THE FOLLOWING GROUP OF SLIDES WAS PRESENTED AT THE ROCKY MOUNTAIN ASPHALT USER PRODUCER GROUP MEETING ON MARCH 3, 2004. SLIDES WHICH HAVE A RED \( N \) IN THE UPPER LEFT HAND CORNER HAVE NOTES WRITTEN FOR THEM TO DISCUSS THE DATA PRESENTED. YOU SHOULD READ THESE NOTES FOR THE DETAILS BEHIND THE DATA.
ON MARCH 3, 2004 SIX INDIVIDUALS PRESENTED DISCUSSIONS ON THE USE AND IMPACT OF ACID MODIFICATION IN ASPHALT AT THE ROCKY MOUNTAIN ASPHALT USER PRODUCER GROUP MEETING.

IN ORDER OF PRESENTATION THE WERE

DAVE JONES-TRUMBULL ASPHALT

GERALD REINKE-MTE SERVICES, INC.

GAYLON BAUMGARTNER- PARAGON TECHNICAL SERVICES

BRUNO MARCANT-RHODIA

LAIRD WEISHAN- NEBRASKA DEPT OF ROADS

BOB MCGENNIS-KOCH PAVEMENT SOLUTIONS
MOISTURE SENSITIVITY OF ACID MODIFIED ASPHALT & MIXTURES WITH and WITHOUT ANTI-STRIPPING AGENTS

FOR PRESENTATION AT THE ROCKY MOUNTAIN ASPHALT USER PRODUCER GROUP MEETING

By Gerald Reinke—MTE Services, Inc.

MARCH 3, 2004  SANTE FE, NM
“It’s not what we don’t know that hurts, it’s what we know that ain’t so” – Will Rogers
What man wishes were true, he more readily believes.
SOME BACKGROUND INFORMATION

1. DESPITE RECENT FLURRY OF CONCERNS RELATED TO ACID MODIFICATION OF ASPHALT THE INCORPORATION OF ACIDIC CHEMICALS INTO ASPHALTIC PRODUCTS & BITUMINOUS PAVING MATERIALS HAS BEEN THE SUBJECT OF RESEARCH FOR MANY YEARS.

- PATENT REFERENCE FROM 1939 (BURK 2179208) STANDARD OIL, DIRECTED TOWARDS MANUFACTURING ASPHALT WITH THE USE OF ACIDS AND REDUCED TIMES OF AIR BLOWING

- ALEXANDER IN 1973 (3751278), TOSCO-LION REFINING CO., DIRECTED TOWARDS THE USE OF PHOSPHORIC ACIDS TO PRODUCE PAVING GRADE ASPHALT WITHOUT BLOWING
BACKGROUND CONTINUED

- McGINNIS (ED) 1991 (CHEVRON) USE OF SOLVENT EXTRACTED ASPHALT, A BITUMINOUS MATERIAL AND PHOSPHORIC ACID
- Reinke, Engber (MTE) 2001, 2003 USE OF ACID WITH EPOXY GROUP BEARING TERPOLYMERS
- Baumgartner, et. al (ERGON) 2000, 2001 METHODS OF PREPARING POLYPHOSPHORIC ACID AND POLYMER ASPHALT BLENDS
- Puzic, et. al (EXXON RESEARCH) 1996, 1997 USE OF ACID AND DIENE CONTAINING POLYMERS
BACKGROUND CONTINUED

- **VAN DER WERFF, ET. AL (SHELL OIL) 1996**
  Use of acid and glycidyl containing polymers. (Mainly directed towards roofing applications)

- **GERMANAUD ET. AL (ELF FRANCE) 1997**
  Use of SBS, sulfur and acid to produce PMA

- **PLANCHE, ET. AL (ELF FRANCE) 2000**
  Use of epoxy bearing polymers, acid in conjunction with SBS
I KNOW WHAT YOU’RE THINKING

JUST BECAUSE INDIVIDUALS AND COMPANIES ENGAGE IN OBTAINING PATENTS ON A PARTICULAR TECHNOLOGY DOESN’T NECESSARILY MEAN THAT IT IS WORTHWHILE!
THERE ARE REALLY 2 AND PERHAPS 3 ISSUES WHEN IT COMES TO THE DISCUSSION OF ACID MODIFICATION OF ASPHALTS AND HMA MIXTURES

1. THE REACTION OF ASPHALT WITH AN ACID (GENERALLY POLYPHOSPHORIC ACID TODAY) TO YIELD AN IMPROVED PG GRADE RELATIVE TO THE BASE ASPHALT

2. THE USE OF AN ACID REACTANT ALONG WITH A POLYMER MODIFICATION OF THE ASPHALT. GENERALLY TODAY THE POLYMER IS EITHER SBS, SB, OR AN EPOXY BEARING ETHYLENE TERPOLYMER

3. THE USE OF AN ACID CATALYST AS PART OF THE OXIDIZING PROCESS TO PRODUCE A PG GRADED BINDER.
BUT LET’S NOT FORGET OL’ WILL ROGERS
WHAT IS IT THAT WE KNOW AND WHAT IS IT THAT
WE KNOW THAT AIN’T SO

WE KNOW? THAT BITUMINOUS MIXES MADE WITH
ACID IN THE ASPHALT

1. AGE FASTER (THAN ?)
2. ARE MORE SUSCEPTIBLE TO THERMAL CRACKING
3. ARE MORE SUSCEPTIBLE TO FATIGUE FAILURE
4. ARE MORE SUSCEPTIBLE TO MOISTURE (THAN ?)
5. CAN’T BE BLENDED WITH ANTI-STRIPS
6. WILL REACT DETRIMENTALLY WITH CERTAIN TYPES OF AGGREGATES
IMPACT OF THE ADDITION OF ACID ON THE PROPERTIES OF ASPHALT BINDERS AND MIXES
IMPACT ON HIGH TEMPERATURE PG GRADE
ADDITION OF 1.2% OF DIFFERENT TYPES OF
POLYPHOSPHORIC ACID
IMPACT ON CRITICAL CRACKING TEMPERATURE OF BINDER

ADDITION OF 1.2% (0.6% FOR ONE SAMPLE) OF DIFFERENT TYPES OF POLYPHOSPHORIC ACID

Asphalt C
Asphalt B
Asphalt T
Asphalt M
Asphalt A

IMPACT ON CRITICAL CRACKING TEMPERATURE OF BINDER
ADDITION OF 1.2% (0.6% FOR ONE SAMPLE) OF DIFFERENT TYPES OF POLYPHOSPHORIC ACID
ASPHALT M 64-22, RTFO, 64°C, 300 PA CUM CRT-0001c

- NEAT ASPHALT M 64-22, RTFO, 64°C, 300 PA
- ASPHALT M 64-22, 1.2% 105% SPA, RTFO, 64°C, 300 PA

% strain vs. global time (s)
PG 58-28 & PG 64-28 MADE FROM IT, 58°C, 300 PACUM CRT-0001c

- PG 64-28 USING 0.75% 105% ACID, 58°C, 300 PA
- PG 64-28 USING POLYMER, 58°C, 300 PA
- PG 58-28, RTFO, 58°C, 300 PA
FLOW NUMBER FROM REPEATED CREEP & RECOVERY TEST
3.5% & 7% AIR VOIDS GRANITE MIXES: 68 KPA STRESS, 58° C TEST TEMP
FLOW NUMBER = TIME TO TERTIARY FLOW
FLOWNUMBER FROM REPEATED CREEP & RECOVERY TEST
68 KPA STRESS, 58° C TEST TEMP
FLOWNUMBER = TIME TO TERTIARY FLOW

- **GRANITE AGG UNMODIFIED BINDER**
- **GRANITE AGGREGATE, ACID MODIFIED BINDER**
- **LIMESTONE AGG UNMODIFIED BINDERS**
- **LIMESTONE AGG ACID MODIFIED BINDERS**

FLOWNUMBER TO FAILURE, SEC'S

- AC B PG 64-22
- AC B PG 64-22 + ACID
- AC B PG 64-22 + ACID
- AC C PG 64-22 + ACID
- AC C PG 67-22 + ACID
- AC C 67-22 + ACID

3.5% AIR VOIDS MIXES
FLOWNUMBER TO FAILURE FOR ASPHALTS B AND C WITH AND WITHOUT ACID AT 7% AIR VOIDS, 68 KPA STRESS, 58° C
TEST TEMP FOR GRANITE & LIMESTONE AGGREGATES
IMPACT OF AGING ON PROPERTIES OF MIXES PRODUCED WITH ACID CONTAINING BINDERS
Area Determination

Area = 1.43 cm⁻¹
Aging Study

64-28 ACID MODIFIED

Abs vs cm⁻¹

Binder Unaged
Binder RTFO
Binder PAV
Mix Unaged
Mix 5 Day Aged
Mix 15 Day Aged
Mix 25 Day Aged
This region is unique to the Elvaloy polymer.
\begin{align*}
\text{Log10}(Y) &= 8.72858 - 3.43684X \\
\text{EMS} &= 8.78553 \times 10^{-5} \\
R^2 &= 1.000
\end{align*}

\begin{align*}
\text{Log10}(Y) &= 9.96424 - 4.33581X \\
\text{EMS} &= 0.0359668 \\
R^2 &= 0.949
\end{align*}
Log10(Y) = -1.91135 + 3.4656X
EMS = 0.0303806
R² = 0.934

Log10(Y) = -4.33471 + 4.45565X
EMS = 0.127725
R² = 0.886
CRITICAL CRACKING TEMPERATURE OF BINDER RECOVERED FROM AGED MIXES FOR PG 64-28P & PG 64-28 C

Days of Mix Aging @ 85°C in Air Oven

Critical Cracking Temperature in Deg K

PG 64-28C
PG 64-28 P
R^2 = 0.96
R^2 = 0.95
COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED

- PG 64-28 POLYMER MIX, UNAGED
- PG 64-28 ACID REACTED MIX, UNAGED
COMPARISON OF FATIGUE FAILURE BETWEEN
PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED

- PG 64-28 POLYMER MIX, UNAGED
- PG 64-28 ACID REACTED MIX, UNAGED
- PG 64-28 POLYMER MIX, 5 DAY AGED
- PG 64-28 ACID REACTED MIX, 5 DAY AGED
COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED
AGING COMPARISON OF SBS WITHOUT ACID & ELVALOY WITH ACID CATALYST
AGGREGATE USED WAS A CRUSHED GRANITE

ELVALOY + ACID MODIFIED PG 70-34
SBS MODIFIED PG 70-34

ALL VALUES WHERE DSR = 2.2 kPa
UNAGED  61.1°C
RTFO  69.7°C
PAV  22.35°C

ALL VALUES WHERE DSR = 2.2 kPa
UNAGED  62.2°C
RTFO  69.7°C
PAV  22.5°C
DAYS OF MIX AGING @ 85°C, FORCED DRAFT OVEN
Mix Flowtime test conducted at 58°C & 68 kPa Stress
IMPACT OF MOISTURE ON
1. ACID MODIFIED ASPHALT
2. POLYMER MODIFIED + ACID
3. BLENDS CONTAINING PHOSPHATE ESTER ANTI-STRIP ADDITIVE
T-283 AND HAMBURG DATA
TENSILE STRENGTH TEST RESULTS FOR SOURCE C 67-22 AND SOURCE C 67-22 + 1.2% OR 0.6% POLYPHOSPHORIC ACID USING LIMESTONE AND GRANITE MIXES

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>1.2% Acid</th>
<th>0.6% Acid</th>
<th>Control</th>
<th>1.2% Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIMESTONE</td>
<td>TSR 88.2</td>
<td>TSR 66.1</td>
<td>TSR 73.0</td>
<td>GRANITE</td>
<td>TSR 87.4</td>
</tr>
<tr>
<td>GRANITE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TSR 94.1</td>
</tr>
</tbody>
</table>

TENSILE STRENGTH VALUES IN KPA

TENSILE STRENGTH VALUES IN PSI
TENSILE STRENGTH TEST RESULTS FOR SOURCE B 64-22 AND SOURCE B 64-22 + 1.2% POLYPHOSPHORIC ACID USING LIMESTONE AND GRANITE MIXES

- **Dry Strength Values**
- **Wet Strength Values**

**Materials**: Control, 1.2% Acid, Limestone, Granite

**Results**:
- **Limestone**
  - TSR 90.2
  - TSR 86.8
  - TSR 83.8
- **Granite**
  - TSR 93.4

**Units**:
- Tensile Strength Values in KPA
- Tensile Strength Values in PSI
MATHY RUT TEST WITH PG 64-34 TESTED IN PMW HAMBURG WET AT 50° C

ONSET OF STRIPPING OCCURS @ 7100 CYCLES

GRANITE E-10 MIX PG 64-34 @ 50° C WET rerun RIGHT WHEEL 7.2&6.8%VOIDS

RUT DEPTH IN mm

RUT CYCLES AT 50° C & 158 LBS (702 N)
HAMBURG ONSET OF STRIPPING

LIMESTONE AGG FROM MINNESOTA PROJECT

CYCLES TO STRIPPING ONSE

<table>
<thead>
<tr>
<th>Material</th>
<th>Cycles to Stripping Onset</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG 58-28</td>
<td>3200</td>
</tr>
<tr>
<td>PG 58-34C+ NO AS</td>
<td>500</td>
</tr>
<tr>
<td>PG 58-34C+ GRIPPER X</td>
<td>1500</td>
</tr>
<tr>
<td>PG 58-34P+ NO AS</td>
<td>1100</td>
</tr>
<tr>
<td>PG 58-34P+ GRIPPER X</td>
<td>3500</td>
</tr>
<tr>
<td>PG 64-28C+ NO AS</td>
<td>2800</td>
</tr>
</tbody>
</table>
PG 58-34 ACID MODIFIED
4.5 MILES, PAVED JULY 2002

FEB 26 2004
HAMBURG ONSET OF STRIPPING FOR LIMESTONE MIX

CYCLES TO STRIPPING ONSET

ONSET OF STRIPPING

FIELD MIX FROM MINNESOTA PROJECT

PG 64-28C
PG 64-28C + GRIPPER X
PG 64-28P
PMW HAMBURG RUT TEST OF PG 70-22
AND PG 64-22 BINDERS-- 70-22 AB, 70-22 PPA,
70-22 PPA + GRIPPER, 70-22 STRAIGHT RUN & 70-22 PMA

SAME MIX FOR ALL BINDERS
LIMESTONE AGGREGATE

TEST CYCLES @ 50° C & 703 N (158 LBS)
RUT TEST GRANITE E-3 MIX & PG 70-28
TESTED WET AT 50° C
“When you have eliminated the impossible, whatever remains, however improbable, must be the truth.”

Arthur Conan Doyle
NEBRASKA I-80 CRACKING

COMPARISON OF PG 70-28 MADE WITH STYLINK & 70-28 MADE WITH ELVALOY + ACID

CONSTRUCTED 1999, SOME OF THE FIRST SUPERPAVE PROJECTS IN NEBRASKA

EXTENSIVE CRACKING IN ELVALOY + ACID SECTIONS & MINIMAL CRACKING IN STYLINK SECTIONS

ACID MODIFICATION WAS BLAMED FOR THIS PROBLEM
Acid Type Modification

POLYMER MODIFICATION
TO INVESTIGATE THIS PROBLEM CORES WERE CUT FROM BOTH THE STYLINK AND ELVALOY + ACID SECTIONS. ONE PORTION OF THE ELVALOY + ACID SECTIONS DID NOT EXHIBIT ANY CRACKING AND CORES WERE TAKEN FROM THIS LOCATION AS WELL.

THE PROJECT CONSISTED OF A 80 mm BOTTOM LIFT AND A 50 mm TOP LIFT. BOTH LIFTS WERE CONSTRUCTED WITH THE SAME MIX AND BINDER
UNCRAKED SECTION

TOP LIFT ~ 50 mm

BOTTOM LIFT ~ 80 mm
## Properties of Binder Recovered from Top 2” of Identified Cores

**Shipped Grade = PG 70-28**

<table>
<thead>
<tr>
<th>Core</th>
<th>Grade</th>
<th>Temperature</th>
<th>Stress @ Temperature</th>
<th>Modulus @ Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>405.9W—</td>
<td>Stylink, #11</td>
<td>79.4°C</td>
<td>2.2 kPa</td>
<td>5000 kPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-18°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>S=252 Mpa</td>
<td>M=0.306</td>
</tr>
<tr>
<td>425E—</td>
<td>Elvaloy + acid, #3</td>
<td>77.2°C</td>
<td>2.2 kPa</td>
<td>5000 kPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.1°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-18°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>S=264 Mpa</td>
<td>M=0.324</td>
</tr>
</tbody>
</table>
Nebraska I-80, Rec AC FROM BOTTOM LIFT
70°C Frequency Sweeps, $G^*/\sin(\delta)$

TEST FREQUENCY IN RADIANS/SEC

$G^*/\sin(\delta)$, kPa

- Elv, Sec 425 E, Core 6, Slice B-3; 2.939
- KMC, Sec 416 W, Core 1, Slice B-3; 4.405
- Elv, Sec 419 E, Core 13, Slice B-3; 2.874
- KMC, Sec 405.9 W, Core 11, Slice B-3; 3.536
- Elv, Sec 400 E, Core 10, Slice B-2; 2.876
Nebraska I-80, Rec AC FROM BOTTOM LIFT
19°C Frequency Sweeps
$G^* \times \sin(\delta)$, kPa

**STYLINK, Sec 416 W, Core 1, Slice B-3; $$G''=3686$$**

**Elv, Sec 419 E, Core 13, Slice B-3; $$G''=2692$$**

**Elv, Sec 400 E, Core 10, Slice B-2; $$G''=3331$$**

**Elv, Sec 425 E, Core 6, Slice B-3; $$G''=3216$$**
NE I-80 ELV 400E, 9B-1, master curve @ 20°C, AR2, Step
NE I-80 ELV 400E, 10B-1, master curve @ 20°C, AR1, Step
NE I-80 ELV 419E, 13B-1 #3, master curve @ 20°C, Step
NE I-80 ELV 425E, 6B-1#2, master curve @ 20°C, AR1, Step
NE I-80 KMC 416E, 1B-1, master curve @ 20°C from 10-30°C sweep AR1, Step
NE I-80 KMC 405.9W#2, 11B-1, master curve @ 20°C, AR-2, Step
CYCLES TO FAILURE @ 20°C AS A FUNCTION OF MIX FLOWTIME TO FAILURE AT 58°C, 34 kPa STRESS

Cycles to fatigue failure @ 20°C, 10 Hz

MIX FLOWTIME FROM DSR CREEP TEST 58°C & 34 kPa STRESS

Elvaloy 400E
Elvaloy 419E
Elvaloy 425E
Stylink 405.9W
Stylink 416W

R² = 0.48
FATIGUE CYCLES TO FAILURE @ 1000 µSTRAIN & 20°C
AS A FUNCTION OF COMPLEX MODULUS OF THE MIX
TESTED AT 20°C

\[ Y = 661773.39 - 2.1964948 \times 10^{23} / X^2 \quad R^2 = 0.20 \]

Elvaloy 400E
Elvaloy 425E
Stylink 405.9W
Stylink 416W

02/22/04 22:50:22 C:\DRIVE_E\AR2000\RESULTS\2004\NEI-80\CYCLES TO FAILURE @ 1000 MS = F(MIX G star @ 20C).spf
CYCLES TO FATIGUE FAILURE @ 1000 µSTRAIN AND 20°C AS A FUNCTION OF MIX AIR VOIDS

Y = (19,928,907 - 934,756.86 * LOG(X)); R^2 = 0.93
Fine at Opt. AC Content

3.9 Million

No Cracking

Air Void Content

Low

Med

High
BUT LET’S NOT FORGET OL’ WILL ROGERS

WHAT IS IT THAT WE KNOW AND WHAT IS IT THAT WE KNOW THAT AIN’T SO

WE KNOW THAT BITUMINOUS MIXES MADE WITH ACID IN THE ASPHALT

1. AGE FASTER (THAN ?)
2. ARE MORE SUSCEPTIBLE TO THERMAL CRACKING
3. ARE MORE SUSCEPTIBLE TO FATIGUE FAILURE
4. ARE MORE SUSCEPTIBLE TO MOISTURE (THAN ?)
5. CAN’T BE BLENDED WITH ANTI-STRIPS
6. WILL REACT DETRIMENTALLY WITH CERTAIN TYPES OF AGGREGATES
WHAT DO WE KNOW NOW?
MAYBE LESS THAN WHEN WE STARTED

1. MIXES MADE WITH ACID MODIFIED BINDERS DO SEEM TO AGE MORE RAPIDLY THAN THOSE MADE WITH POLYMER + ACID—BUT DO THEY AGE FASTER THAN UNMODIFIED BINDERS?

1. DOES THAT MATTER IF THE LOW TEMPERATURE PROPERTIES REMAIN INTACT?

1. STIFFER MIXES RESIST RUTTING

2. FATIGUE IS THE QUESTION
WHAT DO WE KNOW NOW?

THE ISSUE OF FATIGUE

1. OUR DATA INDICATES THAT FATIGUE OF MIXES USING POLYMER IS BETTER THAN THAT OF MIXES WITH ACID ONLY—UP TO A POINT

1. ONCE THE MIX HAS BEEN AGED THE MIX FATIGUE RESULTS SEEM TO MERGE.

2. BAHIA, ET. AL PRESENTED RESULTS AT 2004 TRB SHOWING COMPARABLE FATIGUE PROPERTIES FOR ACID AND POLYMER MODIFIED PAV RESIDUES
WHAT DO WE KNOW NOW?

THE ISSUE OF MOISTURE SENSITIVITY

1. THIS IS A MIX PROBLEM AND SHOULD BE TREATED AS A MIX PROBLEM

2. THERE ARE COMPATIBLE ANTI-STRIPPING ADDITIVES AVAILABLE—USE THEM WHEN NEEDED

1. FOR MANY AGGREGATES THE PPA APPEARS TO SERVE AS AN ANTI-STRIP

3. THE TOOLS ARE AVAILABLE TO PREVENT INCOMPATIBLE SYSTEMS FROM REACHING THE ROAD—USE THEM
SOME FINAL COMMENTS

1. ACID MODIFICATION $\neq$ POLYMER MODIFICATION

1. USE THE MIX ANALYSIS TOOLS WE HAVE TO DETERMINE WHERE AND WHEN POLYMER IS NEEDED

2. ACID MODIFICATION CAN FILL A NICHE WHEN SOME ADDITIONAL BINDER STIFFNESS IS NEEDED

2. ABOVE ALL ELSE COMMUNICATION BETWEEN AGENCY, SUPPLIER AND CONTRACTOR IS ESSENTIAL TO SUCCESS
“Errors using inadequate data are much less than those using no data at all”—Charles Babbage