Effect and efficiency of rejuvenators on aged asphalt binder – German experiences

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ABSTRACT

Due to aging process of bitumen and its corresponding increase in viscosity, the stiffness of asphalt pavement increases during its lifetime. Therefore, high addition rates of Reclaimed Asphalt Pavement (RAP) in asphalt mixtures may negatively influence a mixture's quality. As a consequence, asphalt recycling is predominantly used in the asphalt's base layers (asphalt and unbound). Yet, with regards to the current importance of sustainability and protection of resources, it is becoming increasingly desirable to raise the addition rates of RAP in top layers. Rejuvenating agents can assist in this process by decreasing the aged bitumen's viscosity and restoring its original properties. Chemically, the relation between solid asphaltenes and liquid maltenes in the bitumen shifts towards a higher maltene content.

The german research project "Use of Rejuvenators for Asphalt Recycling" concerns itself with the efficiency of rejuvenators as well as with the effect such additives have on aged bitumen properties. To this end, all rejuvenators available worldwide (21) have been acquired and then mixed with extracted bitumen of asphalts of differing ages. Furthermore, the rheological and physical properties of the mixtures were investigated before and after laboratory aging. Finally, selected mixes of the rejuvenators and the extracted bitumen were subjected to performance tests. This project's goal is to provide a technology for the use of rejuvenators in Germany by defining the properties of rejuvenators that are necessary to enable the efficient recycling of existing asphalt pavements.

Keywords: Reclaimed asphalt pavement (RAP) Recycling, Rejuvenators, Testing

1. INTRODUCTION

Due to the ageing process of bitumen and its corresponding increase in viscosity, the stiffness of asphalt pavement increases during its lifetime. Therefore, high addition rates of Reclaimed Asphalt Pavement (RAP) in asphalt mixtures may negatively influence a mixture's quality. As a consequence, RAP is predominantly used in the asphalt's base courses (asphalt and unbound). Yet, with respect to the current importance of sustainability and protection of resources, it is becoming increasingly desirable to raise the addition rates of RAP in surface layers. Rejuvenating agents can assist in this process by decreasing the aged bitumen's viscosity and restoring its original properties. Chemically, the relation between solid asphaltenes and liquid maltenes in the bitumen shifts towards a higher maltene content.

Today a wide range of additives promising RAP rejuvenation exists on the market. Both ingredients and effectiveness vary from product to product, obstructing definition of rejuvenators and their effect on RAP. This research project concerns itself with the efficiency of rejuvenators as well as the effect such additives have on aged bitumen properties. Therefore 21 rejuvenators available worldwide were acquired and tested. By characterising them and comparing them with each other and to the effects soft paving grade bitumen has on aged bitumen, a technology for specific use of these products as well as a general definition of additives called rejuvenators was supposed to be provided. Furthermore possible applications of these products were to be determined, testing their short- and longtime ageing behavior.

Beneath this and based on the detailed experiences gained on aged bitumen throughout the tests, a practically useful laboratory method for describing aged bitumen's quality was tested. Until now, RAP is only characterised by its softening point Ring and Ball, being insufficient regarding the complexity of bitumen. Yet, knowledge on its quality is required for specific use of high RAP amounts, as favoured nowadays.

Because the research project is still in progress, this paper contents preliminary results at the moment.

2. TESTING PROGRAM

Due to the variation of additives sold as rejuvenators on the market, no general advice for practical application has previously been available, which is one of the main goals of this project. Rejuvenators offered on the market worldwide were requested, whereupon nearly all producers sent samples of their products. The testing programme was divided into four consecutive steps along with the development of a simplified laboratory method for determining the quality of aged bitumen, starting with collecting rejuvenators and describing them via datasheets and production information (**step 1**). Next to the 21 rejuvenators, the effect of soft paving grade bitumen grading 650/900, 500/650, 250/330 and 160/220 as rejuvenators was tested.
Step 2 included the categorisation of the products, using the same base bitumen and adding each rejuvenator in up to three different dosages in order to compare their impact. All 21 rejuvenators were added in amounts of 3.0 %, 5.0 % and 7.0 %. Additionally, dosages of 1.0 % of the soft paving grade bitumen were tested. To eliminate any influence through ageing on extracted bitumen from RAP, a hard paving grade bitumen 20/30 was chosen for mixing in this step. Approximately 100 ml fresh bitumen 20/30 and the particular amount of rejuvenator were stirred at 150 °C for ten minutes, guaranteeing a homogeneous mixture, on which the characteristics mainly used for bitumen quality description in Europe, softening point Ring and Ball [1] and needle penetration [2], were evaluated.
In a **3rd step**, 22 different RAP were extracted and analysed, regarding softening point Ring and Ball [1], needle penetration [2], DSR parameters phase angle and complex shear modulus [3] and BBR parameters stiffness and m-value [4]. Beneath this the amount of binder extracted from the different RAP types, playing an important role in choosing 5 out of the 22 binders for mixing with rejuvenators since a minimum amount of binder was necessary to fully analyse the mixtures, was determined for each RAP [5]. Regarding the extracted binders, a wide range of ageing stages of bitumen were determined, from which five of the most differing were chosen for further tests.
The five chosen bitumen were each mixed with the rejuvenating products in **step 4** and analysed analogous to step 3 in three different states: freshly mixed, short-time aged in RTFOT [6], triple-aged in RTFOT and long-time aged in PAV [7], entailing the analysis of approximately 100-150 mixtures. The results of this analysis gave an overview on the right dosage of each product, its effect on aged bitumen, its effectiveness regarding different stages of bitumen ageing and its rejuvenating features in general, answering the question whether a rejuvenating effect is visible or not.

The large quantity of results characterising bitumen contained in RAP enabled the evaluation of RAP qualities and its properties apart from softening point Ring and Ball [1]. Based on this a testing method for determination of the quality of aged bitumen in RAP, called "simplified laboratory method", was developed in order to gain fast and easy information.

Mainly three different processes take place during bitumen ageing, called oxidative, distillation and structural ageing [8] [9]. Bitumen mainly consists of carbon compounds, which are arranged in a colloidal system with solid particles, asphaltenes, and a fluid phase, maltenes [10]. Bitumen ageing causes decreasing amounts of maltenes whilst increasing the amount of asphaltenes [9].
Whereas different methods of analysis exist where solvents are added to bitumen to determine its chemical properties, ZENKE [11] offered a method for not only determining the amount of maltenes and asphaltenes of bitumen, but distinguishing light-, middle- and high-solubility of asphaltenes, concluding that bitumen ageing results in forming high-soluble asphaltenes. Therefore, the amount of high-soluble asphaltenes is a parameter describing the ageing state of bitumen as well as its usability. The simplified laboratory method is based on ZENKE's findings. The solvents cyclohexane and isooctane were successively added to bitumen in a 1:1 blending ratio. Whilst cyclohexane dissolves bitumen, isooctane causes precipitation of high-soluble asphaltenes. Quantification of the precipitated asphaltenes takes place using turbidimetry. A turbidimeter quantifies the amount of solid parts in a liquid by beaming light at it and using light sensors to measure the amount of light which passes the liquid or is diffracted by solids (Figure 1).
Altogether the focus lay on economic efficiency, simplicity and speed of the test method.

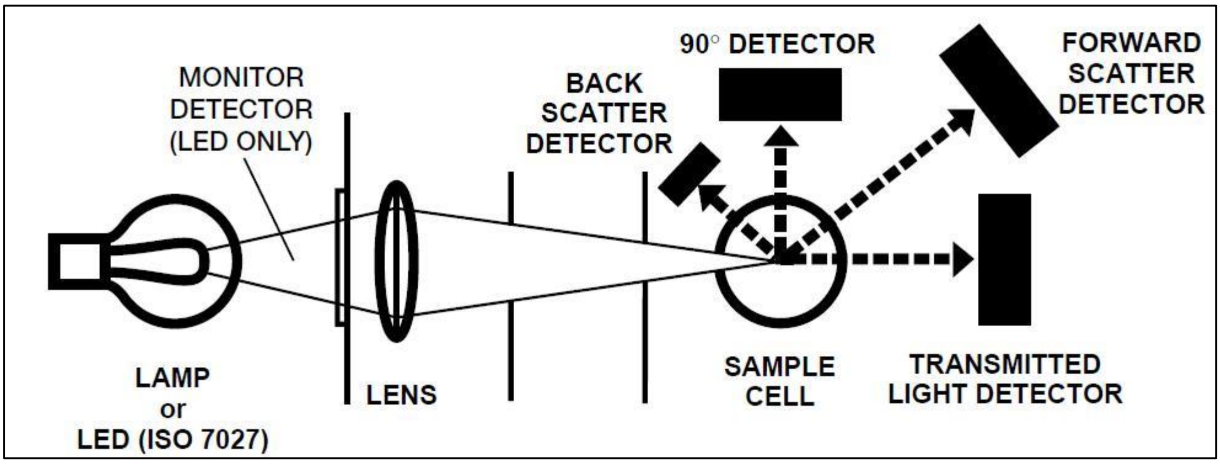

Figure 1: Draft of a turbidimeter's functional principle

3. TEST RESULTS

3.1 Step 1 and Step 2

All products were provided with product data sheets, safety data sheets and some additional information on the handling and use from most of the producers. Although details on ingredients were company secret, a broad classification of the products in three categories was still feasible in step 1. 16 of 22 products were offered as rejuvenators on the market. Regarding the effect they were supposed to have on aged bitumen, these products were divided into groups of "rheologically effective", augmenting the maltene phase of aged bitumen, and "chemically effective" causing a reversible effect on oxidised intermediates. For the latter, the producer insisted on precise mixing temperature, rate and dosage of the rejuvenator.
Next to these rejuvenators, some companies provided products, which were originally designed for other use in bitumen, but which were found to also have rejuvenating effects or were supposed to rejuvenate. These additives were pooled in a separate category as "other products". Beneath that, a fourth category of soft paving grade bitumen existed.
The results of step 2 with increasing dosage, show that each product has a specific effect on the bitumen, one having more influence on softening point ring and ball and the other mainly influencing needle penetration. None of the products provide linear rise of softness subject to increasing dosage, except of the soft paving grade bitumen. Chemically effective products have stiffening effects on the base bitumen.
To gain an overview on different effects, seven additives and two soft paving grade bitumen were chosen for further tests.

3.2 Step 3

Due to German guidelines [12], re-use of reclaimed asphalt, whose soluble binder has a softening point Ring and Ball higher than 70 degrees, is not usable. Actually, as Figure 2 implies, 29 % of today's reclaimed asphalts exceed this limit. The data has been obtained from several studies conducted by Ruhr University Bochum.

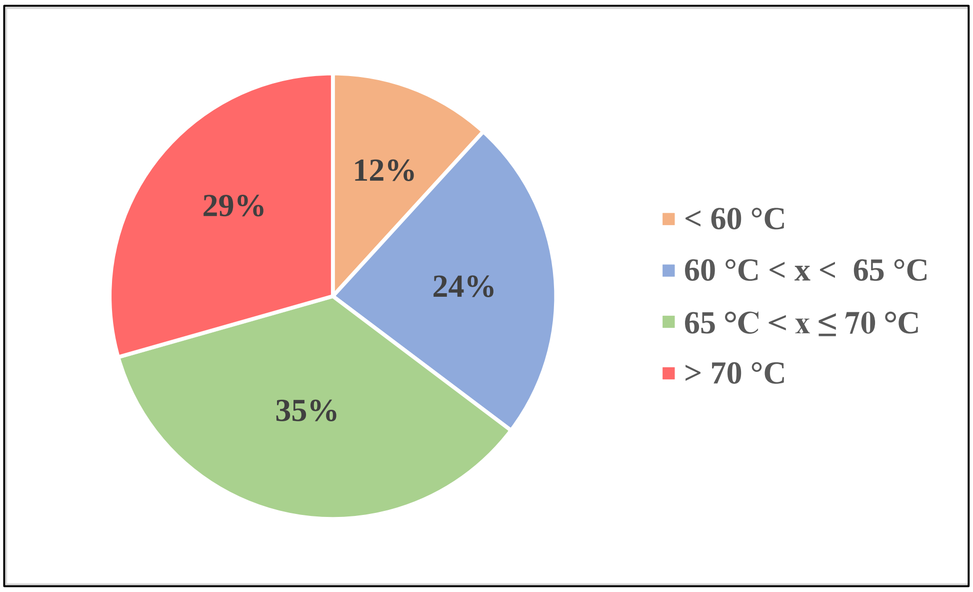

Figure 2: Statistical distribution of softening point of soluble binder in reclaimed asphalt

As a result the examination of if and how rejuvenators reactivate aged binders gains more importance. Furthermore a proper test method for describing actually this reactivation process and enabling information on the properties of the mixture of aged binder and rejuvenator presented an issue.

Characterisation of reclaimed asphalts

Within the scope of the research project 22 different reclaimed asphalts were examined with regard to their physical, chemical and rheological properties. Ten of them were chosen for further tests. Table 1 shows their extraction results, including the softening point Ring and Ball and the needle penetration of the soluble binder.

Table 1: Extraction results, softening point and needle penetration

Name	Filler content	Fine aggregates	Coarse aggregates	Binder content	Softening point	Needle penetration
	[M.-%]	[M.-%]	[M.-%]	[M.-%]	[° C]	[1/10 mm]
AG 4	14.7	73.3	12.0	6.6	78.0	14
AG 5	17.5	72.7	9.7	6.5	50.6	31
AG 6	15.5	63.3	21.2	6.8	65.4	21
AG 7	18.0	80.3	1.7	6.7	57.0	30
AG 9	9.5	47.5	43.0	4.0	105.0	7
AG 12	8.4	15.6	76.0	5.6	68.8	20
AG 18	21.4	72.8	5.8	6.6	82.0	18
AG 20	7.6	37.3	55.1	5.4	68.8	21
AG 21	10.0	22.3	67.8	6.6	70.0	21
AG 22	4.9	38.9	56.2	3.7	66.6	18

Various asphalt mixes and very different softening points ranging from 50.6° C up to 105° C can be seen. These contrasts in physical properties were not as significant in the chemical tests including SARA fractionation [13] and state of asphaltenes according to ZENKE [11]. However, the determination of complex shear modulus and phase angle also show the wide ageing range of the reclaimed asphalts. These results are summarized in a Black Diagram in Figure 3, compared to a fresh bitumen 50/70.

A Black Diagram depicts the magnitude of the complex modulus G* versus the phase angle, δ, obtained from the dynamic test. The frequency and the temperature are eliminated from the plot. AIREY [14] proved the utility of the Black diagram for assessing and comparing rheological properties of bitumen. Therefore, all results of DSR measurements are presented as Black diagram here.

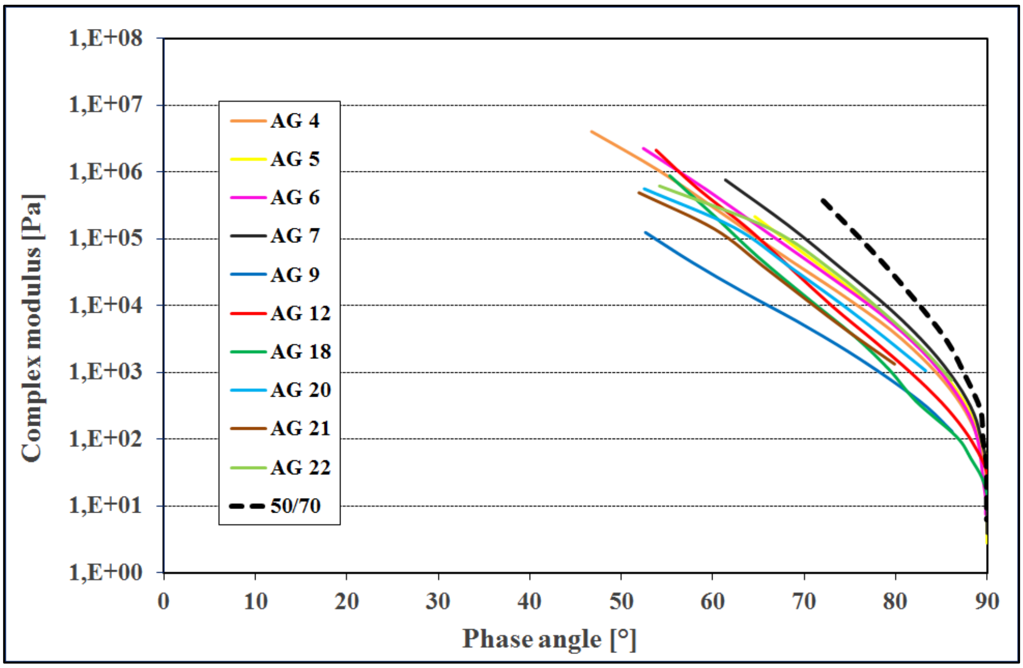

Figure 3: Black Diagram of ten aged bitumen

Addition of rejuvenators

The next step was to mix seven rejuvenators (R1-R7) and two soft bitumen (R8 and R9) with five aged bitumen. Considering previous results, bitumen AG 4, AG 7, AG 9, AG 18 and AG 20, highlighted in grey in Table 2, were selected. At first, the required dosage of each rejuvenator for adding to the aged bitumen had to be determined. The aim for all rejuvenators was to replicate the physical and rheological properties of a bitumen 50/70 and thereby to examine if the rejuvenator can do it and to determine the required dosage and the corresponding physical and rheological parameters. Because manufacturer information was not sufficient for this task, preliminary tests with fresh bitumen and different quantities of rejuvenators were necessary. Based on the results of step 2 (compare 3.2), the amount of rejuvenator was calculated. Because of the great difference between actual softening point of RAP and targeted softening point of a 50/70 dosages had to be higher than in step 2. Softening point and needle penetration were measured of the blends. The results for mixtures 1-9 (R1-R9) with AG 4 and AG 20 are presented in Table 2, including dosage, softening point and needle penetration of the aged bitumen and of the mixtures. Highlighted in grey are softening points and needle penetration fulfilling the requirements for a bitumen 50/70. It can be seen that most materials failed to achieve the physical properties of a bitumen 50/70. Just a few mixtures met the specifications for softening point or needle penetration, while only two mixtures (20.3 and 20.5) meet both. This trend was confirmed by mixtures with AG 7, AG 9 and AG 18. Evidently, for most rejuvenators, no linear dependency determination of dosage based on the softening point is possible. Moreover, values within the limits of a bitumen 50/70 are reached by different rejuvenators, so that reliable information on suitability of each individual rejuvenator only by means of physical parameters cannot be gained. Further purpose should be an optimization of dosages and to test their impact on the blends, so that the statement for each rejuvenator can be confirmed or disproved.

Table 2: Mixture results after addition of rejuvenators to AG 4 and AG 20

Name/ Mix	Dosage	Softening point	Needle penetration		Name/ Mix	Dosage	Softening point	Needle penetration
	[M.-%]	[° C]	[1/10 mm]			[M.-%]	[° C]	[1/10 mm]
AG 4	-	78.0	14		AG 20	-	68.8	21
4.1	24.0	51.1	106		20.1	14.0	44.3	138
4.2	24.0	46.1	132		20.2	10.0	56.3	47
4.3	20.0	40.0	169		20.3	10.0	52.2	50
4.4	31.0	57.3	36		20.4	10.0	59.9	30
4.5	20.0	41.5	164		20.5	10.0	53.3	56
4.6	20.0	57.8	61		20.6	15.0	58.5	47
4.7	20.0	69.9	37		20.7	15.0	66.6	41
4.8	50.0	55.4	43		20.8	40.0	57.1	36
4.9	50.0	46.7	84		20.9	35.0	58.5	54

However, results of DSR measurements, presented in Figure 4 and Figure 5 for AG 4 and AG 20 allow better differentiation between the rejuvenators as their rheological impact can easily be determined in the Black diagram, because at the same complex modulus there can be seen corresponding different phase angles providing a statement of diverse visco-elastic behaviour.

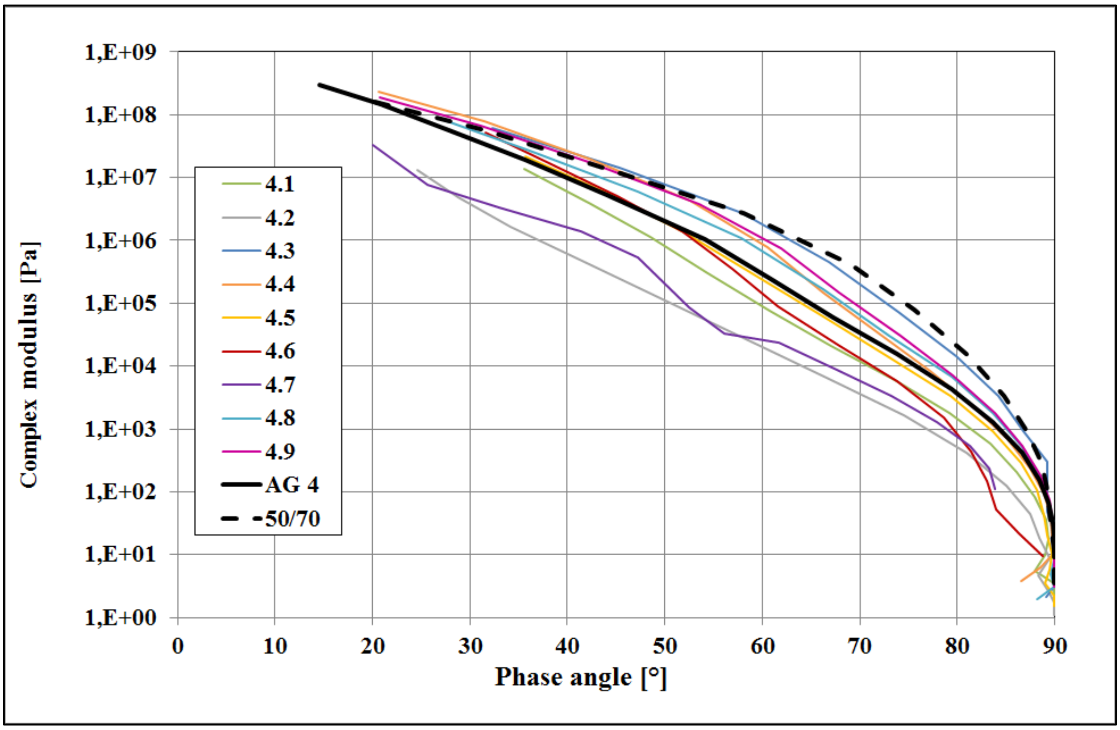

Figure 4: Black diagram of mixtures of AG 4 with rejuvenators R1-R9

The curve of AG 4 without rejuvenator lies in the middle of the eleven curves displayed. For comparative purposes the dashed black line represents a curve progression of a fresh bitumen 50/70. Some rejuvenators (e.g. mixtures 4.3 and 4.4) succeed in changing the ratio between viscous and elastic components in such a way that the curve progress is similar to the fresh bitumen, while rejuvenator 3 has the best impact. From a rheological perspective, these products have a “rejuvenating” effect. Others (e.g. R5 / mixture 4.5) act in a “fluxing” manner: stiffness of a bitumen 50/70 can probably be reached, but the ratio of viscous and elastic components remains largely unchanged. The third group of rejuvenators (e.g. R2 and R7) causes a shift of the ratio towards higher elastic components (“structural hardening”). Based on this knowledge, this is an undesirable result. Conclusions concerning the different effect of rejuvenators can analogically be transferred to mixtures with AG 7, AG 9, AG 18 and AG 20, underlined by Figure 5.

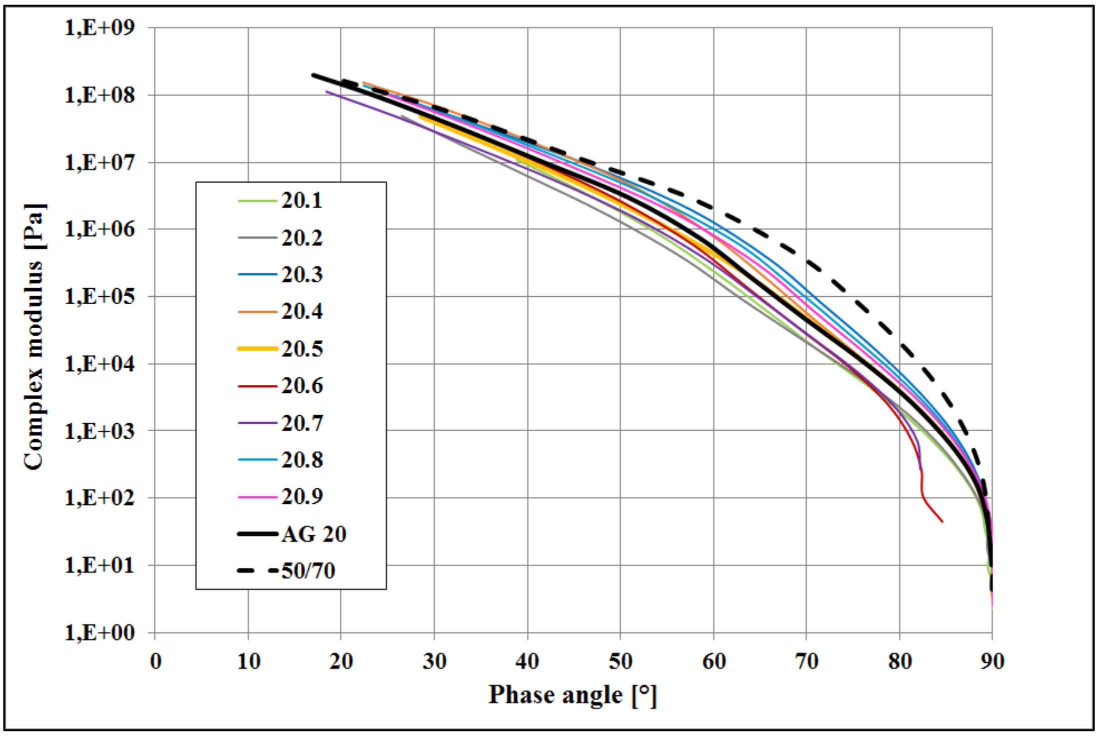

Figure 5: Black diagram of mixtures of AG 20 with rejuvenators R1-R9

Rejuvenator R3 shows a rejuvenating effect as well as the soft bitumen R8 and R9, while most of the others, especially R2 or R6 do not have any impact in such a way.

Regarding Bending Beam Rheometer (BBR) tests, it was detected, that mixtures with rejuvenators having a rejuvenating effect, improve the relaxation behaviour compared to the aged bitumen.

3.3 Test results step 4

After selecting three “rejuvenating” additives, the simulation of short time- and longtime ageing was undertaken to assess how the mixture properties change if the mixture is subjected to ageing processes. Figure 6 shows the softening point of AG 20 and mixtures after ageing compared to the initial state without rejuvenator and to the non-aged mixture.

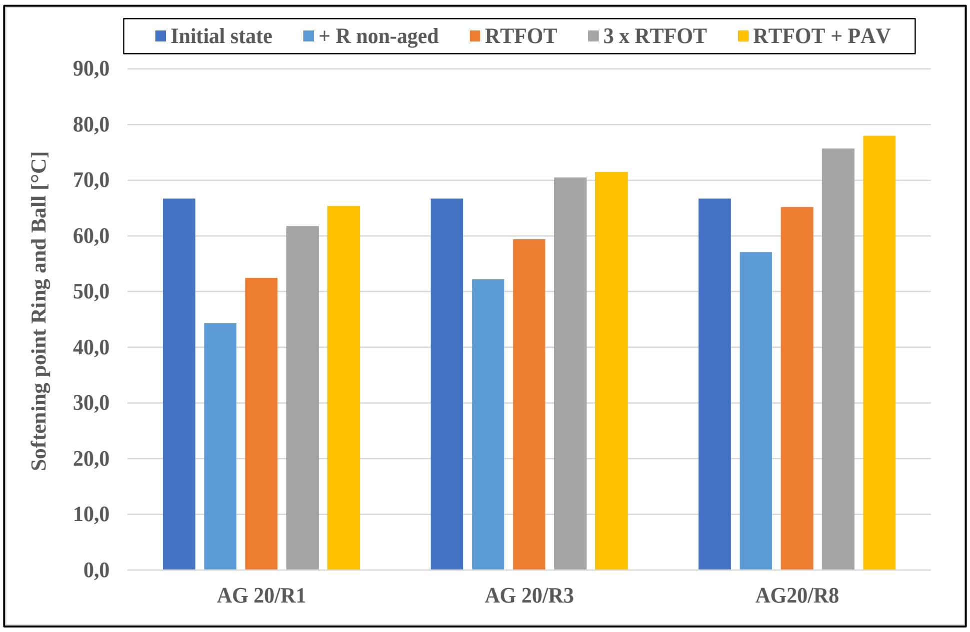

Figure 6: Softening point of mixtures of AG 20 with rejuvenators R1, R3, R8 before and after ageing tests

Independent of the rejuvenator some general statements can be concluded. After addition of rejuvenators the softening point initially decreases. After the short term ageing (RTFOT) the softening point increases but does not reach the value of the initial state. The latter is exceeded after three times RTFOT ageing. The highest softening point is measured for the combined long term ageing process RTFOT and PAV. Due to the previous insights that the softening point permits only limited conclusions regarding rheological efficacy, additional DSR tests were made. Results of AG 20 after short term (RTFOT) and long term ageing (RTFOT and PAV) are represented in the following figures. For the purpose of comparison, the graphs also include the DSR curves for initial state of AG 20 and the particular mixture before ageing.

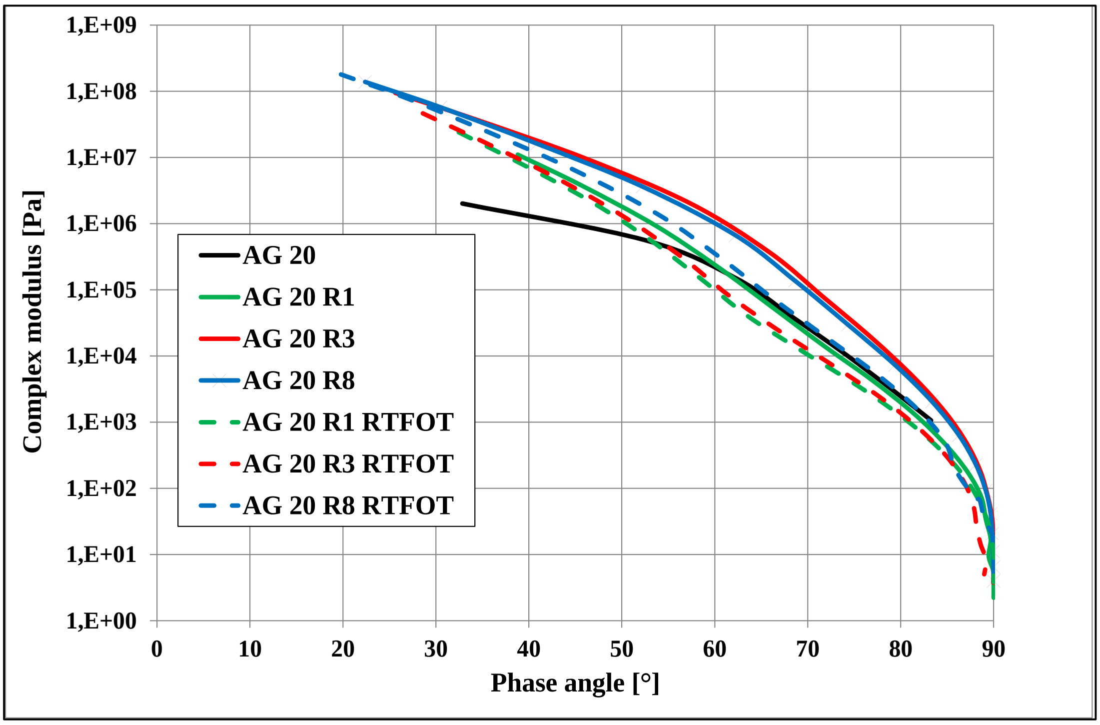

Figure 7: Black diagram of AG 20 and mixtures after short term ageing

Figure 7 and Figure 8 conclude that R3 and R8 achieve ”rejuvenating” effects while R1 does not. Because of the smaller gap between the curves compared to R3 and R8 before and after ageing, R1 appears to be more resilient to ageing. After long term ageing the ratio between elastic and viscous components is displaced in favour of elastic components. This effect can be observed after both ageing processes and is, according to the softening points, stronger for long term ageing. The special curve characteristics if the mixture AG 20 with R3 after RTFOT and PAV has to be examined further.

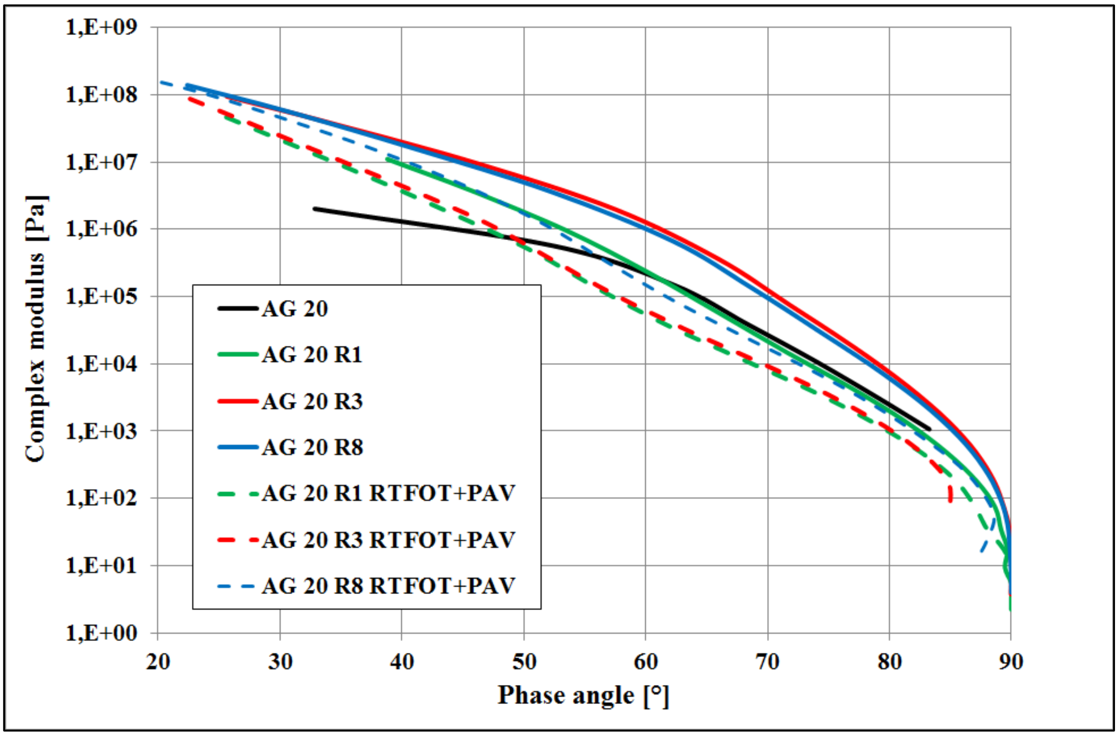

Figure 8: Black diagram of AG 20 and mixtures after long term ageing

3.4 Test results simplified laboratory method

Altogether more than 50 different bitumen (initial state) were used for developing the simplified laboratory method. Parameters such as the mixture’s colour, dependant from the bitumen dosage, solving and precipitating times and temperature were varied and tested. Also different methods for partitioning the precipitated solids off from the mixture were taken into account.

Ultimately, a test method for the implementation of the simplified laboratory method was outlined, requiring a solvent (cyclohexane), a precipitating agent (isooctane), devices for exact weighing of a small bitumen amount, closable flasks for preventing solvent evaporation, a turbidimeter and appropriate tubes and an ultrasonic bath. The test method contained the following steps:

1. Weighing
   Tests regarding the mixture’s colour showed that for altogether 100 ml cyclohexane and isooctane (1:1 rate), a max. amount of 0.1 g bitumen had to be weighed in a very accurate way. Higher dosages of bitumen caused dark mixture colours which prevented accurate turbidity measurements. Furthermore the exact dosage of bitumen proved to play an important role as even slight differences of ≥ 10 mg affected the resulting turbidity grades so that comparability was not fulfilled.
2. Addition of the solvent (cyclohexane)
   Bitumen and Cyclohexane were mixed in a flask for 30 minutes. To guarantee homogenous mixing, the flask was put into an ultrasonic bath, its vibration causing continual movement of the liquid. The slightly increased temperature of approx. 40 °C of this water bath had a positive impact on the dissolving time.
3. Determination of the “basic turbidity”
   After the bitumen was completely dissolved, the first turbidity measurement took place. The determined turbidity rate was called “basic turbidity”.
4. Addition of precipitant (isooctane)
   The bitumen-cyclohexane mixture was filled up with isooctane and again mixed in an ultrasonic bath for 30 minutes at approx. 40 °C.
5. Determination of turbidity after precipitation

The mixture including precipitated solids was measured via turbidimeter, as per 3.

6. Determination of the final turbidity rate
   The final turbidity rate was determined by the difference between basic turbidity and turbidity after precipitation.

For validating this instruction, the absolute rates of high-solving asphaltenes of 39 different bitumen were determined using ZENKE's method. Afterwards the same bitumen samples were used for turbidity measurements. Figure 9 shows the results of the comparison of this data. Noticeably some basic correlation between high-solving asphaltene rate and turbidity rate is proved, regarding the coefficient of determination of 0.72. Yet, outliers and inaccuracies are displayed, which were mainly determined on bitumen of harder grades.

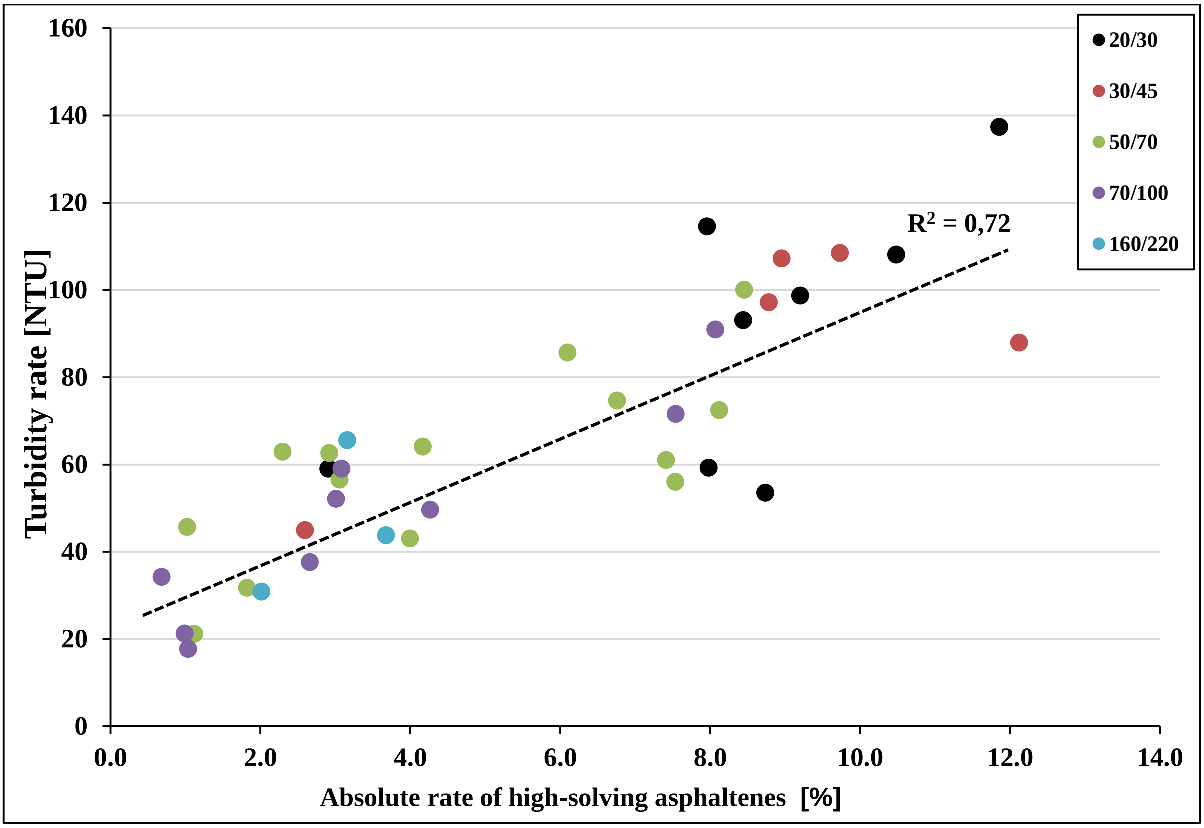

Figure 9: Comparison of turbidity rates and absolute rates of high-solving asphaltenes of 39 different bitumen

4. Conclusions

The following conclusions can be drawn so far from the research reported in this paper:

- Black diagrams allow a good assessment of rheological behavior of mixtures of bitumen with rejuvenators regarding the rejuvenating effects when trying to achieve same mixture properties with each rejuvenator.
- The displacements in the Black diagram are suitable for evaluation of state of bitumen ageing.
- The grade of ageing of bitumen and the quantity of rejuvenator added show no linear relation.
- Impact of rejuvenators is quite different: some have "rejuvenating" effects, some "fluxing" effects and others cause "structural" hardening (cf. chapter 3.2).
- Ageing behaviour of rejuvenated bitumen differs and needs further observation.
- Dosages of rejuvenators should be adjusted according to the results and more blends with other dosages should be tested.
- The simplified laboratory method offers a useful and scientific approach for determining aged bitumen's quality.

5. PERSPECTIVES

Further research should be undertaken to determine the required quantity of rejuvenator added in order to gain specific physical and rheological properties. Ongoing tests show that results of DSR tests may be used for this. Moreover, only laboratory tests with bitumen mixtures were carried out until now raising the question whether the effects of rejuvenators on asphalt mixtures are similar, and making performance tests on such mixtures necessary. As a further step, a test track is planned in Hamburg using rejuvenators on the surface layer of a main road. Additionally, the validation of the simplified laboratory method should take place.

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