Report on comparison of Residue Recovery Methods and Rheological Testing of Latex and Polymer Modified Asphalt Emulsions

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This report compares the 177ºC distillation method with the BASF low temperature evaporation procedure[1] on emulsions formulated using latexes normally used for micro-surfacing emulsions. Laboratory produced emulsions and plant manufactured emulsions were both used in the evaluation process. Asphalt emulsions used for non micro-surfacing applications using latex and polymer modification are compared along with unmodified emulsions in these recovery techniques as well. The grades of asphalt used in the emulsion production ranged from a PG64-22 grade to a soft grade of a PG51-34, shown as a PGXX-34.

Various rheological tests were completed on the residues from each of the recovery methods to test for any differences there may be between the procedures. The rheological tests used were the original DSR procedure for bitumen and the MSCR (Multiple Stress Creep Recovery) procedure, which is designated as ASTM D7405. The ISSA Loaded Wheel Test (TB109 and TB147) was used as an attempt to verify the residue testing in a micro-surfacing mixture application.

Recovery methods

The 177ºC distillation procedure is a modification of the ASTM D6997 procedure by utilizing a 20 minute hold at 177ºC. The modification to the procedure is one that many agencies have incorporated based on input from emulsion and polymer suppliers. The temperature reduction is due to the degradation of many polymers used for asphalt modification, and latexes used in asphalt emulsion production, at the original 260ºC distillation temperature. After the distillation is completed, the residue can be poured into the molds for further testing.

The BASF evaporation procedure utilizes a silicone mat to hold 60 grams of emulsion which is a spread ratio of 1.9 kg/m^2. The emulsion is placed in a 25ºC oven for 24 hours followed by a 60ºC oven cure for 24 hours. The 25ºC oven time is to “slow cure” the emulsion to not allow the skin formation to trap moisture before placing in the 60ºC oven for final water evaporation. The emulsion can be peeled off of the mats after the curing time to be tested as required. A wooden tongue depressor was used to scrape the residue off of the mat, and nitrile gloves were used to take pieces of the residue from the sample to make specimens for rheological testing. The residue was not heated for pouring the rheological test specimens and it should be noted that heating may affect the residue testing with some emulsifiers and polymers. This evaporation procedure is very close to the EN 13074 European procedure and is currently being balloted for ASTM approval.

The reason for comparing these residue recovery methods is the temperature difference between the methods. The distillation procedure uses a much higher temperature than the emulsion applications see during application and use. The BASF evaporation procedure is much closer to the road temperatures seen during the curing process for emulsion applications.

Micro-surfacing Emulsion Test Results

The Table below shows the distillation test results of lab run emulsions that are typical of micro-surfacing grades. The PG64-22 grade is typical of micro-surfacing emulsion manufacture, while

the PG58-28 is used from the same refinery for comparison. Latex A and latex B are of two different polymer types, both of which have been used for micro-surfacing application.

	Original DSR Testing on Residue from Distillation (350ºF/177ºC) @ 10rad/sec @ test temperature										
		58ºC		64ºC		70ºC		76ºC		82ºC	
Emulsion	% Latex	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta
PG58-28	3.75A	5.163	69.79	2.739	72.87	1.504	75.20	0.8567	76.70		
PG64-22	3.75A	8.025	67.78	4.149	72.07	2.218	75.01	1.233	76.92	0.716	77.94
PG58-28	3.75B	5.891	69.00	3.223	69.53	1.893	69.48	1.178	68.88	0.7689	67.71
PG64-22	3.75B	9.050	70.09	4.764	70.80	2.675	70.92	1.575	70.45	0.9921	69.27

The next Table shows the BASF evaporation test results of the lab run emulsions.

	Original DSR Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour) @ 10rad/sec @ test temperature										
		58ºC		64ºC		70ºC		76ºC		82ºC	
Emulsion	% Latex	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta
PG58-28	3.75A	10.060	70.42	5.147	72.61	2.706	74.39	1.483	75.46	0.8531	75.65
PG64-22	3.75A	14.640	69.52	7.29	71.32	3.738	73.19	2.013	74.76	1.135	75.64
PG58-28	3.75B	10.280	71.57	5.296	73.52	2.835	74.83	1.592	75.43	0.9392	75.27
PG64-22	3.75B	18.060	71.61	8.903	73.80	4.570	75.44	2.455	76.29	1.400	76.38

The Evaporation procedure gives higher overall values for the G*/sin delta than the distillation procedure, which may be an indication of less degradation of the polymer. An interesting observation between latex A and B, is that at the higher residue recovery temperatures from the distillation procedure the delta values are lower in latex B than those from the evaporation procedure. This may be an indication of ”vulcanization” being done to latex B at the distillation temperature. Since the delta change is not happening at the evaporation temperatures, the distillation procedure may not be giving an accurate value for the residue properties at normal field conditions.

To verify the lab run results on the original DSR testing, four plant run micro-surfacing emulsions were tested. The Table below shows the distillation results.

	Original DSR Testing on Residue from Distillation (350ºF/177ºC) @ 10rad/sec @ test temperature										
		58ºC		64ºC		70ºC		76ºC		82ºC	
Emulsion	% Latex	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta
Plant A	3.6	9.118	69.35	4.695	69.32	2.5480	69.88	1.442	70.94	0.8548	71.76
Plant B	3.9	9.394	68.05	4.986	68.14	2.781	68.75	1.617	69.81	0.975	70.78
Plant C	4.2	11.000	66.79	5.937	67.38	3.357	68.23	2.007	69.00	1.262	69.45
Plant D	3.8	12.240	67.87	6.347	68.18	3.472	68.56	1.995	68.90	1.206	68.94

The next Table shows the evaporation results of the plant run micro-surfacing emulsions.

	Original DSR Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour) @ 10rad/sec @ test temperature										
		58ºC		64ºC		70ºC		76ºC		82ºC	
Emulsion	% Latex	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta
Plant A	3.6	16.450	69.36	8.395	70.35	4.3710	71.8	2.351	73.14	1.325	73.76
Plant B	3.9	18.370	66.62	9.571	68.13	5.108	69.63	2.842	70.3	1.66	69.68
Plant C	4.2	18.400	66.16	9.6	68.11	5.141	69.88	2.857	70.80	1.676	70.47
Plant D	3.8	19.090	65.54	10.01	67.12	5.346	68.69	2.959	69.5	1.726	69.08

The results are comparable to the PG64-22 based emulsions using latex A in the lab run emulsions used for the initial evaluation.

The next table shows the average percent recovery rheological results at 0.1 and 3.2 kPa shear stress levels using the MSCR (Multiple Stress Creep Recovery) procedure on residue from evaporation. The procedure was followed as indicated by the ASTM D7405 procedure, but the residue was not run through the rolling thin film oven testing. This is due to the lack of hot mix plant aging for these emulsions.

Multiple Stress Creep Recovery Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour)							
		58ºC		64ºC		70ºC	
Emulsion	% Latex	100Pa	3200Pa	100Pa	3200Pa	100Pa	3200Pa
PG58-28 LR	3.75A	**45.97**	**34.82**	**53.14**	**31.74**		
PG64-22 LR	3.75A			**55.27**	**33.46**	**53.36**	**26.74**
PG58-28 LR	3.75B	**52.00**	**26.72**	**60.29**	**24.00**		
PG64-22 LR	3.75B			**58.20**	**23.78**	**64.35**	**19.21**

The MSCR testing is proposed to be run on the warm temperature for the climate area based on the LTPP Bind weather station data. The PG58-28 base was tested at 58ºC and 64ºC, while the PG64-22 was tested at 64ºC and 70ºC. The 3200 Pa values are those that are suggested to be indicative of a rheological comparison to the Elastic Recovery test method. The latex A gives a much greater % recovery regardless of the base stock or temperature tested. This type of rheological testing has been said to be indicative of fatigue in polymer testing.

The next table shows the J_{nr} (non-recoverable creep compliance) percent difference between the 0.1 and 3.2kPa shear stress levels.

Multiple Stress Creep Recovery Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour)							
		52ºC	58ºC	64ºC	70ºC		
Emulsion	% Latex	Jnr diff.	Jnr diff.	Jnr diff.	Jnr diff.	Comments	
PG58-28 LR	3.75A		25.60	44.28			
PG64-22 LR	3.75A			40.55	46.51		
PG58-28 LR	3.75B		40.53	56.04			
PG64-22 LR	3.75B			51.39	63.74		

This table shows there is a greater percent difference with each base and at each temperature between the 0.1 and 3.2 kPa shear stress levels using polymer B. This pattern may be used to show differences in polymer types. This is not a calculation method that has been proposed in any literature, but one that is shown for informational purposes only.

Recently the J_{nr} at the reciprocal kPa level has been promoted as a possible rutting test correlation for various traffic levels[2]. This J_{nr} value (non-recoverable creep compliance) is determined by dividing the non-recoverable shear strain by the applied shear stress on the RTFO residue. The values recommended for possible specification purposes are as follows:

Standard Traffic (S)	$J_{nr} <= 4\ kPa^{-1}$
Heavy Traffic (H)	$J_{nr} <= 2\ kPa^{-1}$
Very Heavy Traffic (V)	$J_{nr} <= 1\ kPa^{-1}$

These are to be tested at the environmental temperature rather than a grade bumped temperature for traffic. The following table gives the J_{nr} values for the 0.1 and 3.2 kPa shear stress levels for the same emulsions tested previously. The residue was not aged in the RTFO due to the lack of that aging in the emulsion applications.

Multiple Stress Creep Recovery Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour)							
		58ºC		64ºC		70ºC	
		Jnr kPa-1		**Jnr kPa -1**		**Jnr kPa -1**	
Emulsion	% Latex	.1 kPa	3.2kPa	.1 kPa	3.2kPa	.1 kPa	3.2kPa
PG58-28 LR	3.75A	**0.433**	**0.582**	**0.709**	**1.272**		
PG64-22 LR	3.75A			**0.392**	**0.660**	**0.813**	**1.520**
PG58-28 LR	3.75B	**0.352**	**0.591**	**0.608**	**1.383**		
PG64-22 LR	3.75B			**0.453**	**0.933**	**0.794**	**2.190**

To verify the MSCR testing on the lab run emulsions, the plant run emulsions used in the original DSR tests were evaluated using residue from the BASF evaporation procedure. The J_{nr} values for the 0.1 and 3.2 kPa shear stress levels are tabulated below for this evaluation.

Multiple Stress Creep Recovery Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour)					
		64ºC		70ºC	
		Jnr kPa -1		**Jnr kPa -1**	
Emulsion	% Latex	.1 kPa	3.2kPa	.1 kPa	3.2kPa
Plant A	3.6A	**0.456**	**0.645**	**0.921**	**1.669**
Plant B	3.9A	**0.268**	**0.464**	**0.387**	**1.160**
Plant C	4.2A	**0.238**	**0.382**	**0.372**	**0.914**
Plant D	3.8A	**0.230**	**0.357**	**0.473**	**1.026**
PG64-22 LR	3.75A	**0.392**	**0.660**	**0.813**	**1.520**

The lab run PG64-22 based emulsion results were added to the Table for ease of comparison. The results show good consistency between plant run emulsions and the lab run emulsion. It should be noted that the J_{nr} at the 3.2 kPa stress levels are well below the 1.0 specification level for very heavy traffic. Micro-surfacing has been used in rut fill applications very successfully and this shows some good evidence of that success.

Micro-surfacing Mixture Testing Verification

The data in the MSCR testing of the emulsion residue identifies a possible potential to show differences in polymer type as it is used in micro-surfacing. The Loaded Wheel Test (ISSA TB 109 and TB 147) has been used to show differences in slurry seal and micro-surfacing materials. Mixtures were made using emulsions above that were manufactured using the PG58-28 and PG64-22 asphalts and also latex A and Latex B from the residue testing completed previously. The aggregate used in the mixture was a Guernsey, Wyoming aggregate. Two specimens of each of the materials were made and the results averaged to give the data below.

	Vertical Displacement	Lateral Displacement
PG64-22 and 3.75% Latex A	**9.4%**	**3.7%**

PG58-28 and 3.75% Latex A	**9.7%**	**4.7%**
PG64-22 and 3.75% Latex B	**9.7%**	**2.9%**
PG58-28 and 3.75% Latex B	**11.7%**	**6.6%**

The PG64-22 based emulsions with both latexes give very similar values. The interesting results are with the PG58-28 based emulsions. The latex A results are similar, whether the base is a PG64-22 or a PG58-28, while the latex B based emulsions had a noticeable increase in the displacements when the softer base was used in the mixture. This is only one set of test results, but is something that should be further evaluated.

MSCR Testing of Emulsion Bases for non micro-surfacing emulsions

For comparison purposes, the Table below shows the % recovery MSCR results of the emulsion bases used in the emulsion production without emulsification or polymer modification. There is also a test result for two typical plant manufactured modified asphalt emulsion bases using the same polymer as comparison. The PG58-28 results are included because that is the likely grade used as the base to modify. A PG64-22 is also included as comparison.

Multiple Stress Creep Recovery Testing on Emulsion Base Bitumens							
		58ºC		64ºC		70ºC	
Emulsion	% Polymer	100Pa	3200Pa	100Pa	3200Pa	100Pa	3200Pa
PG58-28	0.00	**2.338**	**0.2606**				
PG64-22	0.00			**1.732**	**0.21**		
PM Base2	3.00	**55.480**	**39.9**	**52.38**	**24.90**		
PM Base1	3.00	**53.190**	**39.38**	**49.74**	**28.97**		

It is obvious that the polymer modification is identifiable by the MSCR test and that the creep recovery for unmodified asphalts near the high PG temperature is near zero as would be expected.

A CRS-2P was manufactured with one of the modified asphalt emulsion base stocks (PMB2) with a standard rapid setting emulsifier. The results with the PG58-28 based emulsions manufactured with latex A and latex B are included for comparison. The comparison of the evaporation and distillation techniques can be seen for these emulsions in the following table for the MSCR test.

Multiple Stress Creep Recovery Testing on Residue from Evaporation or Distillation						
		58ºC		64ºC		Method
Emulsion	% Latex	100Pa	3200Pa	100Pa	3200Pa	
PG58-28 LR	3.75A	**45.970**	**34.82**	**53.14**	**31.74**	Evaporation (BASF)
PG58-28 LR	3.75B	**52.000**	**26.72**	**60.29**	**24.00**	Evaporation (BASF)
CRS-2P (PMB2)	3.0P	**51.280**	**44.25**	**49.99**	**34.01**	Evaporation (BASF)
CRS-2P (PMB2)	3.0P	**50.410**	**35.23**	**51.82**	**21.01**	Distillation (177C)

Regardless of the polymer used, it is easy to identify the polymer in the residue shown as the percent recovery from the MSCR test.

The next two tables show the J_{nr} test results for two plant manufactured CRS-2P and two plant manufactured HFRS-2P emulsions using the evaporative and distillation recovery techniques. These emulsions are all made using a polymer modified asphalt as a base stock and are shown to compare the emulsion grades made with similar polymers.

Multiple Stress Creep Recovery Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour)							
		58ºC		64ºC		70ºC	
		Jnr kPa-1		**Jnr kPa -1**		**Jnr kPa -1**	
Emulsion	% L/P	.1 kPa	3.2kPa	.1 kPa	3.2kPa	.1 kPa	3.2kPa
CRS-2P (PMB2)	3.0P	**0.611**	**0.763**	**1.315**	**2.016**		
CRS-2P (CO)	3.0P	**0.789**	**1.166**	**1.920**	**3.072**		
HFRS-2P (ATX)	3.0P	**1.027**	**1.640**	**1.768**	**3.409**		
HFRS-2P (CO)	3.0P	**4.489**	**6.595**				

Multiple Stress Creep Recovery Testing on Residue from Distillation (177ºC minute hold)							
		58ºC		64ºC		70ºC	
		Jnr kPa-1		**Jnr kPa -1**		**Jnr kPa -1**	
Emulsion	% L/P	.1 kPa	3.2kPa	.1 kPa	3.2kPa	.1 kPa	3.2kPa
CRS-2P (PMB2)	3.0P	**1.202**	**1.761**	**2.330**	**4.562**		
CRS-2P (CO)	3.0P	**1.613**	**2.396**	**4.056**	**6.248**		
HFRS-2P (ATX)	3.0P	**1.564**	**3.236**	**3.480**	**8.243**		
HFRS-2P (CO)	3.0P	**4.397**	**6.585**				

The CRS-2P emulsion results are fairly similar in results while there is a significant difference between the HFRS-2P emulsions due to the specifications that these are designed to meet. The distillation technique does seem to have a negative effect on the J_{nr} results for both of the emulsions. The HFRS-2P emulsions have a much larger difference in J_{nr} between the stress levels. This is likely due to the effect of the "gelling" that happens at higher temperatures in the distillation procedure with the emulsifier used for production.

Asphalt Base Testing (Recovery Technique Comparison)

There have been questions about the differences that the recovery techniques may have on the residue testing. To show differences that may occur, the following information is provided on the DSR testing of the unmodified base stock and emulsion residues recovered from the evaporation and modified distillation techniques.

The following Table shows the Original DSR results of asphalt base stocks used for emulsion production that follows

		Original DSR Testing on Base Asphalt							
		52ºC		58ºC		64ºC		70ºC	
Asphalt Grade	% L/P	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta
PGXX-34	0	0.9009	87.775						
PG58-28	0			1.501	86.82	0.7054	88.05		
PG64-22	0			3.1355	85.515	1.419	86.955	0.6913	88.025

Emulsions were manufactured using the emulsion bases above and the results for the original DSR are shown in the Table below for the distillation and evaporation recovery methods.

	Original DSR Testing on Residue from Distillation (350ºF/177ºC) @ 10rad/sec @ test temperature										
		52ºC		58ºC		64ºC		70ºC		76ºC	
Emulsion	% Latex	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta
PGXX-34 base	**0.0**	**0.95985**	**87.39**								
PG58-28 base	**0.0**			**1.5755**	**85.88**	**0.7777**	**86.49**				
PG64-22 base	**0.0**			**3.6575**	**84.22**	**1.6635**	**85.78**	**0.80495**	**86.93**		

	Original DSR Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour) @ 10rad/sec @ test temperature										
		52ºC		58ºC		64ºC		70ºC		76ºC	
Emulsion	% L/P	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta	g*/sin delta	delta
PGXX-34 base	**0.0**	**2.0485**	**84.74**	**0.93585**	**86.14**						
PG58-28 base	**0.0**			**2.408**	**84.92**	**1.119**	**86.45**	**0.546**	**87.55**		
PG64-22 base	**0.0**			**6.4015**	**82.25**	**2.854**	**84.40**	**1.324**	**86.16**	**0.6475**	**87.49**

It can be seen from these results that the distillation procedure gives the closest results that are comparable to the original base stock used. The effect of the type of emulsifier on the evaporative technique and how it is affected in the distillation is likely the difference in the results.

The following tables show the MSCR testing results, J_{nr} (0.1 and 3.2 kPa shear stress levels), using two polymer types using the evaporative and distillation recovery techniques. The base asphalts used without polymer above were used in the manufacture of these emulsions.

Multiple Stress Creep Recovery Testing on Residue from Evaporation (25ºC 24 hour & 60ºC 24 hour)							
		58ºC		64ºC		70ºC	
		Jnr kPa-1		**Jnr kPa -1**		**Jnr kPa -1**	
Emulsion	% Latex	.1 kPa	3.2kPa	.1 kPa	3.2kPa	.1 kPa	3.2kPa
PGXX-34 LR	3.75A	**0.615**	**1.457**				
PG58-28 LR	3.75A	**0.568**	**0.892**	**1.110**	**2.298**		
PG58-28 LR	3.75C	**0.6661**	**1.093**	**1.133**	**2.480**		
PG64-22 LR	3.75A			**0.686**	**0.980**	**1.55**	**2.417**
PG64-22 LR	3.75C			**1.417**	**3.099**	**0.774**	**1.302**

Multiple Stress Creep Recovery Testing on Residue from Distillation (177ºC minute hold)							
		58ºC		64ºC		70ºC	
		Jnr kPa-1		**Jnr kPa -1**		**Jnr kPa -1**	
Emulsion	% Latex	.1 kPa	3.2kPa	.1 kPa	3.2kPa	.1 kPa	3.2kPa
PGXX-34 LR	3.75A	**0.645**	**2.318**	**1.143**	**5.110**		
PG58-28 LR	3.75A	**0.847**	**1.505**	**1.600**	**3.523**		
PG58-28 LR	3.75C	**0.67**	**1.266**	**1.131**	**2.692**		
PG64-22 LR	3.75A			**1.098**	**1.874**	**2.08**	**4.321**
PG64-22 LR	3.75C			**0.762**	**1.323**	**1.340**	**3.018**

The distillation residue gives lower values with polymer C than polymer A, while the evaporation method gives slightly higher results. This may be due to modification of the polymer in the temperature of the distillation.

Conclusions

The BASF residue recovery technique does show a difference in the residue properties of the various asphalt base stocks used as well as possible polymer differentiation. The rheological

techniques described in this report can be used on emulsion residues and may be used to identify polymer differences in type and quantity for various emulsion applications. These differences are driven by the type of asphalt base stock used and test values are not an indication of polymer/latex quantity unless similar asphalt bases are compared.

The MSCR test has great potential to be used in the identification of appropriate polymers used in the micro-surfacing emulsion manufacture. Further testing should be done on mixture analysis to verify the residue test results will show performance results that are required in the field. The % recovery at 3.2kPa or the J_{nr} at the required stress levels for the traffic conditions both show great results with emulsion residues for micro-surfacing or other emulsion applications.

Further testing should be done to identify properties of modified asphalt residues used in other applications such as seal coats and bond coats. The appropriate specifications for recovered residues for various applications need to be considered during the testing.

References

1. Takamura, K, Comparisons of Emulsion Residues Recovered by the Forced Air Flow and RTFO Drying, Presentation to the AEMA-ARRA-ISSA joint meeting, March 2000.
2. Anderson, M, "A New High Temperature Specification Parameter for Asphalt Binders", Asphalt Magazine – Summer 2008.