

CHEMICAL ANALYSES OF SEALER - REJUVENATORS

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2004 SYMPOSIUM ON ADDITIVES IN ROADWAY ASPHALTS

Cheyenne, Wyoming

June 24, 2004

SEALER – REJUVENATORS WHAT ARE THEY?

- Spray-applied Products to Seal Pavement Surface or Restore Pavement Properties.
- Applied as Maintenance Treatments to Preserve Pavement Performance.
- Generally Applied at about 0.10 gal/yd².



CHEMICAL ANALYSES OF SEALER - REJUVENATORS

Background

- Chemical Analyses Have Been Used to Differentiate Asphalts.
- Variability of Asphalt Composition Has Been Used to Explain Differences in Physical Properties.
 - Amount of Crystallizable Fraction is Directly Related to the Low-Temperature Specification Value.
 - Asphaltene Content and Compatibility Related to Temperature Susceptibility.

CHEMICAL ANALYSES OF SEALER - REJUVENATORS

WORK PLAN

- Chemical Similarity of Products.
- Determination of Chemical Compatibility.
- Oxidation and Aging Propensity.
- Analysis for Surface-Active Agents.
- Investigation of the NMR “Mouse”.

CHEMICAL SIMILARITY OF PRODUCTS

What are the Goals of Chemical Analyses?

- Determine the Consistency of Products Placed in Different Locations.
- Determine the Chemical Similarities Between Different Products.
- Quantify the Chemical Characteristics Important to Performance.

CHEMICAL SIMILARITY OF PRODUCTS

TECHNIQUES

- Percent Residue
- Sulfur Content
- Non-Aqueous Potentiometric Titration (NAPT)
- Infrared Analysis
- NMR Analysis

PERCENT RESIDUE

- Glass Pan with a Film Thickness of about 1/32" and 1/64".
- Oven Heating at 95°C for 1.5 hr with Argon Gas Sweep.
- Weight of Pan Before and After.

PERCENT RESIDUE



PERCENT RESIDUE

Salton Sea Site

	Reclamite %	PASS %	CQS-1h %	SS-1h %
Concentrate	62.75	71.12	53.25	60.00
Mixture	47.75	33.50	41.50	46.13

PERCENT RESIDUE

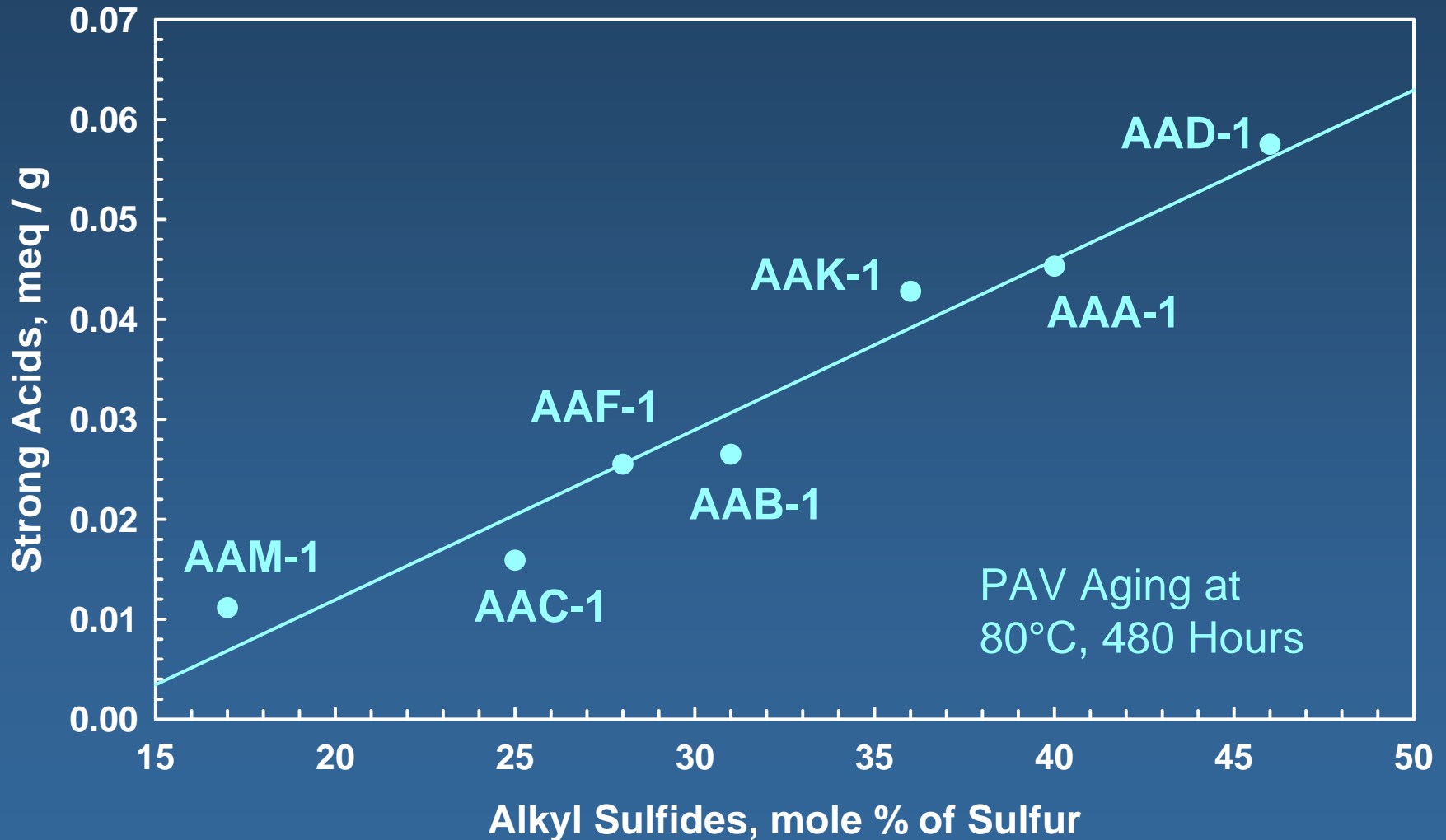
Winslow Site

	Reclamite %	PASS %	ERA-1 %	ERA-25 %	CSS-1h %
Concentrate	67.75	76.50	67.25	NS	NS
Mixture	32.00	27.75	34.87	28.50	28.63

SULFUR CONTENT

- Sulfur is Easily Oxidized.
- Highly Oxidized Sulfur Forms Sulfonic and Sulfenic Acids Which Are Strongly Acidic.
- Strong Acids Containing Sulfur Are Related to Soaps and May Be Displaced By Water.
- Sulfur Analyzed using ASTM Method D 1552, High-Temperature Combustion.

SULFUR CONTENT RELATED TO FORMATION OF STRONG ACIDS DURING AGING



SULFUR CONTENT

Salton Sea Site

	Reclamite	PASS	CQS-1h	SS-1h
Concentrate	1.03	4.33	4.32	2.86
Mixture	1.08	3.82	4.33	4.21

SULFUR CONTENT

Winslow Site

	Reclamite	PASS	ERA-1	ERA-25	CSS-1h
Concentrate	1.33	1.71	1.49	NS	NS
Mixture	1.45	2.22	2.78	2.48	0.66

SULFUR CONTENT

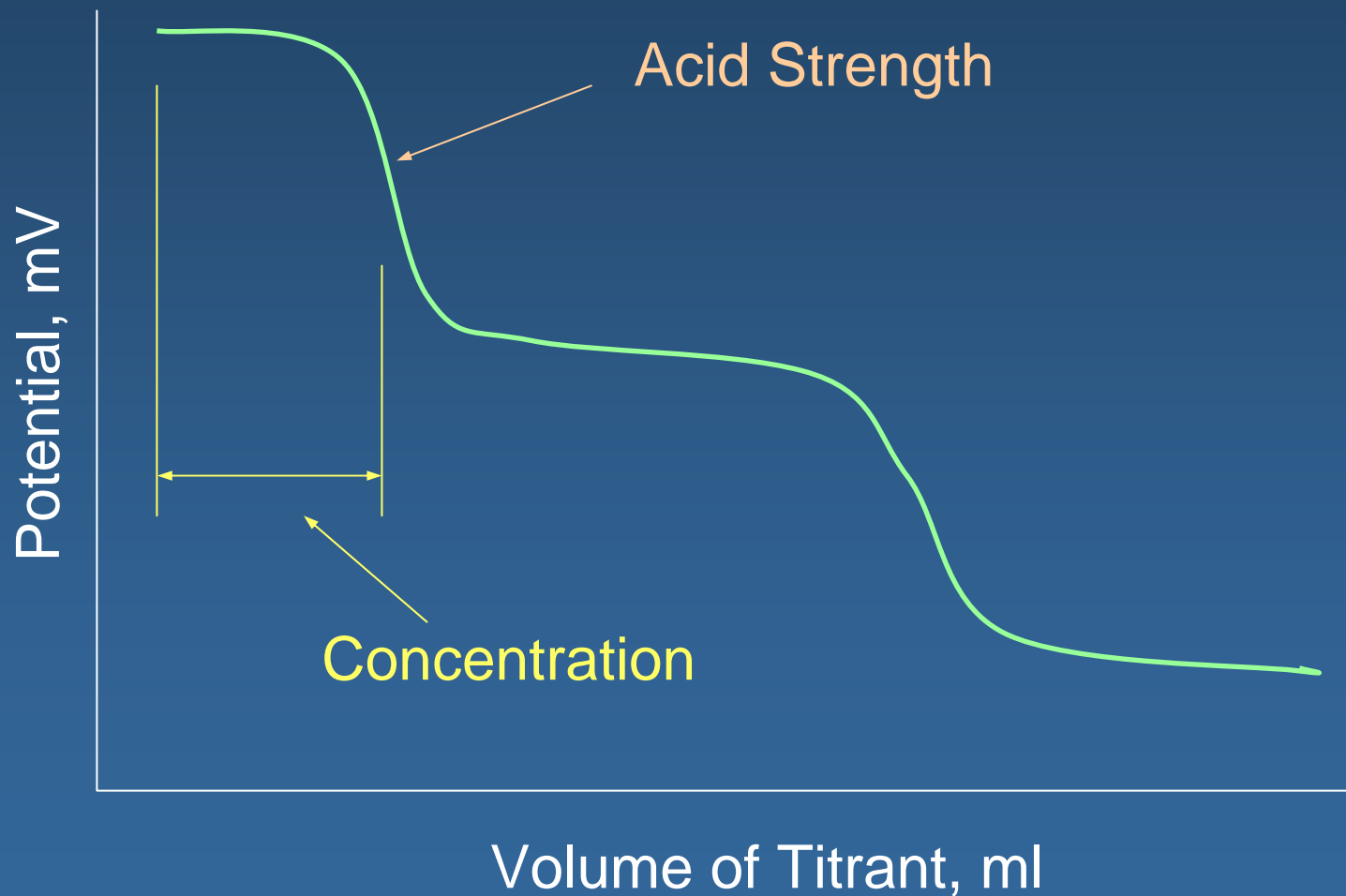
Site	Reclamite	PASS	GSB-B	CQS-1h	CSS-1h
Salton Sea	1.08	3.82	-	4.33	4.21*
Winslow	1.45	2.22			0.66
Minnesota	1.04	3.28	2.54	-	4.15

* SS-1h

NON-AQUEOUS POTENTIOMETRIC TITRATION

- Used to Measure the Acid Strengths.
- Differentiates Between Strong Sulfur Acids and Weaker Carboxylic Acids.
- Also Quantifies the Amount of Acid Present or Formed During Aging.

NON-AQUEOUS POTENTIOMETRIC TITRATION CURVE



NON-AQUEOUS POTENTIOMETRIC TITRATION

Salton Sea Site

	Reclamite	PASS	CQS-1h	SS-1h
HNP #1	-335 mv	-330 mv	-312 mv	-307 mv
Concentration	0.056meq	0.051meq	0.243meq	0.005meq
HNP #2	-75 mv	-75 mv	50 mv	
Concentration	0.003meq	0.0025meq	0.008 meq	

INFRARED ANALYSIS AND NUCLEAR MAGNETIC RESONANCE

- Used to Profile or “Fingerprint” the Products.
- Comparison Will Be Made Between the Same Products Used in Different States. (Is “Brand X” in California the Same As “Brand X” in Illinois.
- Used to Quantitate Chemical Oxidation, Specifically, Oxygen-Containing Molecules.

ASPHALT COMPATIBILITY

- Asphalt Is A Colloidal Mixture.
- Consists of Asphaltenes (Particles) Dissolved in Maltenes (Solvent).
- Compatibility Can Be Affected When Two Different Materials Are Mixed.
- Incompatibility May Explain Some Failures.

DETERMINATION OF CHEMICAL COMPATIBILITY

TECHNIQUE

- Automated Flocculation Titrimetry.
 - More Precise Version of the Heithaus Method.
 - Three Parameters Measured.
 - p_a , p_o , and P.

COMPATIBILITY VALUES OBTAINED BY AFT ON EXTRACTED CORE SLICES

Salton Sea Site

	Reclamite	PASS	CQS-1h	SS-1h	Control
<u>0.08 gal/yd²</u>					
P, (state of peptization)	2.275	2.479	2.595	2.645	2.599
<u>0.12 gal/yd²</u>					
P, (state of peptization)	2.664	3.227	2.655	2.527	2.599

COMPATIBILITY VALUES OBTAINED BY AFT ON EXTRACTED CORE SLICES

Winslow Site

	Reclamite	PASS	ERA-1	ERA-25	CSS-1h	Control
P (state of peptization)	6.662	3.593	3.406	7.689	4.656	3.991

OXIDATION AND AGING PROPENSITY

Aging Prediction

Performance Assessment

OXIDATION AND AGING PROPENSITY

Performance Assessment

- Determine If Treatments Affect Initial Rheological Properties.
 - Compare Rheological Properties of Untreated Sections With Treated Sections.
- Monitor Rheological and Chemical Properties With Time In Service.
 - Compare Rheological Properties of Untreated Sections With Treated Sections.
 - Compare Oxidation of Untreated and Treated Sections Using Infrared Spectroscopy.

RHEOLOGICAL ANALYSIS OF EXTRACTED CORE SLICES

Winslow Site

$G^* \times 10^6$, Pa, 10 radians/second, 25°C

Sample	Reclamite	PASS	ERA-1	ERA-25	CSS-1h	Control
Slice 1	1.74	7.26	4.05	1.98	11.4	9.08
Slice 2	2.43	2.83	4.45	2.53	6.94	5.42

RHEOLOGICAL ANALYSIS OF EXTRACTED CORE SLICES

Winslow Site

G^* , Pa, 10 radians/second, 64°C

Sample	Reclamite	PASS	ERA-1	ERA-25	CSS-1h	Control
Slice 1	4780	19200	13100	7370	27800	26400
Slice 2	7730	9020	12300	7230	18200	15500

INFRARED ANALYSIS OF EXTRACTED CORE SLICES

Winslow Site

Carbonyl Content, au

Sample	Reclamite	PASS	ERA-1	ERA-25	CSS-1h	Control
Slice 1	0.203	0.232	0.242	0.211	0.237	0.254
Slice 2	0.195	0.228	0.225	0.210	0.244	0.242

RHEOLOGICAL ANALYSIS OF EXTRACTED CORE SLICES

Salton Sea Site

$G^* \times 10^6$, Pa, 10 radians/second, 25°C

Treatment Rate	Reclamite	PASS	CQS-1h	SS-1h	Control
0.08 gal/yd ²	1.46	2.58	2.83	3.10	6.49
0.12 gal/yd ²	1.60	2.26	3.09	9.14	

$G^* \times 10^3$, Pa, 10 radians/second, 64°C

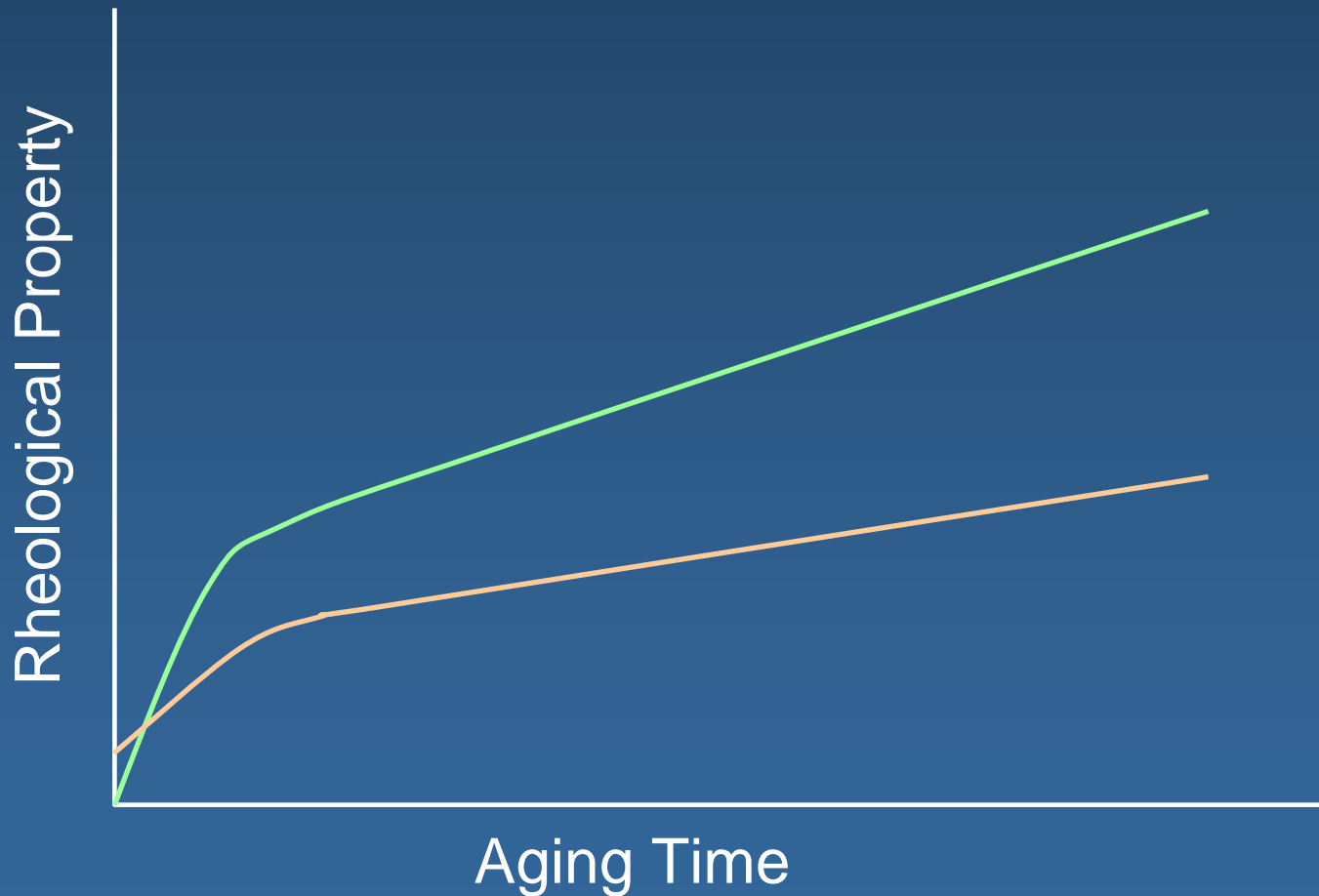
Treatment Rate	Reclamite	PASS	CQS-1h	SS-1h	Control
0.08 gal/yd ²	5.93	10.7	12.4	17.4	25.5
0.12 gal/yd ²	5.74	18.9	52.3	25.9	

OXIDATION AND AGING PROPENSITY

Aging Prediction

- Age Untreated and Treated Samples Using PAV at a Temperature of 60°C.
- Higher Temperature Climates Will Use 70°C PAV Aging.
- Measure Rheological Properties at Mid and High Temperature Using DSR.
- Measure Oxygen-Containing Functional Groups Using Infrared Spectroscopy.
- Compare Aging From PAV With Actual Field Aging.

OXIDATION AND AGING PROPENSITY



RHEOLOGICAL ANALYSIS OF EXTRACTED CORE SLICES AFTER PAV AGING

Winslow Site

G^* , MPa, 10 radians/second, 25°C

Sample	Reclamite	PASS	ERA-1	ERA-25	CSS-1h	Control
Slice 1	1.74	7.26	4.05	1.98	11.4	9.08
PAV #1	2.71	11.2	7.16	4.18	16.3	13.9
Change	1.56	1.54	1.77	2.11	1.43	1.53

PAV Aging at 70°C for 144 hours

RHEOLOGICAL ANALYSIS OF EXTRACTED CORE SLICES AFTER PAV AGING

Winslow Site

G^* , kPa, 10 radians/second, 64°C

Sample	Reclamite	PASS	ERA-1	ERA-25	CSS-1h	Control
Slice 1	4.78	19.2	13.1	7.37	27.8	26.4
PAV #1	14.6	57.6	38.2	29.1	77.7	78.0
Change	3.05	3.00	2.92	3.95	2.79	2.95

PAV Aging at 70°C for 144 hours

INFRARED ANALYSIS OF EXTRACTED CORE SLICES AFTER PAV AGING

Winslow Site

Carbonyl Content, au

Sample	Reclamite	PASS	ERA-1	ERA-25	CSS-1h	Control
Slice 1	0.203	0.232	0.242	0.211	0.237	0.254
PAV #1	0.279	0.307	0.364	0.301	0.302	0.315

ANALYSIS FOR SURFACE-ACTIVE AGENTS

- Surface-Active Materials Formed During Asphalt Aging Form Oil-In-Water Emulsions.
- Investigate If Surface-Active Materials Form In Aged Samples After Treatment Using Aqueous Extraction.
- Determine If Strong Acids Have Been Formed Using pH and Quantify With NAFT.

INVESTIGATION OF THE NMR “MOUSE”

THE BRUKER MINISPEC MOUSE



INVESTIGATION OF THE NMR “MOUSE”

- Use On Sites Where Original Asphalts Are Available.
- Determine If Significant Aging Parameters Can Be Identified Using Lab NMR.
- Determine Aging Parameters Using the “Mouse”.
- Correlate Lab NMR With “Mouse”.
- If Successful, This Device Could Help Determine When To Apply A Surface Treatment.

SUMMARY

- Chemical Evaluation Techniques Developed for Asphalts Are Being Applied To Samples After Surface Treatment.
- The Techniques Selected Are Those That Have The Most Promise.
- The Goal Of The Project Is To Determine If Chemical Techniques Can Predict Performance Or Potential Failures.

