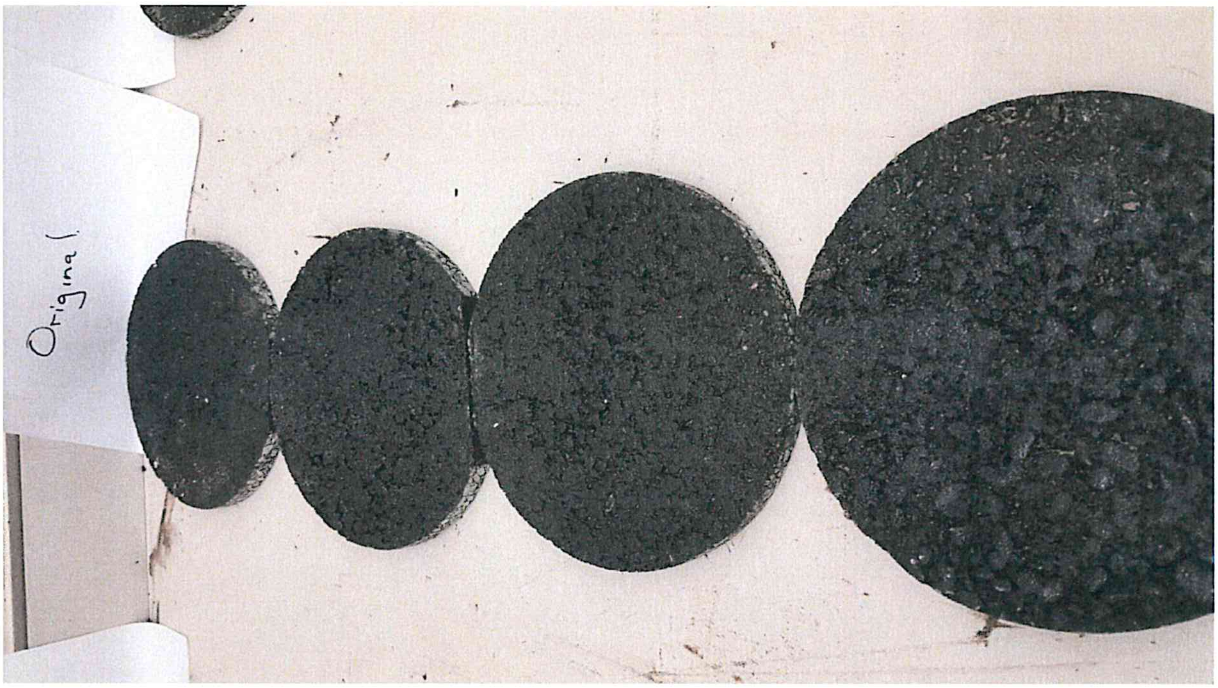


Figure 2-6: Top 10 mm after Application and Short Term Ageing: Original Formulation

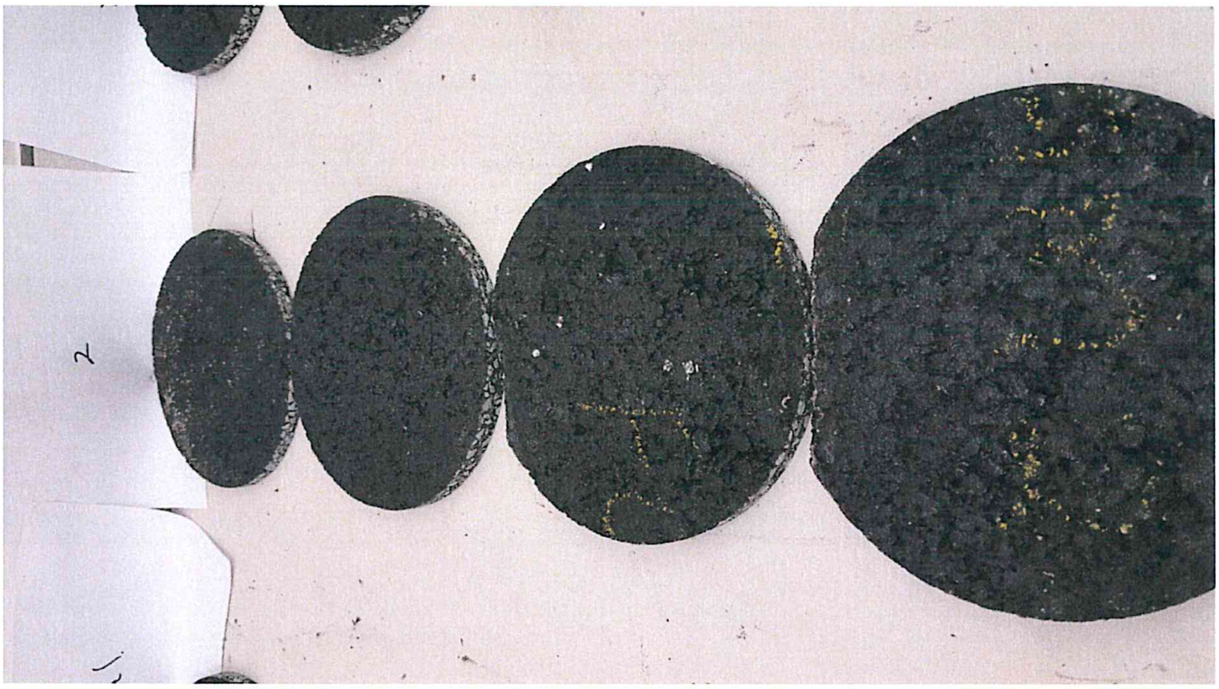


Figure 2-7: Top 10 mm after Application and Short Term Ageing: Formulation 2

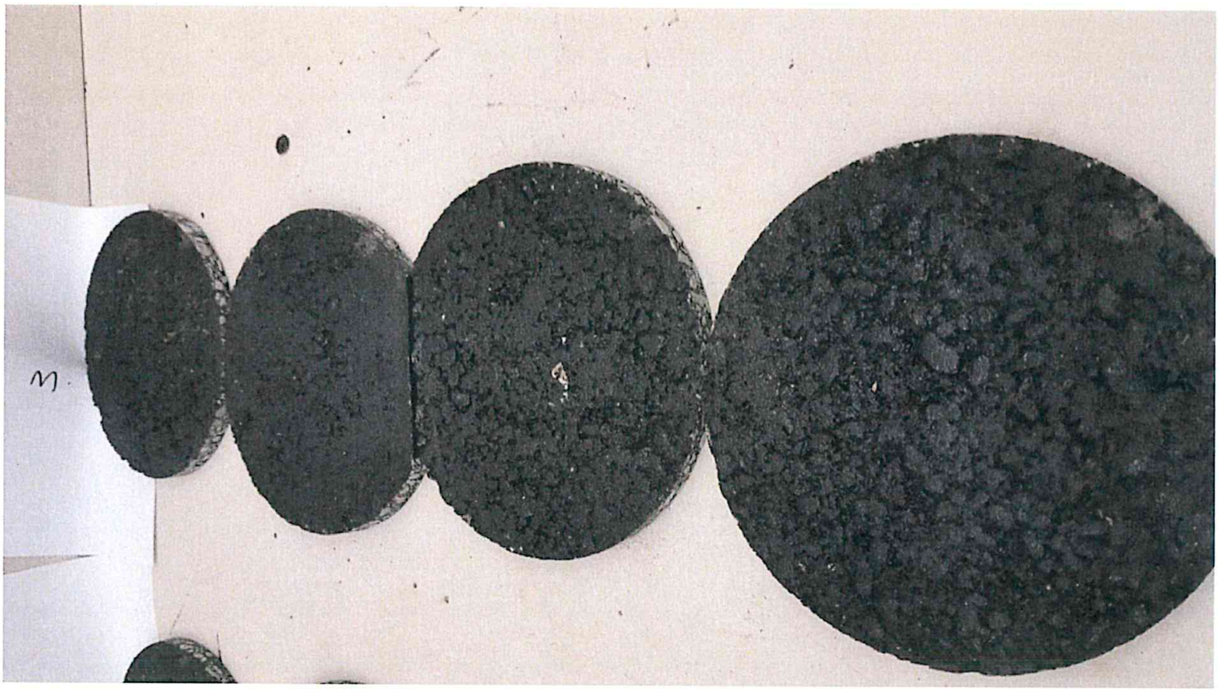


Figure 2-8: Top 10 mm after Application and Short Term Ageing: Formulation 3

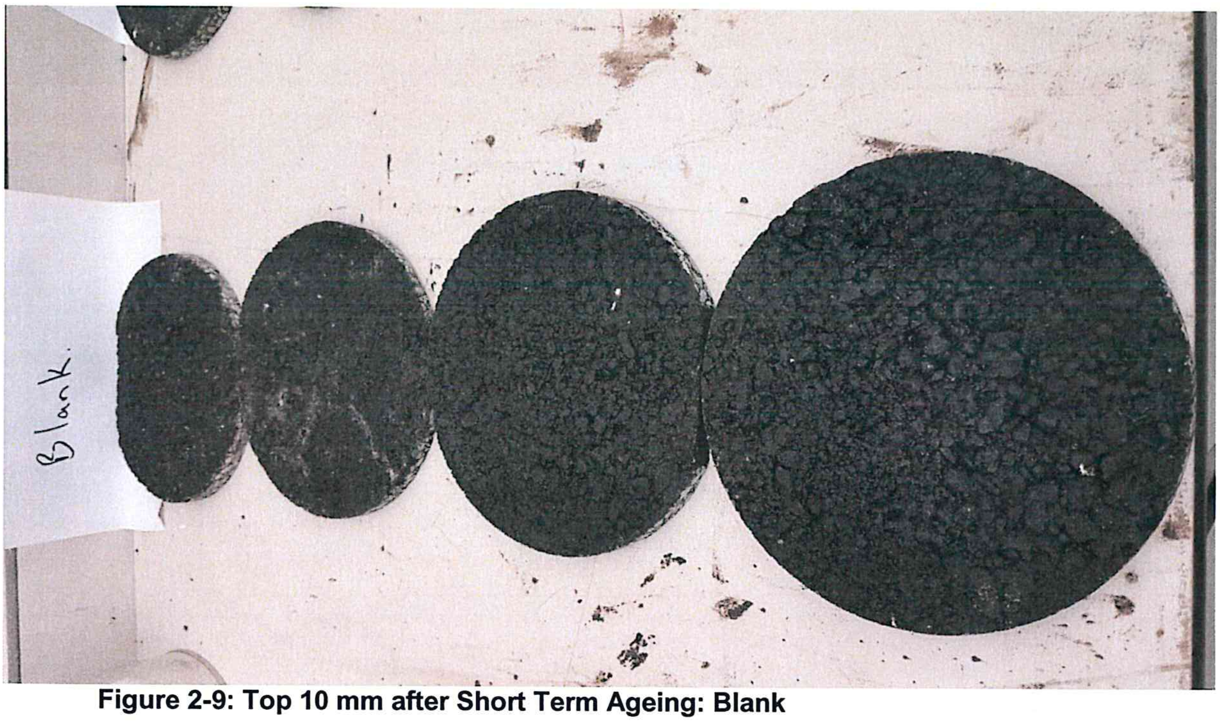


Figure 2-9: Top 10 mm after Short Term Ageing: Blank

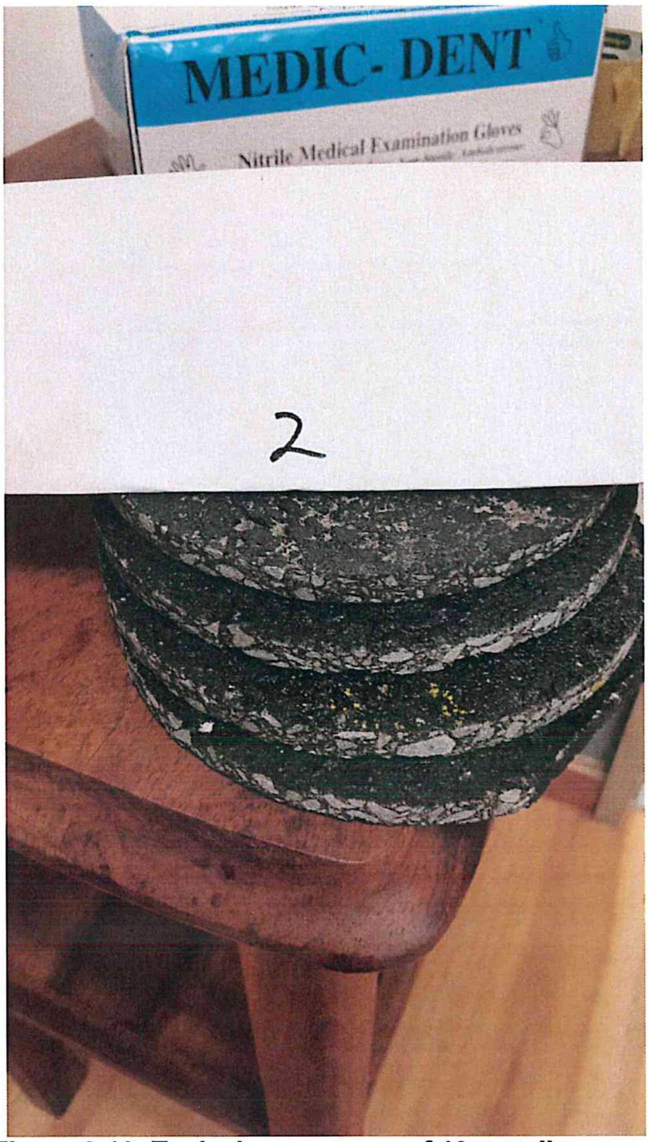


Figure 2-10: Typical appearance of 10mm slices

3 RESULTS

3.1 Binder recovery

The binder was recovered from the asphalt mix cores using test method BE-TM-BINDER-1-2006, a CSIR method based on Abson distillation. The recovered binder properties are given in Table 3-1.

Table 3-1: Recovered Binder Properties

Property	Test Method	Original Formulation	Formulation 2	Formulation 3	Blank
Ash Content (m/m %)	ASTM D482	1.4	1.5	1.1	2.1
Solvent Gas Chromatography (area counts)	BE-TM-BINDER-5-2010	35 600	21 600	29 700	31 600

The ash content and solvent detection using gas chromatography are quality control measures used during the recovery process to ensure that the mineral fines and solvents are sufficiently removed from the recovered binder. Results should be treated with caution when the ash content exceeds 2% or the solvent concentration exceeds 50 000 area counts as these impurities will then have a noticeable effect on the recovered binder properties.

3.2 The Thin Film Chromatographic (TFC) Analysis

The TFC analysis is done according to IP 469/01

During ageing, the saturates have been found to remain largely unchanged. During ageing, however, there is a conversion from aromatics and resins and from resins to asphaltenes. There is thus a significant depletion of aromatics (Ar) and significant increase in asphaltenes (A). There is a direct relationship between the increase in asphaltene content during ageing and the rate of increase in bitumen stiffness. An increase in bitumen stiffness, in turn is related to an increase in fatigue cracking. It should be the aim of the asphalt rejuvenator to increase the aromatic (Ar) fraction of the bitumen, and in so doing, decrease the binder stiffness.

In summary, during the process of weathering or oxidation, the ratio of maltenes to asphaltenes is reduced with resulting in a dry and brittle pavement. The extent to which a rejuvenator can successfully restore the binder, it must be able to penetrate the binder and increase this ratio. A comparison of the ratio (R + Ar) / A of the extracted binders is given in Table 3-2

.

Table 3-2: Recovered Binder Properties

Property	Original Formulation	Formulation 2	Formulation 3	Blank
Ratio: (R + Ar) / A	1.65	0.66	0.84	1.40
Repeat	1.70	0.73	-	1.36
Average	1.68	0.70	0.84	1.38

The graphs of the TLC analyses are presented in Figures 3-1 to 3-4.

Chromatogram: Bitumen10217 Date: 2015/11/24 Time: 12:03

Author:

Notes: OQ-Test Iatroscan S/N 6130603S
Optiplex 7010
Spotter 20131018/111

Orig

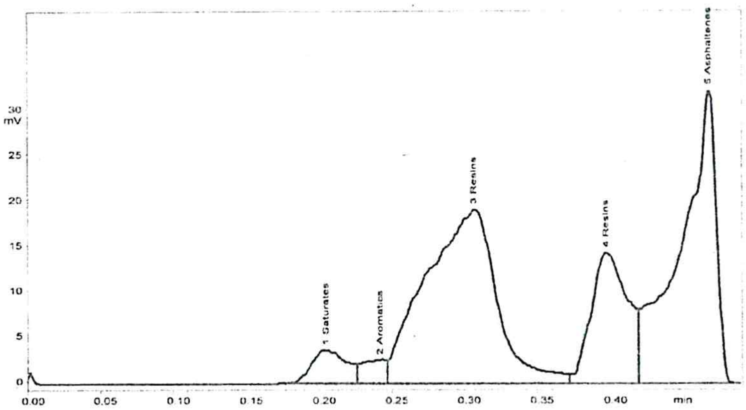
Sample Identifier:

Data Processing Parameters

Injected on:	2015/11/24	Injected at:	12:03
Slice Width (ms):	50	Noise (µV/s):	250
Threshold (mV):	500	Skim Ratio:	3

Parameter Files:

Data Handling File:	Bitumen1	Calculation-File:	Bitumen1



Calculation Method : Normalisation

Peak No	Win No.	Ret.Time (min)	Area	Resp.-Fact.	Area%	Name
1	1	0.205	3207	1.000	3.962	Saturates
2	2	0.243	1603	1.000	1.981	Aromatics
3	3	0.308	34090	1.000	42.125	Resins
4	3	0.398	13356	1.000	16.504	Resins
5	4	0.469	28670	1.000	35.427	Asphaltenes
			80926		100.000	

≈1.65

Page: 1 of: 1

Figure 3-1: TLC Analysis: Original Formulation

Chromatogram: Bitumen10223 Date: 2015/11/25 Time: 11:19

Author:

Notes: OQ-Test Iatroscan S/N 6130603S
Optiplex 7010
Spotter 20131018/111

F2

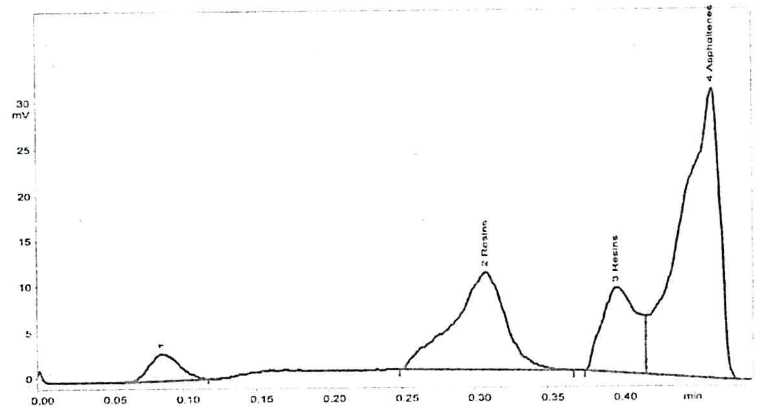
Sample Identifier:

Data Processing Parameters

Injected on:	2015/11/25	Injected at:	11:18
Slice Width (ms):	50	Noise (µV/s):	250
Threshold (mV):	500	Skim Ratio:	3

Parameter Files:

Data Handling File:	Bitumen1	Calculation-File:	Bitumen1



Calculation Method : Normalisation

Peak No	Win No.	Ret.Time (min)	Area	Resp.-Fact.	Area%	Name
1		0.086	2228	0.000	0.000	
2	3	0.308	13758	1.000	26.350	Resins
3	3	0.398	8243	1.000	15.788	Resins
4	4	0.464	30211	1.000	57.862	Asphaltenes
			54440		100.000	

0.73.

Page: 1 of: 1

Figure 3-2: TLC Analysis: Formulation 2

Chromatogram: Bitumen10224 Date: 2015/11/25 Time: 11:19

Author:

Notes: OQ-Test Iatroscan S/N 6130603S
Optiplex 7010
Spotter 20131018/111

F3

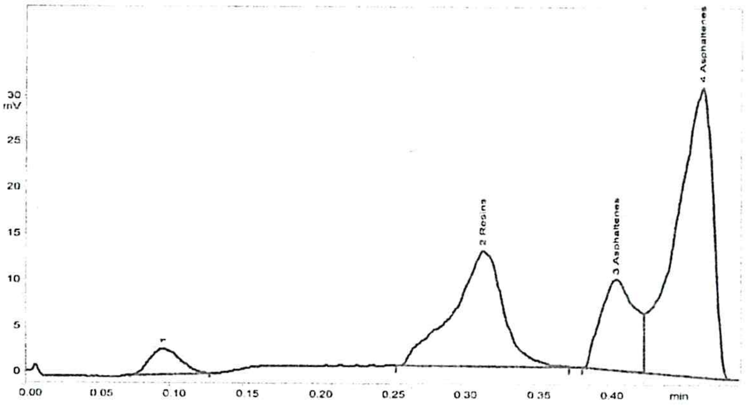
Sample Identifier:

Data Processing Parameters

Injected on:	2015/11/25	Injected at:	11:19
Slice Width (ms):	50	Noise (µV/s):	250
Threshold (mV):	500	Skim Ratio:	3

Parameter Files

Data Handling File:	Bitumen1	Calculation-File:	Bitumen1



Calculation Method : Normalisation

Peak No	Win No.	Ret.Time (min)	Area	Resp.-Fact.	Area%	Name
1		0.096	2152	0.000	0.000	
2	3	0.316	15618	1.000	29.434	Resins
3	4	0.407	8571	1.000	16.153	Asphaltenes
4	4	0.467	28872	1.000	54.413	Asphaltenes
			55213		100.000	

Page: 1 of: 1

0,84.

Figure 3-3: TLC Analysis: Formulation 3

Chromatogram: Bitumen10211 Date: 2015/11/24 Time: 11:58

Author:

Notes: OQ-Test Iatroscan S/N 6130603S
Optiplex 7010
Spotter 20131018/111

blank

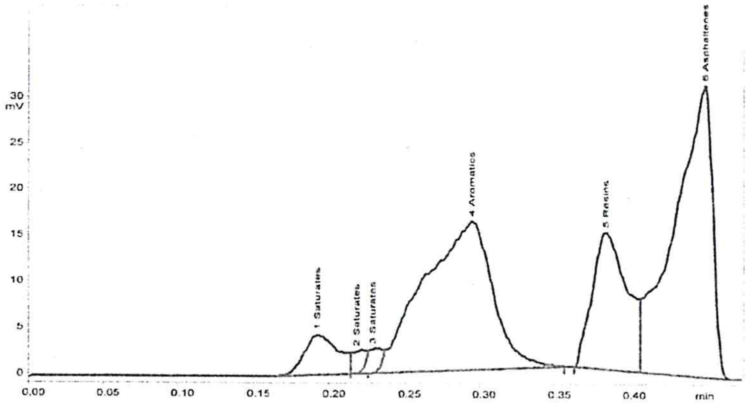
Sample Identifier:

Data Processing Parameters

Injected on:	2015/11/24	Injected at:	11:58
Slice Width (ms):	50	Noise (µV/s):	250
Threshold (mV):	500	Skim Ratio:	3

Parameter Files:

Data Handling File: Bitumen1 Calculation-File: Bitumen1



Calculation Method : Normalisation

Peak No	Win No.	Ret.Time (min)	Area	Resp.-Fact.	Area%	Name
1	1	0.192	3521	1.000	4.718	Saturates
2	1	0.218	728	1.000	0.976	Saturates
3	1	0.229	726	1.000	0.973	Saturates
4	2	0.296	28102	1.000	37.654	Aromatics
5	3	0.384	12484	1.000	16.728	Resins
6	4	0.451	29069	1.000	38.951	Asphaltenes
			74631		100.000	

6.667

1.40.

Page: 1 of: 1

Figure 3-4: TLC Analysis: Blank

3.3 Dynamic Shear Rheometer (DSR)

The DSR determines the viscoelastic properties of the binder, namely:

- The complex modulus (G*)
- The phase angle (δ)

The diagram in Figure 3-5 depicts how two binder samples with the same G* can have different phase angles. The higher the phase angle is, the higher the viscous component of G* is, and the less prone to cracking the binder becomes.

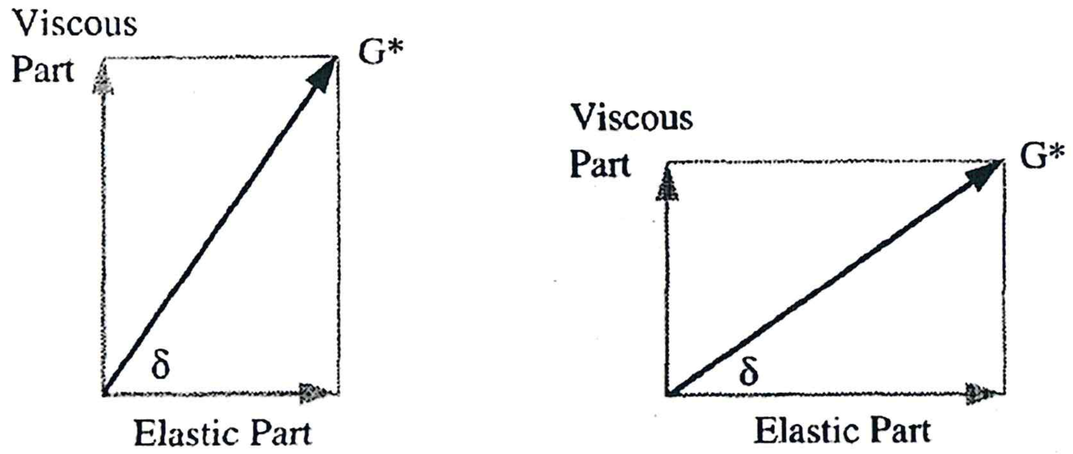


Figure 3-5: Viscous and elastic components of G*

The fatigue life of viscoelastic asphalt mixtures can be described by the dissipated energy criteria where energy is dissipated during loading and unloading periods (see Figure 3-6). In an elastic material, the stored energy during loading (equal to the area under the deflection curve) is fully recovered during the unloading period. In a viscoelastic material, the dissipation of energy occurs in a hysteresis loop during the loading and unloading periods and the area within the loop represents the dissipated energy.

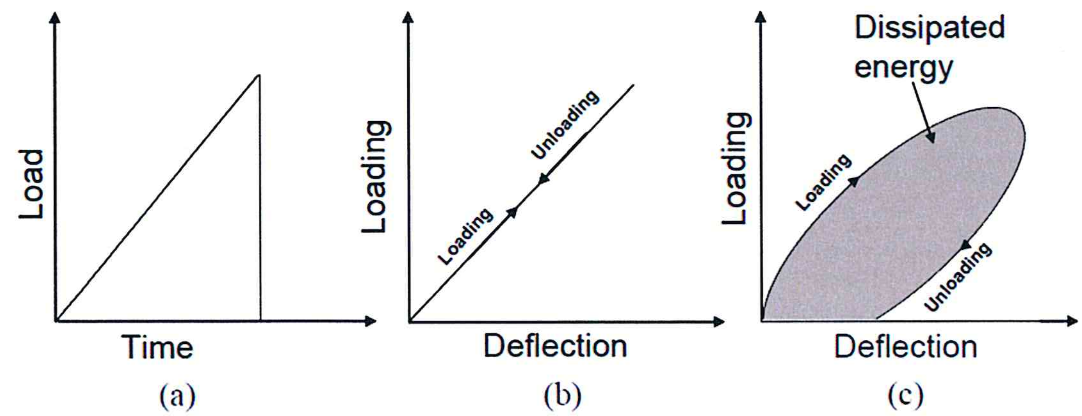


Figure 3-6: Concept of Dissipated Energy and Fatigue Life

The dissipated energy per loading cycle when a viscoelastic material is sinusoidally loaded, with the load/deflection relationship expressed as stress/strain, is given as follows:

$$w_i = \pi\tau\gamma\sin\delta \qquad \text{Equation 3.1}$$

where w_i is the dissipated energy at cycle i, τ is the shear stress, γ is the shear strain, and δ is the phase angle.

The SUPERPAVE® property for predicting binder fatigue performance, G*.sinδ is derived from Equation 5.1 at a constant strain that can be expressed as:

$$w_i = \pi\gamma^2(|G^*|\sin\delta) \qquad \text{Equation 3.2}$$

where G* is the complex shear modulus

According to Equation 3.2, a lower G*.Sin favours improved fatigue performance.

The values for δ and G*Sin δ at 28°C are reported in Table 3-3.

Table 3-3: Recovered Binder Properties

Property	Original Formulation	Formulation 2	Formulation 3	Blank
δ (°C)	65.0	65.2	65.0	63.0
G*Sin δ (kPa)	1 260	1 230	1 210	1 480

4 CONCLUSIONS

Table 3.1 indicates the binders were recovered successfully without excessive solvents or fines being retained.

Table 3-2 shows that the ratio of (R + Ar) / A improved significantly after application of the original formulation compared to the blank. However, the results for Formulation 2 and Formulation 3 made little sense, showing an overall absolute decrease in the binder on the chromarod. It is surmised that these formulations must contain some form of bitumen dispersant making this analytical tool inappropriate.

Table 3-3 shows that the phase angle for the three treated binders are very similar (65.0 – 65.2°C) and better than the blank value (63.0°C). The fatigue parameter $G^*.\sin\delta$ shows that the binder fatigue properties improved with all three formulations, only showing slight differences with:

Formulation 3 > Formulation 2 > Original Formulation