# Effects of Amine-Based Anti-Strip Additives on the Performance Grade of Asphalt Binders

Ray Gore Technical Manager Process Chemicals, L.L.C. ARR-MAZ Products Division

#### Abstract

Amine-based anti-strip additives are commonly added to asphalt to promote adhesion to aggregate. The most common types of adhesion promoters are fatty amines, polyamines based on BHMT, and amidoamines. The objective of this research is to determine the change in performance grade when these adhesion promoters are added to binders from various sources.

After testing the performance grade of the asphalts, the anti-strip additives were added, and the samples were tested again for grade compliance. The change in performance grade varied depending on the crude source, type, and dosage of anti-strip additive.

#### Background

Stripping or moisture damage in asphalt pavement is the loss of adhesion between the aggregate and the asphalt binder. This loss of adhesion may precipitate several types of road failures: rutting, cracking, raveling, and shoving. Many times, this loss of adhesion can be overcome with the aid of anti-stripping additives, also known as active adhesion promoters and wetting agents. These anti-strips additives, when added to asphalt, displace the moisture on the surface of the aggregate and promote adhesion of the binder to the aggregate surface.

Historically, the most common types of anti-strip additives have been amine-based hydrocarbons, such as tallow diamine, polyamines based on bis-hexamethylene triamine (BHMT), and amidoamines. The typical dosage by weight of asphalt is 0.25% - 0.75%. Anti-strip additives often are required by various State Departments of Transportation to increase tensile strength ratios of a mix design under AASHTO T-283 test criteria when the ratios cannot be met simply by using neat or polymer modified binder. Anti-strip additives aid in coating large amounts of fine aggregate or dust. They also are used to aid in adhering high acid value asphalts to acidic aggregates. Acidic groups in asphalt can

cause adhesion problems with acidic or siliceous aggregates, such as granites and quartzite.

Many times binders are tested for performance grades prior to the addition of anti-strip additives; therefore, changes in the performance grade, if any, are not known. The purpose of our research is to determine how the addition of anti-strip additives changes the performance grade of several different binders.

### Method of Investigation

Four unmodified asphalt binders, representing asphalt crudes commonly used for road paving, were heated to the upper range of their mixing temperatures. The viscosity of these asphalts were determined based on a two point viscosity chart, extrapolating to a viscosity of 0.15 Pa\*s. The base asphalts were heated to the corresponding temperature and modified with two dosages of amine-based anti-strip additives. The anti-strip modified samples were held at this temperature while being mixed with a 200-rpm paddle mixer for a period of one hour. The samples then were tested using AASHTO MP1 test criteria for both the original binder and the modified samples. The rotational viscosity for the original and RTFO samples also were tested to determine the change in viscosity after modification of both the original binder and the anti-strip modified binders.

### **Additive Selection**

The additives chosen were tallow diamine, polyamine based on BHMT, and an amidoamine. These liquid anti-stripping additives were added to the asphalt at a dosage of 0.5% and 0.75%. Each sample was blended with one dosage and one anti-strip additive prior to testing. All samples were handled and tested using the same heating schedule and testing criteria.

#### **Asphalt Binder Selection**

The binders chosen were a Venezuelan PG 67-22, a Canadian PG 52-34, a Mexican/ Arabic blended PG 67-22, and an Alaskan North Slope PG 64-22. These binders were chosen due to their diverse base crude locations and their wide range of performance grades. Each of these binders currently is being sold in the United States for paving applications.

## **Test Results**

#### Venezuelan PG 67-22 Original DSR, RTFO DSR, PAV DSR, Stiffness, MPa, m- Value, Original Viscosity, Viscosity after RTFO, $G^*/\sin \delta$ , $G^*/\sin \delta$ , $G^*/\sin \delta$ , -12°C -12°C Rotational, 135°C Rotational, 135°C 64°C 64°C 22°C Neat PG 67-22 1.870 4.674 4089 233 0.315 450 732 0.5% TDA 1.780 4.761 4287 217 0.311 483 715 0.75% TDA 1.894 4.388 4268 220 0.330 460 688 192 765 0.5% BHMT 2.497 6.578 4559 0.311 473 0.75% BHMT 2.233 6.743 4046 226 0.318 449 764 0.5% Amido 2.054 5.768 4222 200 0.317 486 733 0.75% Amido 2.251 220 730 4.956 4158 0.323 444

#### Phase Angle

8	δ, Original DSR 64,°C	δ, RTFO DSR, 64°C	δ, PAV DSR, 22°C
Neat PG 67-22	87.6	84.2	46.1
0.5% TDA	87.4	84.4	46.4
0.75% TDA	87.6	85.0	46.4
0.5% BHMT	87.1	82.9	45.1
0.75% BHMT	87.2	82.9	46.1
0.5% Amido	87.2	84.0	46.2
0.75% Amido	87.2	84.1	45.7

#### Calculated True Grade

	Original DSR	RTFO DSR	PAV DSR	Stiffness	m- value	True Grade	
Neat PG 67-22	68.8	69.7	20.4	-13.7	-13.1	68.8-23.1	
0.5% TDA	69.2	69.7	19.5	-14.1	-13.3	69.2-23.3	
0.75% TDA	69.3	69.4	20.8	-14.0	-14.1	69.3-24.0	
0.5% BHMT	70.9	71.4	21.3	-15.6	-13.1	70.9-23.1	
0.75% BHMT	69.9	72.1	20.1	-13.7	-13.3	69.9-23.3	
0.5% Amido	69.9	71.1	20.6	-15.1	-13.5	69.9-23.5	
0.75% Amido	70.2	69.8	20.5	-14.0	-13.6	69.8-23.6	

#### Change in True Grade from Original Binder

	$\Delta$ Original DSR	$\Delta$ RTFO DSR	$\Delta$ PAV DSR	$\Delta$ Stiffness	$\Delta$ m- value
0.5% TDA	0.4	0.0	-0.9	-0.4	-0.2
0.75% TDA	0.5	-0.3	0.4	-0.3	-1.0
0.5% BHMT	2.1	1.7	0.9	-1.9	0.0
0.75% BHMT	1.1	2.4	-0.3	0.0	-0.2
0.5% Amido	1.1	1.4	0.2	-1.4	-0.4
0.75% Amido	1.4	0.1	0.1	-0.3	-0.5

Note: TDA= Tallow diamine, BHMT= polyamine based on bis-hexamethylene triamine, Amido= amidoamine.

The Venezuelan PG 67-22 maintained a PG 64-22 for all dosage levels and anti-strip additives tested. The high temperature PG for all dosages of anti-strip additives was within 1°C of a PG 70. The trend for the high temperature PG was less than a 2°C increase for all anti-strip additives at each dosage, with the exception of BHMT based amine, which showed a slightly higher increase. The PAV DSR showed less than a 1°C change when compared to the unmodified binder. The BBR stiffness at  $-12^{\circ}$ C for all anti-strip additives and dosage levels was lower than that of the unmodified binder. The lower dosage levels showed a higher reduction in BBR stiffness at  $-12^{\circ}$ C for each individual anti-strip. The change in m- value varied from -1.3% to 4.8%, and all anti-strip modified samples showed 0 to  $-1^{\circ}$ C change in grade. The rotational viscosity did not change more than 8% for any dosage of anti-strip additive. The trend was an increase in viscosity, with the exception of the tallow diamine and the amidoamine after RTFO aging.

## Mexican/Arabic Blend PG 67-22

	Original DSR,	RTFO DSR,	PAV DSR,	Stiffness, MPa,	m- Value,	Original Viscosity,	Viscosity after RTFO,	
	<b>G*/ sin</b> δ,	<b>G*/ sin</b> δ,	<b>G*/ sin</b> δ,	-12°C	-12°C	Rotational, 135°C	Rotational, 135°C	
	64°C	64°C	19°C					
Neat PG 67-22	1.960	4.652	4987	225	0.303	516	738	
0.5% TDA	1.519	3.401	4594	223	0.316	482	685	
0.75% TDA	1.595	3.719	4395	160	0.364	483	661	
0.5% BHMT	2.012	4.251	4752	224	0.305	512	741	
0.75% BHMT	1.686	3.502	4595	223	0.309	487	719	
0.5% Amido	1.767	3.617	4905	218	0.304	496	710	
0.75% Amido	1.937	3.887	4226	218	0.318	503	695	

## Phase Angle

	$\delta$ , Original DSR 64°C	δ, RTFO DSR 64°C	δ, PAV DSR 19°C
Neat PG 67-22	87.4	84.1	41.7
0.5% TDA	87.8	85.1	43.5
0.75% TDA	87.9	85.4	43.9
0.5% BHMT	87.4	84.5	42.4
0.75% BHMT	87.7	84.6	42.4
0.5% Amido	87.6	84.7	42.7
0.75% Amido	87.7	85.1	43.8

## Calculated True Grade

	1		1		1	
	Original DSR	RTFO DSR	PAV DSR	Stiffness	m- value	True Grade
Neat PG 67-22	69.7	69.5	19.0	-14.0	-12.2	69.5-22.2
0.5% TDA	68.4	68.2	18.3	-14.9	-13.9	68.2-23.9
0.75% TDA	68.4	68.1	18.0	-15.9	-15.6	68.1-25.6
0.5% BHMT	69.5	69.1	18.6	-13.9	-12.4	69.1-22.4
0.75% BHMT	68.5	69.5	18.3	-14.9	-13.0	68.5-23.0
0.5% Amido	69.1	68.6	18.9	-14.1	-12.3	68.6-22.3
0.75% Amido	69.4	68.5	17.6	-15.1	-14.1	68.5-24.1

## Change in True Grade from Original Binder

		0			
	$\Delta$ Original DSR	$\Delta$ RTFO DSR	$\Delta$ PAV DSR	$\Delta$ Stiffness	$\Delta$ m- value
0.5% TDA	-1.3	-1.3	-0.7	-0.9	-1.7
0.75% TDA	-1.3	-1.4	-1.0	-1.9	-3.4
0.5% BHMT	-0.2	-0.4	-0.4	0.1	-0.2
0.75% BHMT	-1.2	0.0	-0.7	-0.9	-0.8
0.5% Amido	-0.6	-0.9	-0.1	-0.1	-0.1
0.75% Amido	-0.3	-1.0	-1.4	-1.1	-1.9

Note: TDA= Tallow diamine, BHMT= polyamine based bis-hexamethylene triamine, Amido= amidoamine.

The Mexican/Arabic blend PG 67-22 maintained a PG 64-22 for all dosage levels and anti-strip additives tested. The high temperature PG showed no increase and did not decrease more than 1.4°C. The reduction in RTFO DSR was greater than the reduction in the unmodified binder. The PAV DSR at 19°C was reduced in all anti-strip modified samples with a maximum change in performance grade of -1.4°C. The BBR stiffness at -12°C was reduced in all anti-strip modified samples. The change in BBR stiffness at -12°C ranged from 0.1 to -1.1°C. The m- value at -12°C was increased for all anti-strip modified samples. The m- value at -12°C did not increase more than 5% for all anti-strip modified samples, with the exception of 0.75% tallow diamine, which increased 20% and gave a change in m-value of -3.4°C. The rotational viscosity did not change more than 7.2% for any dosage of anti-strip additive, with the exception of tallow diamine, which decreased 10.4%. The trend was a decrease in viscosity, with the largest change in the tallow diamine modified samples.

## Alaskan North Slope PG 64-22

	Original DSR,	RTFO DSR,	PAV DSR,	Stiffness, MPa,	m- Value,	Original Viscosity,	Viscosity after RTFO,	
	<b>G*/ sin</b> δ,	<b>G*/ sin</b> δ,	G*/ sin δ,	-12°C	-12°C	Brookfield, 135°C	Brookfield, 135°C	
	64°C	64°C	22°C					
Neat PG 67-22	1.334	3.450	3951	195	0.309	358	538	
0.5% TDA	1.410	2.390	3801	194	0.315	336	478	
0.75% TDA	1.056	2.558	3027	181	0.325	330	468	
0.5% BHMT	1.159	3.141	4215	195	0.309	340	517	
0.75% BHMT	1.464	2.849	4065	196	0.313	330	503	
0.5% Amido	1.390	2.771	4232	194	0.312	341	506	
0.75% Amido	1.134	2.774	3669	163	0.328	338	498	

#### Phase Angle

	δ, Original DSR 64°C	δ, RTFO DSR 64°C	δ, PAV DSR 19°C
Neat PG 64-22	88.5	86.2	39.2
0.5% TDA	88.7	87.0	40.3
0.75% TDA	88.9	87.2	41.6
0.5% BHMT	88.7	86.3	39.5
0.75% BHMT	88.5	86.2	39.4
0.5% Amido	88.8	86.4	39.4
0.75% Amido	88.7	86.6	40.7

## Calculated True Grade

	Original DSR	RTFO DSR	PAV DSR	Stiffness	m- value	True Grade	
Neat PG 64-22	66.8	67.8	19.8	-14.9	-12.7	66.8-22.7	
0.5% TDA	67.1	65.0	19.5	-15.2	-13.3	65.0-23.3	
0.75% TDA	64.8	65.5	18.5	-15.5	-14.0	64.8-24.0	
0.5% BHMT	65.6	67.3	20.4	-15.1	-12.8	65.6-22.8	
0.75% BHMT	67.3	66.6	20.0	-15.0	-13.0	66.6-23.0	
0.5% Amido	67.1	66.4	20.4	-15.0	-13.0	66.4-23.0	
0.75% Amido	65.7	66.2	18.7	-16.4	-14.0	65.7-24.0	

## Change in True Grade from Original Binder

	$\Delta$ Original DSR	$\Delta$ RTFO DSR	$\Delta$ PAV DSR	$\Delta$ Stiffness	$\Delta$ m- value	
0.5% TDA	0.3	-2.8	-0.3	-0.3	-0.6	
0.75% TDA	-2.0	-2.3	-1.3	-0.6	-1.3	
0.5% BHMT	-1.2	-0.5	0.6	-0.2	-0.1	
0.75% BHMT	0.5	-1.2	0.2	-0.1	-0.3	
0.5% Amido	0.3	-1.4	0.6	-0.1	-0.3	
0.75% Amido	-1.1	-1.6	-1.1	-1.5	-1.3	

Note: TDA= Tallow diamine, BHMT= polyamine based on bis-hexamethylene triamine, Amido= amidoamine.

The Alaskan North Slope PG 64-22 maintained a PG 64-22 for all dosage levels and antistrip additives tested. The high temperature PG did not change more than 2°C. The trend for the high temperature PG varied for the original binder with a 1.1°C range, with the exception of 0.75% tallow diamine, which decreased 2°C. The change in RTFO DSR was more pronounced, with a -0.5 to -2.8 °C decrease. Again the tallow diamine decreased the most. The PAV DSR at 22°C showed various changes. The maximum change in PAV DSR PG for all anti-strip modified samples was -1.1°C. The BBR stiffness at -12°C was relatively unchanged in all anti-strip modified samples, with the exception of 0.75% BHMT based amine and 0.75% amidoamine. The change in BBR stiffness at  $-12^{\circ}$ C ranged from -0.1 to  $-1.5^{\circ}$ C. The m- value at  $-12^{\circ}$ C was increased for all anti-strip modified samples, with the exception of 0.5% BHMT based amine, which showed no change. The m- value at -12°C did not increase more than 2% for all antistrip modified samples, with the exception of 0.75% tallow diamine and 0.75% amidoamine, which increased 5% and 6% respectively. The greatest change in m- value at -12°C was -1.3°C. The rotational viscosity did not change more than 8% for any dosage of anti-strip additive, with the exception of tallow diamine, which decreased 11% and 13% after RTFO aging. The trend was a decrease in viscosity for all anti-strip modified samples in both the original and RTFO samples.

## Canadian PG 52-34

-							
	Original DSR,	RTFO DSR,	PAV DSR,	Stiffness, MPa,	m- Value,	Original Viscosity,	Viscosity after RTFO,
	<b>G*/ sin</b> δ,	<b>G*/ sin</b> δ,	G*/ sin δ,	-24°C	-24°C	Brookfield, 135°C	Brookfield, 135°C
	52°C	52°C	7°C				
Neat PG 67-22	1.235	3.330	4549	274	0.298	181	279
0.5% TDA	1.160	2.711	4300	236	0.334	181	249
0.75% TDA	1.126	2.448	3124	218	0.344	169	248
0.5% BHMT	1.262	3.419	2855	200	0.350	183	269
0.75% BHMT	1.221	2.992	2687	225	0.340	176	269
0.5% Amido	1.252	2.843	3757	235	0.336	178	265
0.75% Amido	1.315	2.755	3998	250	0.333	175	263

## Phase Angle

	δ, Original DSR 52°C	δ, RTFO DSR 52°C	δ, PAV DSR 7°C
Neat PG 52-34	88.0	84.4	46.7
0.5% TDA	88.3	85.2	44.6
0.75% TDA	87.9	85.1	45.4
0.5% BHMT	87.9	84.2	47.1
0.75% BHMT	87.8	84.0	48.5
0.5% Amido	87.9	84.7	45.1
0.75% Amido	88.2	85.9	47.2

## Calculated True Grade

	Original DSR	RTFO DSR	PAV DSR	Stiffness	m- value	True Grade
Neat PG 52-34	54.0	55.5	6.1	-25.0	-23.8	54.0-33.8
0.5% TDA	53.5	54.1	5.8	-24.9	-25.6	53.5-34.9
0.75% TDA	53.2	53.1	4.3	-25.0	-26.2	53.1-35.0
0.5% BHMT	54.3	55.7	1.8	-25.7	-26.8	54.3-35.7
0.75% BHMT	54.1	54.9	1.7	-25.1	-25.8	54.1-35.1
0.5% Amido	54.3	54.6	4.8	-24.8	-25.6	54.3-34.8
0.75% Amido	54.5	54.1	5.1	-24.7	-25.4	54.1-34.7

## Change in True Grade from Original Binder

	$\Delta$ Original DSR	$\Delta$ RTFO DSR	$\Delta$ PAV DSR	$\Delta$ Stiffness	$\Delta$ m- value
0.5% TDA	-0.5	-1.4	-0.3	0.1	-1.8
0.75% TDA	-0.8	-2.4	-1.8	0.0	-2.4
0.5% BHMT	0.3	0.2	-4.3	-0.7	-3.0
0.75% BHMT	0.1	-0.6	-4.4	-0.1	-2.0
0.5% Amido	0.3	-0.9	-1.3	0.2	-1.8
0.75% Amido	0.5	-1.4	-1.0	0.3	-1.6

Note: TDA= Tallow diamine, BHMT= polyamine based on bis-hexamethylene triamine, Amido= amidoamine.

The Canadian PG 52-34 maintained a PG 52-34 for all dosage levels and anti-strip additives tested. The high temperature PG did not change more than 1.1°C. The trend for the high temperature PG varied for the original binder with a 1.3°C range. The change in RTFO DSR was more pronounced, with a 0.2 to -2.4°C change. Higher dosages of each individual anti-strip additive showed a higher reduction in PG. The PAV DSR at 7°C was reduced for all anti-strip additives. The decrease was most pronounced in the BHMT based amine modified samples. The change in PAV DSR PG for all antistrip modified samples ranged from -0.3 to -4.3 °C. The BBR stiffness at -12 °C was decreased in all anti-strip modified samples. The change in stiffness ranged from 0.3 to – 0.7°C. The m- value at -12°C was increased for all anti-strip modified samples, with the exception of 0.5% BHMT based amine, which showed no change. The m- value was increased for all samples, with a change in PG of -1.6 to  $3.0^{\circ}$ C. The decrease in m-value ranged from 12 to 17%. The rotational viscosity did not change more than 5.7% for any dosage of anti-strip additive, with the exception of tallow diamine, which decreased 11% after RTFO aging. The trend was a decrease in viscosity for all anti-strip modified samples in both the original and RTFO samples, with the change in RTFO being greater than the change in the original.

#### Conclusions

All anti-strip modified binders retained their original performance grade according to AASHTO MP1 test criteria. The change in original DSR  $\delta$  was never more than 0.5° from the unmodified original DSR. The change in RTFO DSR  $\delta$  was never more than 1.5° from the unmodified RTFO DSR. The change in PAV DSR  $\delta$  was never more than 2.4° from the unmodified PAV DSR. The high temperature performance grade did not change more than 2.1°C for all anti-strip additives when compared to the original binder. The general trend was a larger reduction in RTFO DSR when compared to the original unmodified binder, with the exception of the Venezuelan binder, where the BHMT based amine and amidoamine showed an increase in RTFO DSR. The PAV DSR data varied, with the Canadian and Mexican/Arabic samples being reduced for all anti-strip additives. The Venezuelan sample showed an increase for most additives, and the North Slope samples showed a reduction for half of the modified samples and an increase for the remaining three. The BBR stiffness was reduced in all anti-strip modified samples. The change in BBR stiffness ranged from 0.4 to 27%, with the largest changes occurring in the Venezuelan and Canadian samples. The Mexican/Arabic and Alaskan North Slope samples showed little to no change in BBR stiffness, with the exception of 0.75% tallow diamine in the Mexican/Arabic sample and 0.75% tallow diamine and 0.75% amidoamine in the Alaskan North Slope samples, all three of which showed a decrease. The m- value was increased or unchanged for all modified asphalts, with the exception of the Venezuelan, which showed a 1.3% decrease in the 0.5% tallow diamine and 0.5%BHMT based amine modified samples. The greatest overall increase in m- value was observed in the Canadian anti-strip modified samples, with an increase of 12 to 17%. The trend for the original rotational viscosity was a decrease of up to 8%, with the

exception of the Venezuelan anti-strip modified samples. The Venezuelan modified samples showed an increase in original rotational viscosity for all anti-strip additives, with the exception of 0.75% BHMT based amine and 0.75% amidoamine, both of which increased less than 1.4% over the original unmodified binder. The trend for the RTFO rotational viscosity was a decrease of 3 to 13%, with the exception of the Venezuelan anti-strip modified samples, which showed an increase of approximately 4.5% for both BHMT based amine modified samples and no change for the amidoamine modified samples.

## Appendix