This report includes the binder designs for the Houston, Laredo, Pharr and Bryan Toner Projects where waste toner was used as an asphalt binder modifier. For each of these projects, a binder design was performed, including blending time, performance grading, storage stability, and mixing and compaction temperature calculation. The PG properties of the toner-modified asphalt binders used in each test section varied according to the amount of polymers in the toner. Objectives of the research included determining the toner levels needed to arrive at a given PG grade, as well as a better understanding of the effect of toner level on the PG properties of a binder. Test results indicate that the stiffness of the blend increases at all temperatures as the percentage of the toner content present increases. This stiffening effect is more pronounced when the level of toner content is at higher levels. Results also show that two hours of blending time is sufficient to achieve a homogeneous toner-asphalt mix; significant storage stability problems are expected regardless of the level of toner in the blend; and mixing and compaction temperatures stay at reasonable levels.
DESIGN OF TONER MODIFICATIONS FOR THE HOUSTON, LAREDO, PHARR, AND BRYAN DEMONSTRATION PROJECTS

Yetkin Yildirim, Thomas W. Kennedy, and Jorge Prozzi

Implementation Project # 5-3933-01

Products 5-3933-01-P1, P2, P3, and P4

March 2004
Preface

This is the report summarizing the binder design results conducted for the Project 3933. It presents the toner-modified binder designs for the Houston, Laredo, Bryan and Pharr projects.

Implementation Statement

Every year a large amount of toner is produced for copiers and printers by toner manufacturing companies. Toner, the dry ink used in laser printers and copiers, can be blended into asphalt to improve strength and temperature-resistance properties. Some of the toner does not meet quality specifications for use in copiers or printers and consequently becomes a waste product of the manufacturing process. This manufacturing waste along with the spent toner from copiers and printers is dumped into landfills for lack of a better way to utilize the material.

A cooperative research project, 7-3933, undertaken by the Texas Department of Transportation and the University of Texas at Austin investigated the feasibility and potential benefits of utilizing waste toner in hot-mix asphalt concrete. This implementation project transferred the results from project 7-3933, in which the feasibility and potential benefits of utilizing waste toner in hot-mix asphalt concrete was investigated.

The results of this study can assist industry and state agencies in their efforts to utilize toner in binder modification.
Disclaimers

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Texas Department of Transportation (TxDOT). This report does not constitute a standard, specification, or regulation.

There was no invention or discovery conceived or first actually reduced to practice in the course of or under this contract, including any art, method, process, machine, manufacture, design or composition of matter, or any new and useful improvement thereof, or any variety of plant, which is or may be patentable under the patent laws of the United States of America or any foreign country.

NOT INTENDED FOR CONSTRUCTION, BIDDING, OR PERMIT PURPOSES

Dr. Yetkin Yildirim
P.E. (Texas No. 92787)
Table of Contents

1. DESIGN OF TONER MODIFICATION FOR THE HOUSTON DEMONSTRATION PROJECT
   1.1 Binder Design for Houston Project ................................................................. 3
   1.2 Effective Reaction Conditions ........................................................................ 3
   1.3 Design Toner Modification Level .................................................................... 4
   1.4 Mixing And Compaction Temperatures ......................................................... 6
   1.5 Storage Stability .............................................................................................. 8

2. DESIGN OF TONER MODIFICATION FOR THE LAREDO DEMONSTRATION PROJECT
   2.1 Binder Design for Laredo Project ................................................................. 13
   2.2 Effective Reaction Conditions ...................................................................... 13
   2.3 Design Toner Modification Level .................................................................. 14
   2.4 Mixing and Compaction Temperatures ....................................................... 16
   2.5 Storage Stability ............................................................................................ 17

3. DESIGN OF TONER MODIFICATION FOR THE PHARR DEMONSTRATION PROJECT
   3.1 Binder Design for Pharr Project ..................................................................... 21
   3.2 Effective Reaction Conditions ...................................................................... 21
   3.3 Design Toner Modification Level .................................................................. 21
   3.4 Mixing And Compaction Temperatures ......................................................... 23
   3.5 Storage Stability ............................................................................................ 24

4. DESIGN OF TONER MODIFICATION FOR THE BRYAN DEMONSTRATION PROJECT
   4.1 Introduction ..................................................................................................... 29
   4.2 Effective Reaction Time ................................................................................ 29
   4.3 Mixing And Compaction Temperatures ....................................................... 30
   4.4 Storage Stability ............................................................................................ 31
   4.5 Design Toner Modification Level .................................................................. 32

References .................................................................................................................. 35

Appendix A - Superpave Binder Requirements for the Houston Demonstration Project 37
Appendix B - Superpave Binder Requirements for the Laredo Demonstration Project... 43
Appendix C - Superpave Binder Requirements for the Pharr Demonstration Project .... 49
Appendix D - Superpave Binder Requirements for the Bryan Demonstration Project .... 55
List of Figures

Figure 1.1. Shear Modulus as a Function of Blending Period ........................................ 4
Figure 1.2. Viscosity Shear Rate Relation at 135°C and 165°C ................................. 7
Figure 1.3. Viscosity Temperature Relation at 12.5 Toner Modification Level .......... 8
Figure 1.4. Results of Stability Test at 12.5 Toner Modification Level ....................... 9
Figure 2.1. Shear Modulus as a Function of Blending Period ............................... 13
Figure 2.2. Viscosity Vrs Temperature at 14.5 Toner Modification Level ............... 17
Figure 2.3. Results of Storage Stability Test at 14.5 percent Toner Modification Level 18
Figure 3.1. Shear Modulus as a Function of Blending Period ............................... 21
Figure 3.2. Viscosity Vrs Temperature at 7 percent Toner Modification Level ............ 24
Figure 3.3. Results of Stability Test at 7 percent Toner Modification Level ............. 25
Figure 4.1. Shear Modulus as a Function of Blending Period ............................... 30
Figure 4.2. Viscosity Vs. Temperature at 7% Toner Modification Level ................. 31
Figure 4.3. Results of Stability Test at 7 percent Toner Modification Level ............. 32
List of Tables

Table 1.1. Superpave Binder Requirements for PG 70-16 ....................................................... 4
Table 1.2. Equations for Estimated Relations.......................................................................... 5
Table 1.3. Estimated values of Superpave requirements at different toner modification levels ................................................................. 6
Table 2.1. Superpave PG Binder Requirements for PG 76-16 .............................................. 14
Table 2.2. Equations for Estimated Relations.......................................................................... 14
Table 2.3. Estimated values of Superpave requirements at different toner modification. 15
Table 3.1. Superpave Binder Requirements for PG 64-22 ................................................... 22
Table 3.2. Equations for Estimated Relations.......................................................................... 23
Table 4.1. Superpave Binder Requirements for PG 64-22 ................................................... 33
Table 4.2. Equations for Estimated Relations.......................................................................... 33
1. DESIGN OF TONER MODIFICATION FOR THE HOUSTON DEMONSTRATION PROJECT

Yetkin Yildirim and Thomas W. Kennedy

Implementation Project # 5-3933-01

Products 5-3933-01-P1

SEPTEMBER 2001
1.1 Binder Design for Houston Project

CTR completed the binder design for toner modified binder for the Houston demonstration project. The design included information on the effective reaction time between binder and toner, effective stirring time to achieve a homogeneous mix, effective toner content range to achieve the required performance grade, storage stability of toner modified asphalt binders and mixing and compaction temperatures for toner modified asphalt binders. The amount of toner required to achieve PG 70-16 was found to be between 11 and 14 percent.

Originally, it was intended to use PG 76-16 binder for this project. However, in order to reach PG 76-16, more than 30 percent toner should be added to the base binder. Since adding 30 percent toner might change the characteristics of the binder completely, it was decided to modify the binder to achieve PG 70-16.

1.2 Effective Reaction Conditions

The first consideration in developing a binder design was to determine the effective reaction conditions. In order to obtain a homogenous binder, 7 percent toner was blended and reacted using a “Lightning” mixer with the base asphalt. The mixing took place at 500 revolutions per minute at 163°C. At the end of reaction period the samples were tested for complex shear modulus at 64°C. The change in complex modulus versus blending time was plotted to find the efficient blending time to achieve a homogeneous mix. Figure 1.1 shows this relation.

The results plotted in Figure 1.1 indicated that as the blending time increases, the complex modulus increases for the first 100 minutes. After that, complex modulus values stay constant. From the figure, it can be assumed that after 100 minutes of stirring, a homogenous toner asphalt mixture can be achieved. Based on this information, it was concluded to use a blending time of two hours.
For this study, mixing was conducted using a Lightning mixer (Model L1U08) with a three-blade impeller (7.6-cm diameter) at a rate of 500 revolutions per minute. Different mixing conditions affect the mixing time to achieve a homogenous mixture. During construction of the test sections, mixing process of toner and asphalt might be completely different than mixing conditions at CTR laboratory. To solve this problem, viscosity values will be monitored regularly during mixing process at the plant.

1.3 Design Toner Modification Level

Trial blends containing different percentages of toner were prepared. Full performance grade binder classification testing was conducted on each trial blend. Trial blends were prepared at 0%, 7%, 14%, 21% and 30% toner modification levels. Table 1.1 shows the requirements for PG 70-16 binders.

<table>
<thead>
<tr>
<th>Table 1.1. Superpave Binder Requirements for PG 70-16</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PG 70-16</strong></td>
</tr>
<tr>
<td>Original G*/sinδ</td>
</tr>
<tr>
<td>RTFO G*/sinδ</td>
</tr>
<tr>
<td>PAV G*sinδ</td>
</tr>
<tr>
<td>PAV S</td>
</tr>
<tr>
<td>PAV m-value</td>
</tr>
</tbody>
</table>
All tests listed in Table 1.1 were conducted at required temperatures. Tests were conducted at different toner modification levels to establish the relations between toner modification level and the requirements listed in Table 1.1. Figures showing the relations for these five requirements were included in Appendix A. Equations and $R^2$ values were included in Table 1.2.

Table 1.2. Equations for Estimated Relations

<table>
<thead>
<tr>
<th>Percent Toner vs.</th>
<th>Binder</th>
<th>Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G^*/\sin\Delta$</td>
<td>Original</td>
<td>$Y = -0.4469x^2 + 45.239x + 544.32$</td>
<td>0.9642</td>
</tr>
<tr>
<td>$G^*/\sin\Delta$</td>
<td>RTFO</td>
<td>$Y = -1.2485x^2 + 122.54x + 1306.7$</td>
<td>0.9768</td>
</tr>
<tr>
<td>$G^*/\sin\Delta$</td>
<td>PAV</td>
<td>$Y = 9672.7x^2 + 11789x + 3E+06$</td>
<td>0.9235</td>
</tr>
<tr>
<td>S</td>
<td>PAV</td>
<td>$Y = 43.284x^2 - 310.88x + 53720$</td>
<td>0.634</td>
</tr>
<tr>
<td>m-value</td>
<td>PAV</td>
<td>$Y = -5E-05x^2 - 0.0003x + 0.0773$</td>
<td>0.8666</td>
</tr>
</tbody>
</table>

Based on the equations listed in Table 1.2, values required in the Superpave binder specification were calculated at different toner modification levels. Values were calculated between 7 and 19 percent toner modification for five Superpave requirements listed in Table 1.1. Calculated values were included in Table 1.3.

As can be seen from Table 1.3, binders under 12 percent toner modification do not meet the requirements for $G^*/\sin\delta$ on original binders. For RTFO aged binder, the base binder should be modified with a minimum of 8 percent toner to meet the requirements for $G^*/\sin\delta$. The base binder should be modified less than 14 percent to meet the requirements for $G^*\sin\delta$. Between 7 and 19 percent modification level, in all cases binders meet the requirements for Creep Stiffness (S), but for Logarithmic Creep Rate (m-value) more than 18 percent toner modification did not meet the requirements.
Table 1.3. Estimated values of Superpave requirements at different toner modification levels.

<table>
<thead>
<tr>
<th>Percent Toner</th>
<th>Original G*/sinδ Pascal</th>
<th>RTFO G*/sinδ Pascal</th>
<th>PAV G*sinδ Pascal</th>
<th>PAV S</th>
<th>PAV m-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>839</td>
<td>2103</td>
<td>3556485</td>
<td>95844</td>
<td>0.355</td>
</tr>
<tr>
<td>8</td>
<td>878</td>
<td>2207</td>
<td>3713365</td>
<td>98000</td>
<td>0.350</td>
</tr>
<tr>
<td>9</td>
<td>915</td>
<td>2308</td>
<td>3889590</td>
<td>100601</td>
<td>0.346</td>
</tr>
<tr>
<td>10</td>
<td>952</td>
<td>2407</td>
<td>4085160</td>
<td>103648</td>
<td>0.341</td>
</tr>
<tr>
<td>11</td>
<td>988</td>
<td>2504</td>
<td>4300076</td>
<td>107140</td>
<td>0.337</td>
</tr>
<tr>
<td>12</td>
<td>1023</td>
<td>2597</td>
<td>4534337</td>
<td>111077</td>
<td>0.332</td>
</tr>
<tr>
<td>13</td>
<td>1057</td>
<td>2689</td>
<td>4787943</td>
<td>115459</td>
<td>0.327</td>
</tr>
<tr>
<td>14</td>
<td>1090</td>
<td>2778</td>
<td>5060895</td>
<td>120286</td>
<td>0.322</td>
</tr>
<tr>
<td>15</td>
<td>1122</td>
<td>2864</td>
<td>5353193</td>
<td>125559</td>
<td>0.317</td>
</tr>
<tr>
<td>16</td>
<td>1154</td>
<td>2948</td>
<td>5664835</td>
<td>131277</td>
<td>0.313</td>
</tr>
<tr>
<td>17</td>
<td>1184</td>
<td>3029</td>
<td>5995823</td>
<td>137440</td>
<td>0.308</td>
</tr>
<tr>
<td>18</td>
<td>1214</td>
<td>3108</td>
<td>6346157</td>
<td>144048</td>
<td>0.302</td>
</tr>
<tr>
<td>19</td>
<td>1243</td>
<td>3184</td>
<td>6715836</td>
<td>151101</td>
<td>0.297</td>
</tr>
</tbody>
</table>

The critical values come from G*/sinδ on original binder and G*sinδ on PAV aged binder to achieve PG 70-16. As can be seen from Table 1.3, only 12 and 13 percent toner modification met all the Superpave binder requirements. From this information, it was concluded to use 12.5 percent toner modification for this project.

1.4 Mixing And Compaction Temperatures

Lab mixing and compaction temperatures were calculated at 12.5 percent toner modification level. The method developed by CTR and reported in Research Report 1250-5 for calculation of mixing and compaction temperatures was used in this project. Viscosity of modified binders depends on both shear rate and temperature. Therefore, in viscosity calculations effect of these factors was included. A relation between shear rate and viscosity was established by Brookfield viscometer to estimate the shear rate dependency of the toner modified binder. Measurements were conducted at 135°C and 165°C. Figure 4 shows the relations at these temperatures.
Based on the relations calculated in Figure 1.2, viscosity values at 500 1/s shear rate were calculated. These viscosity values were used to establish the relation between viscosity and temperature. CTR recommends 275 cP viscosity value for calculation of mixing temperature and 550 cP viscosity value for calculation of compaction temperature. These viscosity values were used to estimate the mixing and compaction temperatures. Figure 1.3 shows the relation between viscosity and temperature at 12.5 toner modification level. Based on the relation shown in Figure 1.3, mixing temperature was found to be 147°C and compaction temperature was found to be 136°C.
1.5 Storage Stability

Storage stability was measured using AASHTO PP5-93 at 12.5 toner modification level. A modified asphalt sample was poured into an aluminum tube and held in vertical position throughout the aging portion of the test. The top of the tube is sealed and the sample is placed in a 163°C oven for 2 hours. The sample is removed from the oven, and immediately placed and left in a freezer at –5°C. The tube is cut into three pieces. The top and bottom pieces are each placed in a different container and held at 163°C to remove the aluminum pieces. The resulting specimens are tested for complex shear modulus. The results were tabulated in Table 1.2.

The specimens taken from the bottom part of the tube, showed 15 percent higher viscosity than the binder taken from the top portion. In this study, the specimen was left in the oven only for 2 hours. However, according to AASHTO PP5-93, the required duration of the specimen in the oven is 48 hours. The difference in viscosity exhibited between the top and bottom in such a short time shows a significant storage stability problem.
Figure 1.4. Results of Stability Test at 12.5 Toner Modification Level
2. DESIGN OF TONER MODIFICATION FOR THE LAREDO DEMONSTRATION PROJECT

Yetkin Yildirim and Thomas W. Kennedy

Implementation Project # 5-3933-01

Product 5-3933-01-P2

JUNE 2002
2.1 Binder Design for Laredo Project

The binder design for toner modified binder for the Laredo demonstration project included information on the effective reaction time between binder and toner, effective stirring time to achieve a homogeneous mix, effective toner content range to achieve the required performance grade, storage stability and mixing and compaction temperatures. The base binder was a PG 64-22, and the amount of toner required to achieve a PG 76-16 was between 13 and 14 percent. For this project, it is recommended to use 14.5% percent toner to modify the base binder.

2.2 Effective Reaction Conditions

The results of the effect of stirring period are presented in Figure 2.1. In order to obtain a homogenous binder, 5 percent toner was blended and reacted using a “Lightning” mixer with the base asphalt. The mixing took place at 500 revolutions per minute at 163°C. At the end of reaction period the samples were tested for complex shear modulus at 64°C. The change in complex modulus versus blending time was plotted to find the efficient blending time to achieve a homogeneous mix.

![Figure 2.1. Shear Modulus as a Function of Blending Period](image-url)
2.3 Design Toner Modification Level

Trial blends containing different percentages of toner were prepared to calculate the toner modification level to achieve PG 76-16. The toner-binder blends were prepared at 0%, 5%, 10%, and 15% toner modification levels. Full performance grade binder classification testing was conducted on each toner modification level. Superpave binder specifications for PG 76-16 is shown in Table 2.1

Table 2.1. Superpave PG Binder Requirements for PG 76-16

<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>Original</th>
<th>RTFO</th>
<th>PAV</th>
<th>PAV</th>
<th>PAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>G*/sinδ</td>
<td>G*/sinδ</td>
<td>G*/sinδ</td>
<td>S</td>
<td>m-value</td>
</tr>
<tr>
<td>Test Temperature</td>
<td>76</td>
<td>76</td>
<td>28</td>
<td>-6</td>
<td>-6</td>
</tr>
<tr>
<td>Requirement</td>
<td>Min. 1.0Kpa</td>
<td>Min 2.2Kpa</td>
<td>Max. 5000Kpa</td>
<td>Max.300Mpa</td>
<td>Min 0.30</td>
</tr>
</tbody>
</table>

All tests listed in Table 2.1 are conducted at the specified temperatures. Tests were conducted at different toner modification levels to establish the relations between toner modification level and the requirements listed in Table 2.1. Figures showing the relations for these five requirements were included in Appendix B. Equations and R² values are included in Table 2.2.

Table 2.2. Equations for Estimated Relations

<table>
<thead>
<tr>
<th>Percent Toner v.s.</th>
<th>Binder</th>
<th>Equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>G*/sin Delta</td>
<td>Original</td>
<td>Y = 0.9819x² + 65.982x + 458.5</td>
<td>0.71</td>
</tr>
<tr>
<td>G*/sin Delta</td>
<td>RTFO</td>
<td>Y = 6.5396x² + 8.0997x + 966.63</td>
<td>0.9556</td>
</tr>
<tr>
<td>G*/sin Delta</td>
<td>PAV</td>
<td>Y = 2376.9x² + 109113x + 2E+06</td>
<td>0.9334</td>
</tr>
<tr>
<td>S</td>
<td>PAV</td>
<td>Y = 62.167x² + 1287.8x + 71481</td>
<td>0.8711</td>
</tr>
<tr>
<td>m-value</td>
<td>PAV</td>
<td>Y = -1E-05x² - 0.0025x + 0.3922</td>
<td>0.8591</td>
</tr>
</tbody>
</table>
Based on the equations listed in Table 2.2, values required in the Superpave binder specification were calculated at different toner levels. These results are presented in Table 2.3 for values between 7 and 19 percent toner modification for the five Superpave requirements listed in Table 2.1.

As can be seen from Table 2.3, binders below 8 percent toner modification do not meet the requirements for $G*/\sin\delta$ on original binders. For RTFO aged binder, the base binder should be modified with a minimum of 14 percent toner to meet the requirements for $G*/\sin\delta$. Therefore, the base binder should be modified in more than 14 percent to meet the requirements for $G*\sin\delta$, since the RTFO aged specification is hardly satisfied. Other than this, Creep Stiffness (S), and Logarithmic Creep Rate (m-value) meet the specification requirements for toner modification level between 7 and 19 percent.

Table 2.3. Estimated values of Superpave requirements at different toner modification levels.

<table>
<thead>
<tr>
<th>Percent Toner</th>
<th>Original $G*/\sin\delta$ Pascal</th>
<th>RTFO $G*/\sin\delta$ Pascal</th>
<th>PAV $G*\sin\delta$ Pascal</th>
<th>S Pascal</th>
<th>m-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>968.4871</td>
<td>1383.4424</td>
<td>2880259</td>
<td>83541.78</td>
<td>0.37421</td>
</tr>
<tr>
<td>8</td>
<td>1049.198</td>
<td>1479.1124</td>
<td>3025026</td>
<td>85762.09</td>
<td>0.37156</td>
</tr>
<tr>
<td>9</td>
<td>1131.872</td>
<td>1584.3536</td>
<td>3174546</td>
<td>88106.73</td>
<td>0.36889</td>
</tr>
<tr>
<td>10</td>
<td>1216.51</td>
<td>1699.166</td>
<td>3328820</td>
<td>90575.7</td>
<td>0.3662</td>
</tr>
<tr>
<td>11</td>
<td>1303.112</td>
<td>1823.5496</td>
<td>3487848</td>
<td>93169.01</td>
<td>0.36349</td>
</tr>
<tr>
<td>12</td>
<td>1391.678</td>
<td>1957.5044</td>
<td>3651630</td>
<td>95886.65</td>
<td>0.36076</td>
</tr>
<tr>
<td>13</td>
<td>1482.207</td>
<td>2101.0304</td>
<td>3820165</td>
<td>98728.62</td>
<td>0.35801</td>
</tr>
<tr>
<td>14</td>
<td>1574.700</td>
<td>2254.1276</td>
<td>3993454</td>
<td>101694.9</td>
<td>0.35524</td>
</tr>
<tr>
<td>15</td>
<td>1669.158</td>
<td>2416.796</td>
<td>4171498</td>
<td>104785.6</td>
<td>0.35245</td>
</tr>
<tr>
<td>16</td>
<td>1765.578</td>
<td>2589.0356</td>
<td>4354294</td>
<td>108000.6</td>
<td>0.34964</td>
</tr>
<tr>
<td>17</td>
<td>1863.963</td>
<td>2770.8464</td>
<td>4541845</td>
<td>111339.9</td>
<td>0.34681</td>
</tr>
<tr>
<td>18</td>
<td>1964.312</td>
<td>2962.2284</td>
<td>4734150</td>
<td>114803.5</td>
<td>0.34396</td>
</tr>
<tr>
<td>19</td>
<td>2066.624</td>
<td>2685.4616</td>
<td>4931208</td>
<td>118391.5</td>
<td>0.34109</td>
</tr>
</tbody>
</table>
The numbers in italics in each column represent the specification results for the corresponding toner percent which do not meet a particular criterion. The critical figure stems from $G*/\sin\delta$ on RTFO aged binder to achieve PG 76-16, with a value of 13.9 percent toner modification needed to meet all Superpave binder requirements. Since the abovementioned parameter is barely met (see Appendix B Figure 2), and to be on the safe side, it was decided to use 14.5% percent toner to modify the base binder.

### 2.4 Mixing and Compaction Temperatures

Lab mixing and compaction temperatures were calculated at 14.5 percent toner modification level. The method developed by CTR and reported in Research Report 1250-5 for calculation of mixing and compaction temperatures was used in this project. Viscosity of modified binders depends on both shear rate and temperature. Therefore, the effect of these factors was included in the viscosity calculations. A relationship between shear rate and viscosity was established by Brookfield viscometer to estimate the shear rate dependency of the toner modified binder. Measurements were conducted at 135°C and 165°C.

Based on the relations calculated in Figure B4 (in the appendix), viscosity values at 500 1/s shear rate were calculated. These viscosity values were used to establish the relationship between viscosity and temperature. CTR recommends 275 cP viscosity value for calculation of mixing temperature and 550 cP viscosity value for calculation of compaction temperature. These viscosity values were used to estimate the mixing and compaction temperatures. Figure B5 (see Appendix B) shows the relationship between viscosity and temperature at 14.5 percent toner modification level. Based on the relationship shown in Figure 2.2, mixing temperature was found to be 156°C, and compaction temperature was found to be 141°C.
2.5 Storage Stability

Storage stability was measured using AASHTO PP5-93 at 14.5 toner modification level. A modified asphalt sample was poured into an aluminum tube and held in vertical position throughout the aging portion of the test. The top of the tube was sealed and the sample placed in a 163°C oven for 2 hours. The sample was then removed and immediately placed and left in a freezer at –5°C. The tube was cut into three pieces, with the top and bottom pieces placed in a different container and held at 163°C to remove the aluminum pieces. The resulting specimens were subsequently tested for complex shear modulus.

The specimens taken from the bottom part of the tube, showed up to 4 times higher viscosity than the binder taken from the top portion. In this study, the specimen was left in the oven only for 2 hours, contrasting with AASHTO PP5-93, which requires a duration of the specimen in the oven of 48 hours. However, the difference in viscosity exhibited between the top and bottom in such a short time shows a significant storage stability problem. Figure 2.3 shows the results of the storage stability test.
Figure 2.3. Results of Storage Stability Test at 14.5 percent Toner Modification Level
3. DESIGN OF TONER MODIFICATION FOR THE PHARR DEMONSTRATION PROJECT

Yetkin Yildirim and Thomas W. Kennedy

Implementation Project # 5-3933-01

Product 5-3933-01-P3

June 2002
3.1 Binder Design for Pharr Project

CTR completed the work to evaluate the effect of 7% toner modification design for a specified non-magnetic toner-modified binder corresponding to the Pharr demonstration project. This project intends to arrive to a better understanding of the effect of toner on the relationship between PG specifications and toner level. The project included information on the effective reaction time between binder and toner, effective stirring time to achieve a homogeneous mix, effective 7% toner content on the PG64-22 base binder. Storage stability, mixing and compaction temperatures for non-magnetic toner modified asphalt binders were also determined.

3.2 Effective Reaction Conditions

7 percent toner was used and blending was carried out at 500 revolutions per minute at 163°C. The samples were taken throughout the blending process and tested for complex shear modulus at 64°C. The change in complex modulus versus blending time was plotted to find the efficient blending time to achieve a homogeneous mix. Figure 3.1 shows this relation. It is concluded that after 60 minutes of mixing, the binder-toner mastic is sufficiently homogenous.

![Figure 3.1. Shear Modulus as a Function of Blending Period](image)

3.3 Design Toner Modification Level

Full performance-grade binder classification testing was conducted on a blend prepared at 7 percent toner modification level. Initially, it was believed that a PG 70-22 binder with 7
percent toner would satisfy specifications; however, the RTFO aged binder did not comply with the minimum 2.2Kpa requirement, having thus a diminishment on the high temperature side towards a PG 64-22, as shown in Figure C2, Appendix C. As for the intermediate temperature properties, the PG 64-22 did not comply with the Pressure Aging Vessel (PAV) aged binder test at 25°C, which requires a maximum 5000Kpa. Therefore, a 7% toner-modified binder finally met all the PG grading requirements for a PG 64-16. The testing sequence and corresponding temperatures and specifications are shown in Table 3.1.

Table 3.1. Superpave Binder Requirements for PG 64-22

<table>
<thead>
<tr>
<th>Test</th>
<th>Original</th>
<th>RTFO</th>
<th>PAV</th>
<th>PAV</th>
<th>PAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>G*/sinδ</td>
<td>G*/sinδ</td>
<td>G*/sinδ</td>
<td>S</td>
<td>m-value</td>
</tr>
<tr>
<td>PG 70-22 Test Temperatures</td>
<td>70</td>
<td>70</td>
<td>25</td>
<td>-12</td>
<td>-12</td>
</tr>
<tr>
<td>PG 64-22 Test Temperatures</td>
<td>64</td>
<td>64</td>
<td>25</td>
<td>-12</td>
<td>-12</td>
</tr>
<tr>
<td>PG 64-16 Test Temperatures</td>
<td>64</td>
<td>64</td>
<td>28</td>
<td>-6</td>
<td>-6</td>
</tr>
<tr>
<td>Requirement</td>
<td>Min. 1.0KPa</td>
<td>Min 2.2Kpa</td>
<td>Max. 5000Kpa</td>
<td>Max.300Mpa</td>
<td>Min 0.30</td>
</tr>
</tbody>
</table>

All tests listed in Table 3.1 were conducted at the required temperatures. Although the toner percent amount was fixed, tests were conducted at different toner modification levels to establish the relations between toner modification levels so as to verify compliance with the requirements listed in Table 3.1. Figures showing the relationship between toner modification level and the binder properties for these five requirements are included in Appendix C. Equations and R² values are included in Table 3.2.
Table 3.2. Equations for Estimated Relations

<table>
<thead>
<tr>
<th>Percent Toner v.s.</th>
<th>Binder</th>
<th>Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G*/sin Delta (64)</td>
<td>Original</td>
<td>$Y = 37.776x^2 - 223.54x + 1295.4$</td>
<td>0.9375</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Y = 29.468x^2 - 195.65x + 624.04$</td>
<td>0.9561</td>
</tr>
<tr>
<td>(70)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G*/sin Delta</td>
<td>RTFO</td>
<td>$Y = 98.599x^2 - 664.09x + 3406.2$</td>
<td>0.8779</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Y = 53.828x^2 - 384.61x + 1535.8$</td>
<td>0.8592</td>
</tr>
<tr>
<td>(25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(28)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G*/sin Delta</td>
<td>PAV</td>
<td>$Y = 234850x + 5E+06$</td>
<td>0.9717</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Y = 156114x + 3E+06$</td>
<td>0.9741</td>
</tr>
<tr>
<td>S (-6)</td>
<td>PAV</td>
<td>$Y = 4088.3x + 86523$</td>
<td>0.9516</td>
</tr>
<tr>
<td>m-value (-6)</td>
<td>PAV</td>
<td>$Y = -0.0033x + 0.4285$</td>
<td>0.9415</td>
</tr>
</tbody>
</table>

3.4 Mixing And Compaction Temperatures

Lab mixing and compaction temperatures were calculated at 7 percent toner modification level. The method developed by CTR and reported in Research Report 1250-5 for calculation of mixing and compaction temperatures was used in this project. Viscosity of modified binders depends on both shear rate and temperature. Therefore, the effect of these factors was included in the viscosity calculations. A relationship between shear rate and viscosity was established by the Brookfield viscometer to estimate the shear rate dependency of the toner modified binder. Measurements were conducted at 135°C and 165°C.

Based on the relations between viscosity and shear rate, viscosity values at 500 l/s shear rate were estimated. These viscosity values were used to establish the relationship between viscosity and temperature. CTR recommends 275 cP viscosity value for calculation of mixing temperature and 550 cP viscosity value for calculation of compaction temperature. These viscosity values were used to estimate the mixing and compaction temperatures. Figure 3.2 shows the relationship between viscosity and temperature at 7 percent toner modification level.
Based on this relationship, mixing temperature was found to be 149°C, and compaction temperature was found to be 135°C.

![Figure 3.2. Viscosity Vrs Temperature at 7 percent Toner Modification Level](image)

### 3.5 Storage Stability

Storage stability was measured using AASHTO PP5-93 at 7 percent toner modification level. A modified asphalt sample was poured into an aluminum tube and held in vertical position throughout the aging portion of the test. The top of the tube was sealed and the sample placed in a 163°C oven for 2 hours. The sample was then removed from the oven, and immediately placed and left in a freezer at –5°C. The tube was cut into three pieces, with the top and bottom pieces placed in a different container and held at 163°C to remove the aluminum pieces. The resulting specimens were subsequently tested for complex shear modulus.

The specimens taken from the bottom part of the tube, showed up to 8 times higher viscosity than the binder taken from the top portion. In this study, the specimen was left in the oven only for 2 hours instead of 48 hours as recommended by AASHTO PP5-93. A significant storage stability problem was observed through the high difference in viscosity exhibited between the top and bottom in such a short time. The results of storage stability test are presented in Figure 3.3.
Figure 3.3. Results of Stability Test at 7 percent Toner Modification Level
4. DESIGN OF TONER MODIFICATION FOR THE BRYAN DEMONSTRATION PROJECT

Dr. Yetkin Yildirim and Dr. Jorge Prozzi

Implementation Project # 5-3933-01

Product 5-3933-01-P4

April 2003
4.1 Introduction

This report summarizes the effect of 7% toner modification on the properties of the binder received from Fina Oil Company for the Bryant Toner Project. The report includes information on effective reaction time between the binder and toner, stirring time to arrival at a homogeneous mixture and effect of 7% toner modification on the PG 64-16 base binder. In addition, storage stability and mixing and compaction temperatures for the 7% toner-modified asphalt binders were tested. Finally, performance grade classification tests on 14 and 21% toner modified binders were conducted to better understand the relationship between PG specifications and toner level.

4.2 Effective Reaction Time

Seven percent toner was used and blending was carried out at 500 revolutions per minute at 163°C. The samples were taken throughout the blending process and tested for complex shear modulus at 64°C. The change in complex shear modulus versus blending time was monitored to determine an effective blending time to achieve a homogeneous mix. Figure 4.1 shows this relation. As can be seen from this figure, shear modulus increases rapidly during the first 30 minutes after blending process started; however, the shear modulus seems to stabilize after this period. Based on this empirical relationship, it was concluded that after 60 minutes of mixing, the binder-toner mastic is sufficiently homogenous.
4.3 Mixing And Compaction Temperatures

Lab mixing and compaction temperatures were calculated at 7% toner modification level. The method developed by the Center for Transportation Research (CTR) and reported in Research Report 1250-5 for calculation of mixing and compaction temperatures was used in this project (Yildirim et al., 2000).

It is known that the viscosity of modified binders depends on both shear rate and temperature. Therefore, the effect of these factors was included in the viscosity calculations. A relationship between shear rate and viscosity was established by the Brookfield viscometer to estimate the shear rate dependency of the toner modified binder. Measurements were conducted at 135°C and 165°C.

Viscosity values at 500 1/s shear rate were estimated based on the relationship between viscosity and shear rate. The viscosity values of 109 cP and 423 cP for 165°C and 135°C respectively were used to establish the relationship between viscosity and temperature. CTR recommends 275 cP viscosity value for calculating mixing temperature and 550 cP viscosity value for calculating compaction temperature. Figure 4.2 shows the relationship between viscosity and temperature at 7% toner modification level. Based on this relationship, mixing temperature was found to be 144°C, and compaction temperature was found to be 130°C.
4.4 Storage Stability

Storage stability was measured using AASHTO PP5-93 at 7% toner modification level. A modified asphalt sample was poured into an aluminum tube and held in a vertical position throughout the aging portion of the test. The top of the tube was sealed and the sample was placed in a 163°C oven for 2 hours. The sample was then removed from the oven, and immediately placed in a freezer at –5°C. The tube was cut into three pieces, with the top and bottom portions placed in different containers and heated to 163°C to remove the aluminum pieces. The resulting specimens were subsequently tested for complex shear modulus.

The specimens taken from the bottom part of the tube, showed up to 6 times higher G*/ Sin δ value than the binder taken from the top portion. In this study, the specimens were left in the oven only for 2 hours instead of 48 hours as recommended by AASHTO PP5-93. A significant storage stability problem was observed through the high difference in viscosity exhibited between the top and bottom in such a short time. This problem should be taken into consideration when storing toner-modified binder. The results of storage stability test are presented in Figure 4.3.
Full performance-grade binder classification testing was conducted on a blend prepared at 7% toner modification level. It was found that seven percent toner modified binder meets the DSR requirements for original and RTFO aged binder at 70°C. In addition, 7 percent toner modified binder complies just within the DSR requirements on the Pressure Aging Vessel (PAV) aged binder test at 28°C. Therefore, a 7% toner-modified binder meets all the PG grading requirements for a PG 70-16. The testing sequence and corresponding temperatures and specifications are shown in Table 4.1. All tests listed in Table 4.1 were conducted at the required temperatures.

Although the toner percent amount was fixed at 7%, tests were also conducted at different toner modification levels to establish the relations between toner modification levels so as to verify compliance with the requirements listed in Table 4.1. Figures showing the relationship between toner modification level and the binder properties for these five requirements are included in Appendix D. The corresponding regression equations and relevant statistics are included in Table 4.2.
Table 4.1. Superpave Binder Requirements for PG 64-22

<table>
<thead>
<tr>
<th>Test</th>
<th>Original</th>
<th>RTFO</th>
<th>PAV</th>
<th>PAV</th>
<th>PAV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>G*/sinδ</td>
<td>G*/sinδ</td>
<td>G*/sinδ</td>
<td>S</td>
<td>m-value</td>
</tr>
<tr>
<td>PG 70-16 Test Temperatures</td>
<td>70</td>
<td>70</td>
<td>25</td>
<td>-12</td>
<td>-12</td>
</tr>
<tr>
<td>PG 64-16 Test Temperatures</td>
<td>64</td>
<td>64</td>
<td>28</td>
<td>-6</td>
<td>-6</td>
</tr>
<tr>
<td>Requirement</td>
<td>Min. 1.0 kPa</td>
<td>Min 2.2 kPa</td>
<td>Max. 5000 kPa</td>
<td>Max.300 MPa</td>
<td>Min 0.30</td>
</tr>
</tbody>
</table>

Table 4.2. Equations for Estimated Relations

<table>
<thead>
<tr>
<th>Percent Toner v.s.</th>
<th>Binder</th>
<th>Equation (t-statistics)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>G*/sin Δ (70)</td>
<td>Original</td>
<td>Y = 4.82x² + 62x + 494 [(5.2) \quad (3.1) \quad (5.8)]</td>
<td>0.99</td>
</tr>
<tr>
<td>G*/sin Δ (70)</td>
<td>RTFO</td>
<td>Y = 7.46x² - 7.07x + 2103 [(2.42) \quad (-0.1) \quad (7.2)]</td>
<td>0.88</td>
</tr>
<tr>
<td>G*/sin Δ (28)</td>
<td>PAV</td>
<td>Y = 11095x² - 46699x + 4.6E+06 [(8.6) \quad (-1.7) \quad (38.2)]</td>
<td>0.99</td>
</tr>
<tr>
<td>S (-6)</td>
<td>PAV</td>
<td>Y = 0.20x² - 0.08x + 103 [(6.9) \quad (-0.1) \quad (37.7)]</td>
<td>0.99</td>
</tr>
<tr>
<td>m-value (-6)</td>
<td>PAV</td>
<td>Y = -8.75E-05x² - 0.00088x + 0.36 [(-4.3) \quad (-2.0) \quad (188.5)]</td>
<td>0.99</td>
</tr>
</tbody>
</table>
References


Appendix A – Information for the Houston Project
Figure A1. Test Results from DSR for the original binder modified with different toner amounts

Figure A2. Test Results from DSR for the RTFO-aged binder modified with different toner amounts
Figure A3. Test Results from DSR for the PAV-aged binder modified with different toner amounts

Figure A4. Creep Stiffness values from BBR
Figure A5. Logarithmic Creep Rate (m-value) values from BBR
Appendix B - Information for the Laredo Project
Figure B1. Test Results from DSR for the original binder modified with different toner amounts

Figure B2. Test Results from DSR for the RTFO-aged binder modified with different toner amounts
Figure B3. Test Results from DSR for the PAV-aged binder modified with different toner amounts

Figure B4. Creep Stiffness values from BBR
Figure B5. Logarithmic Creep Rate (m-value) values from BBR

![Graph showing Logarithmic Creep Rate (m-value) values from BBR at -6C. The equation is y = -1E-05x^2 - 0.0025x + 0.3922 with R^2 = 0.8591.]

Figure B6. Creep Stiffness values from BBR (−12C)

![Graph showing Creep Stiffness values from BBR at -12C. The equation is y = 464.23x^2 - 2406x + 159395 with R^2 = 0.8933.]

Figure B7. Logarithmic Creep Rate (m-value) values from BBR (−12C)

\[ y = -0.0001x^2 - 0.0006x + 0.3269 \]

\[ R^2 = 0.5067 \]
Appendix C - Information for the Pharr Project
Figure C1. Test Results from DSR for the original binder modified with different toner amounts, and for 64 and 70 C
Figure C2. Test Results from DSR for the RTFO-aged binder modified with different toner amounts and for 64 and 70°C

RTFO @ 70°C

\[ y = 53.828x^2 - 384.61x + 1535.8 \]
\[ R^2 = 0.8592 \]

RTFO @ 64°C

\[ y = 98.599x^2 - 664.09x + 3406.2 \]
\[ R^2 = 0.8779 \]
Figure C3. Test Results from DSR for the PAV-aged binder modified with different toner amounts
Figure C4. Creep Stiffness values from BBR

Figure C5. Logarithmic Creep Rate (m-value) values from BBR
Appendix D - Information for the Bryan Project
Figure D1. Test Results from DSR for the original binder modified with different toner amounts, and for 64 and 70 C

\[ y = 4.8203x^2 + 62.499x + 494.65 \]

\[ R^2 = 0.9909 \]
Figure D2. Test Results from DSR for the RTFO-aged binder modified with different toner amounts and for 64 and 70C
Figure D3. Test Results from DSR for the PAV-aged binder modified with different toner amounts
Figure D4. Creep Stiffness values from BBR

Figure D5. Logarithmic Creep Rate (m-value) values from BBR