Polyphosphoric Acid Modified Asphalt Binders – Industry Perspective; Usage, Why, How.

Presented by:

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Workshop on Polyphosphoric Acid (PPA) Modification of Asphalt Binders

Minneapolis, Minnesota

7-8 April 2009

Definition - Asphalt

a high molecular weight, thermoplastic hydrocarbon constituent, found in a large number of petroleum crude oils. Although some asphalts do occur naturally, asphalt as we know it, and as discussed herein, is derived from fractional distillation of petroleum crude oil.

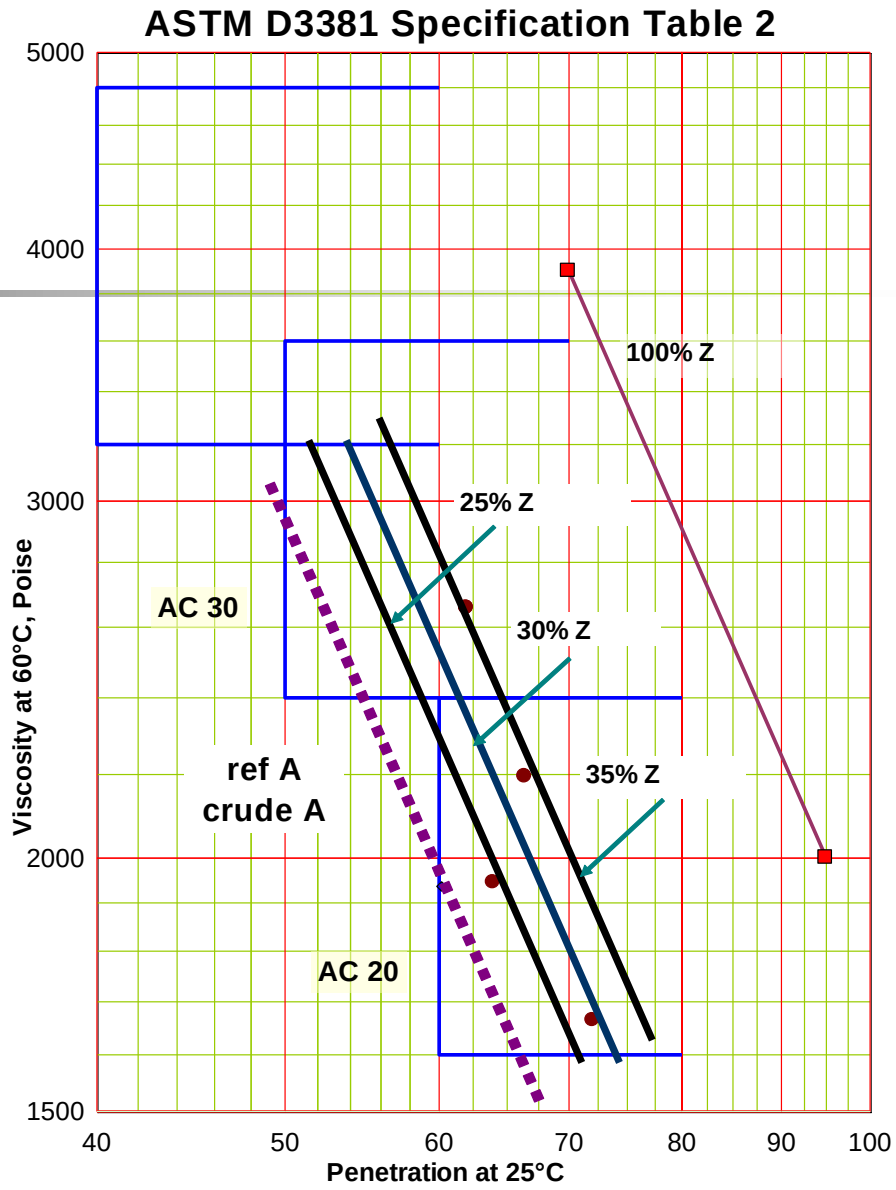
Grading of Asphalt Binders

- Prior to 1970 asphalts were specified as penetration grades.
  - 5/9, 50/60, 60/70, 85/100,140/160 and >300 pen
- Beginning in 1970, asphalts were specified as viscosity grades.
  - AC-5, AC-10, AC-20, AC-30 and AC-40

Effect of crude Z on Crude A (ref A) asphalt properties.

Note: Pen/Vis relationship: AC-30 = 2500-2550 poise min 57 dmm.

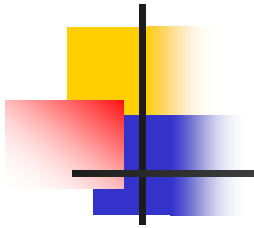
~1 dmm/75 poise



Puzic 2005

Grading of Asphalt Binders Continued

- In the 1990's State DOT's began to specify SHRP or Performance Grades of Asphalts. SuperPave™.
  - PG 58-28, PG 64-22, PG 70-22, PG 76-22, etc
- Though asphalt specifications have been upgraded through time, any of the are previous grading systems are subject to use.

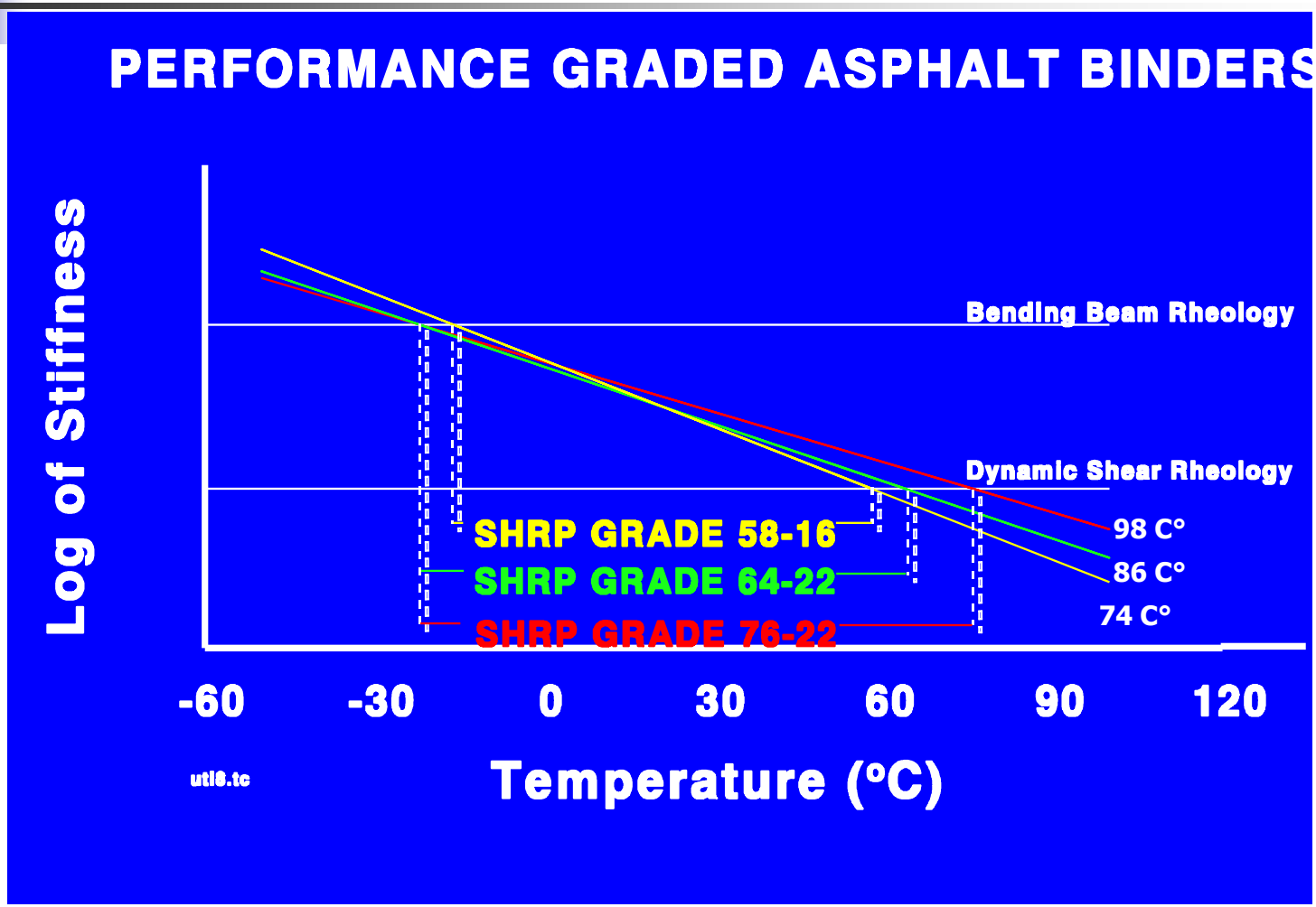


Useful Temperature Interval (UTI) "SuperPave Made Simple"

Useful Temperature Interval

- Simply put, the "useful temperature interval" (UTI) of an asphalt is the differential, or spread in C°, between the high temperature grading and the low temperature grading.

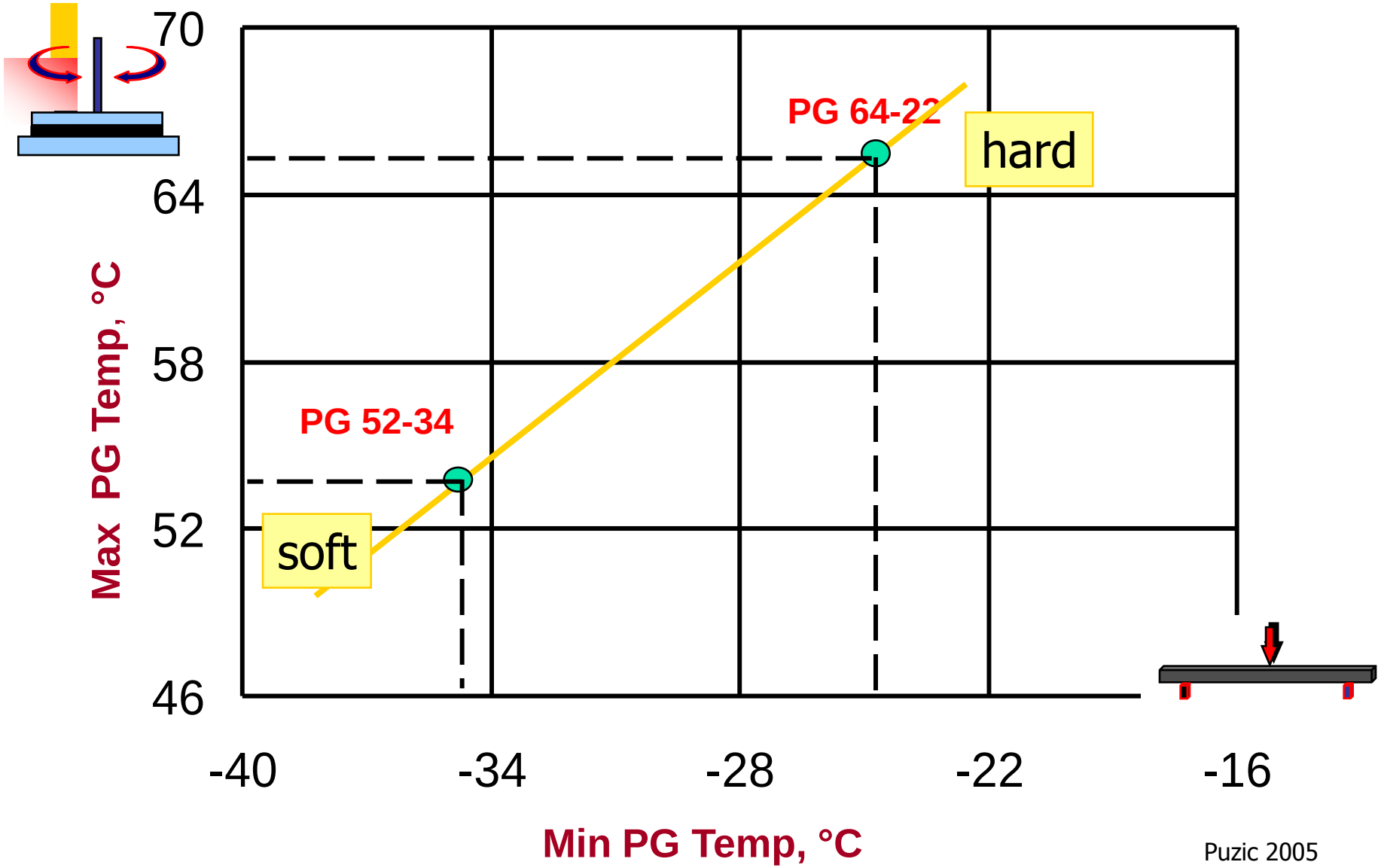
Useful Temperature Interval



UTI of Performance Grade Asphalts

- A PG 64-22 would have a UTI of 86 C°
- A PG 58-28 also has a UTI of 86 C°
- If we needed a PG 76-22, which has a UTI of 98 C° - how is this accomplished?
- As a "rule of thumb", to achieve a UTI of >92 C°, the asphalt has to be "modified".
- Depending on crude source, some binders with more narrow UTI's of 86 and 89 C° may also require modification

SUPERPAVE PERFORMANCE GRADES and PG Line



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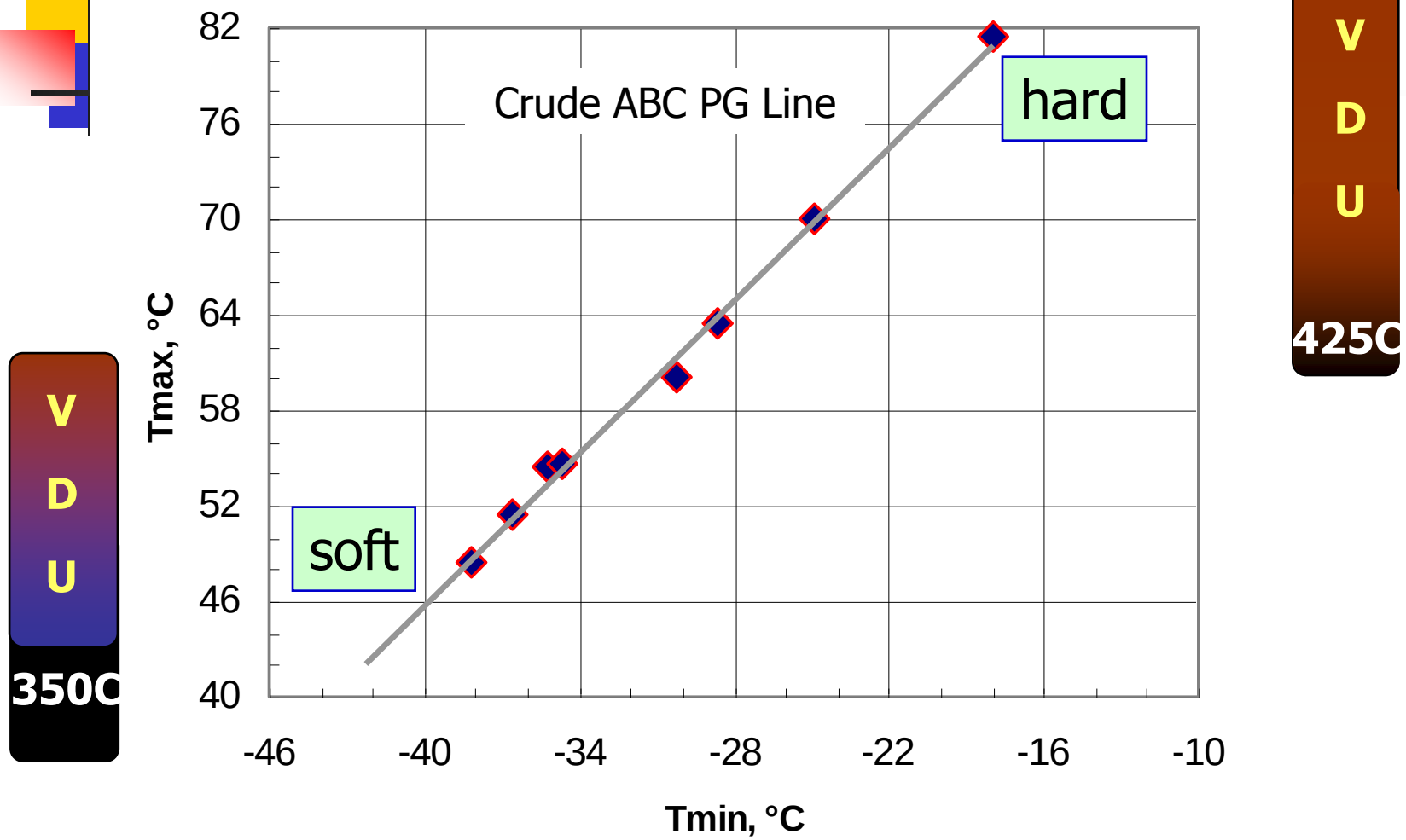
For a given crude, asphalt grade is defined by refinery processing conditions



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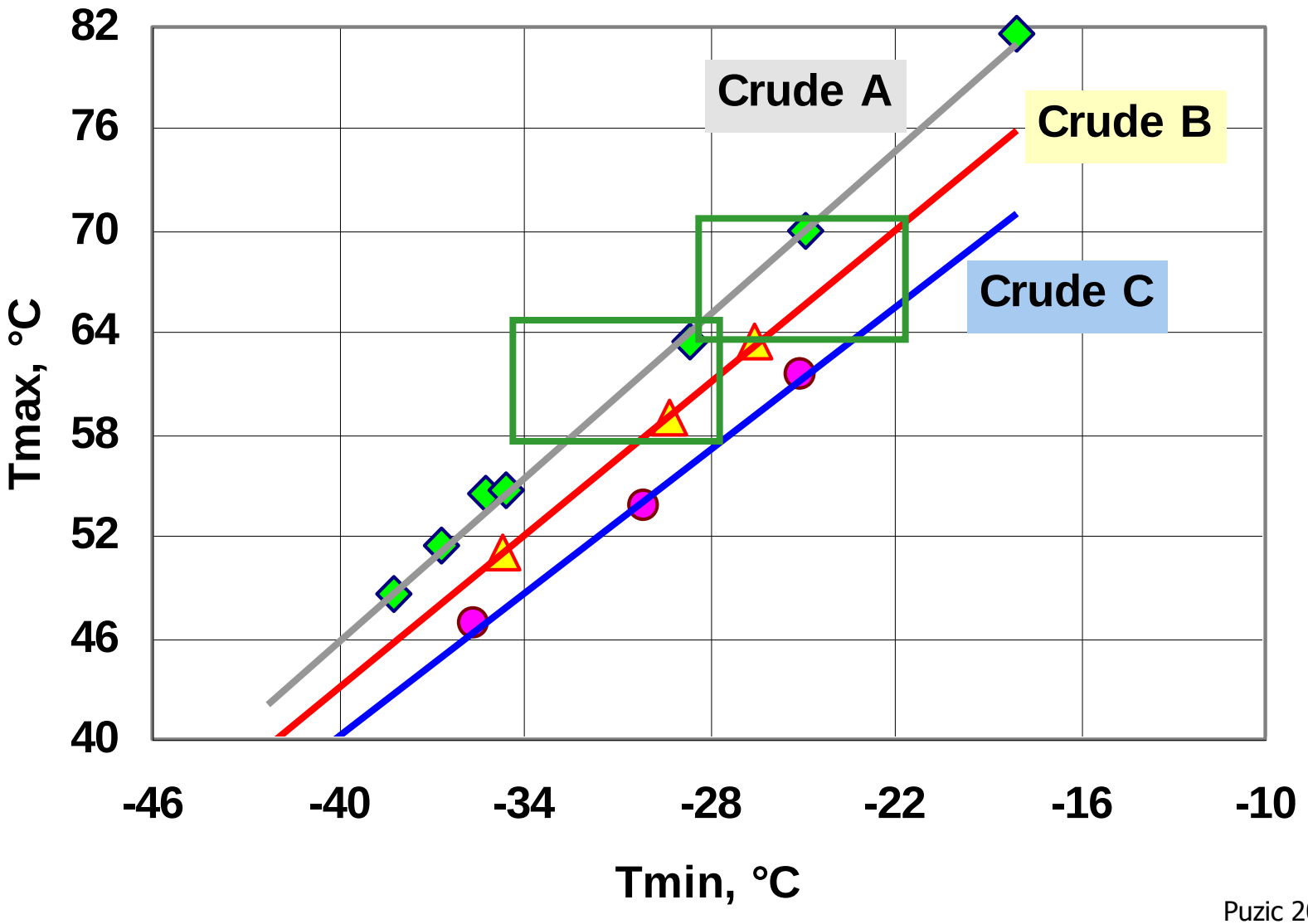
SUPERPAVE PG line is a signature of a crude



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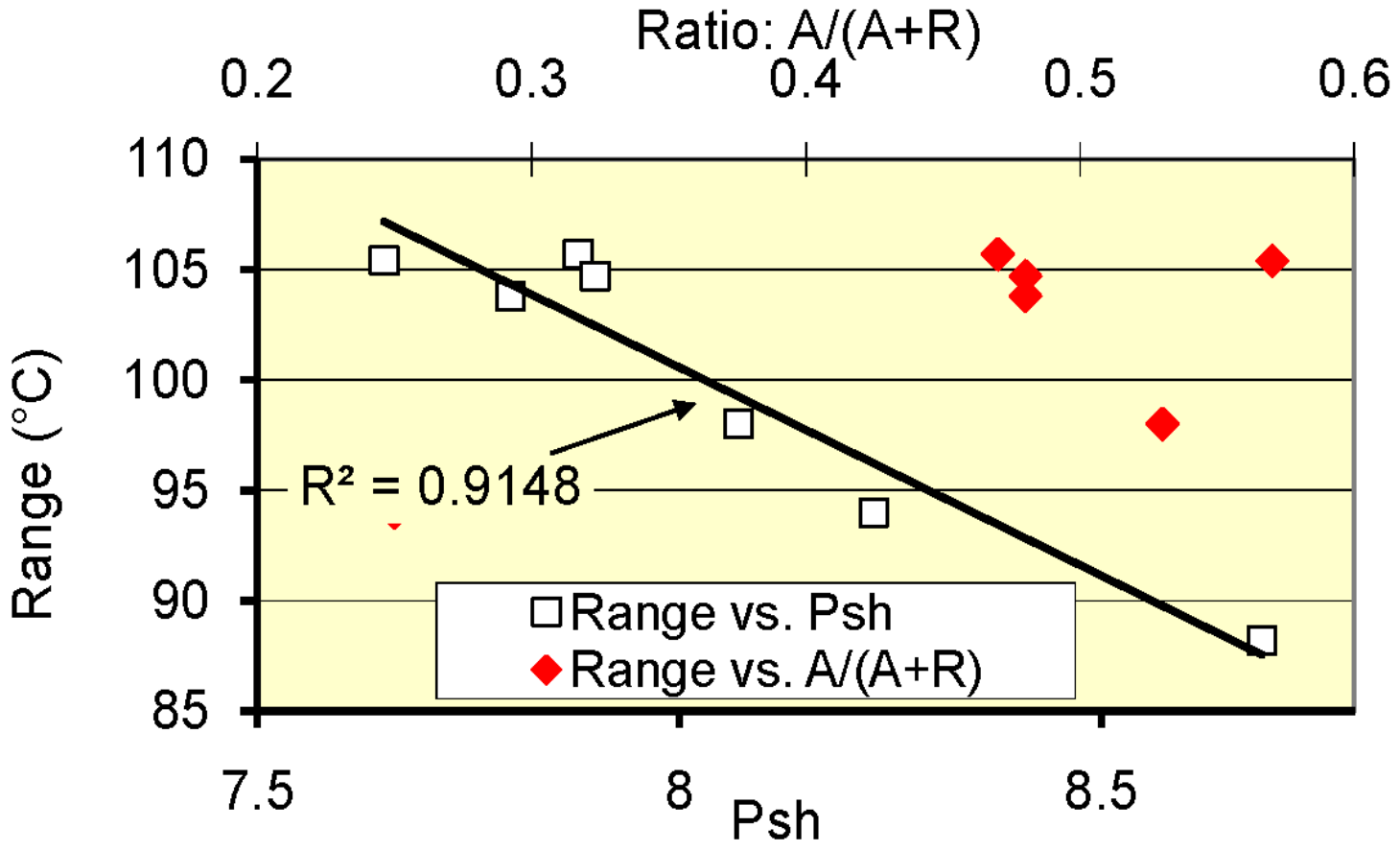
True Grade Range vs. Composition



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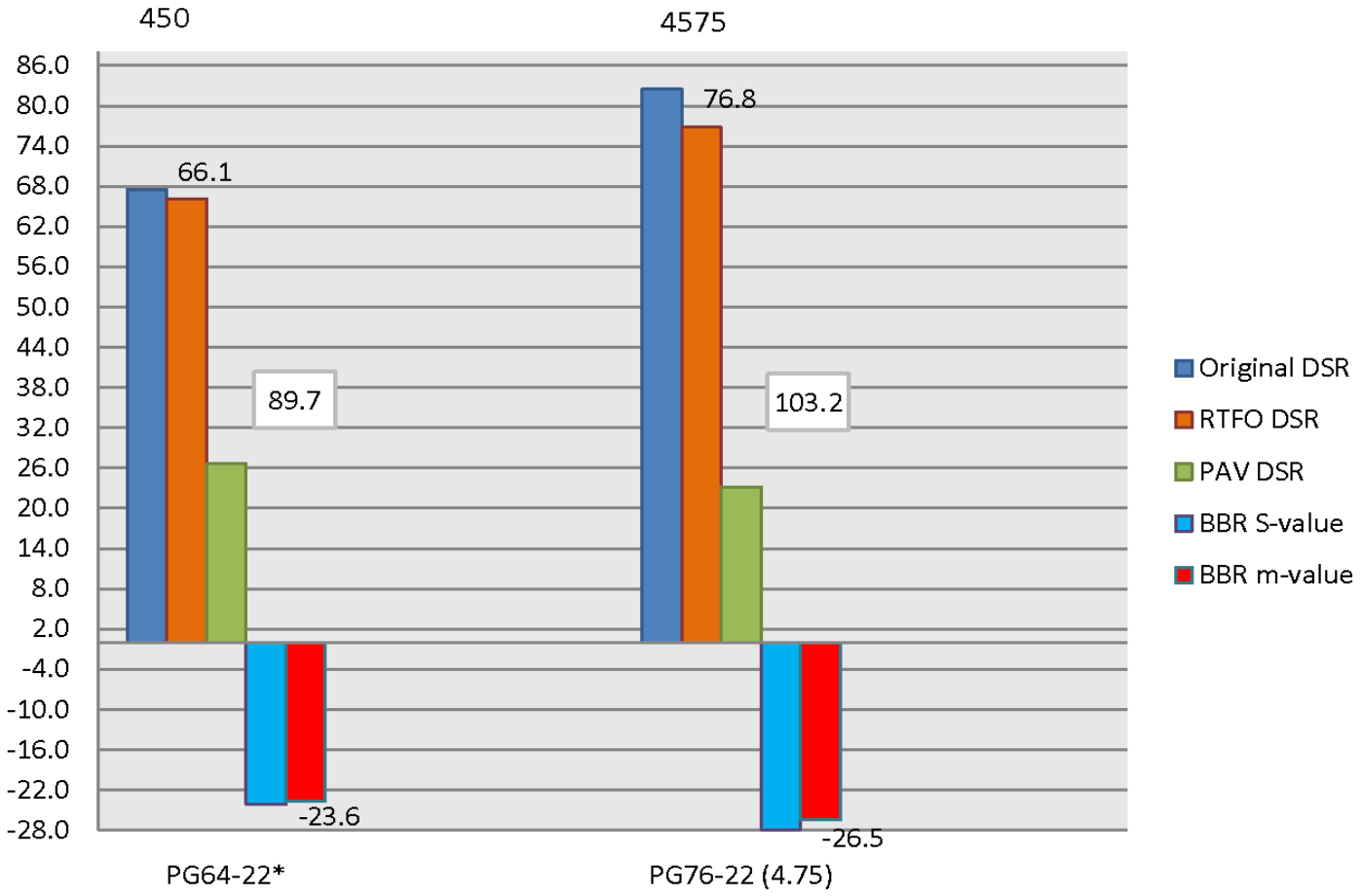
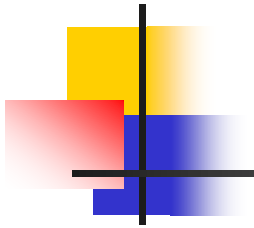
Narrow UTI's of 86 and 89 C° May Require Modification





Phosphoric Acid Modification of Asphalt Binder

Definition – Polyphosphoric Acid

- Inorganic Polymer
- Obtained by Condensation of Monophosphoric Acid or by Hydration of P_2O_5
- 0%wt of Free water
- Viscous liquid (25°C) from 840 cP (105%wt) to 60 000 cP (115%wt)
- Crystallisation temperature below 0 to 15°C
- Medium strong acid : Acidity function (Hammet) = 6 (ref H2SO4 = 12)
- Highly soluble in organics
- Non oxidant compound

Background

- Dr. Arnold Hoiberg
  - US Patent 2,450,756 – October 5, 1948
  - US Patent 3,028.249 – April 3, 1962
- Dr. Stephen Alexander
  - US Patent 3,751,278 – August 7, 1973

Background Contd.

- Gorbaty
- Moran
- Goodrich
- Geviarini
- Reinke
- Puzic
- Planche
- Baumgardner/Burrow
- Et. Al.

Dr. Hoiberg - 1948

- Phosphorous Pentoxide and Stable Acids of Phosphorous, P_2O_5, H_3PO_4
  - Lowered the temperature range of processing air blown asphalt binder from a typical range of 490-500°F to a range of 440 to 450°F (254-260°C to 227-232°C)
  - Typical straight air blown properties 212°F (100°C) softening point with 12-15 dmm penetration, Catalytic air blown properties 212°F (100°C) softening point with 35-40 dmm penetration

Definition

- Catalyst – “a substance that initiates a chemical reaction and enables it to proceed under different conditions (as at lower temperature) than otherwise possible”
  - Cat. Air Blown: 440 to 450°F (227-232°C)

Dr. Hoiberg - 1962

- Phosphorous Pentoxide, Stable Acids of Phosphorous and Phosphorous Pentasulfide, P_2O_5, H_3PO_4, P_2S_5, plus Organic Amine
  - Catalytic Air Blowing Provides Improved Binder Properties (Higher Pen per Softening Point), Amine Added to Catalytically Blown Binder to Promote Adhesion

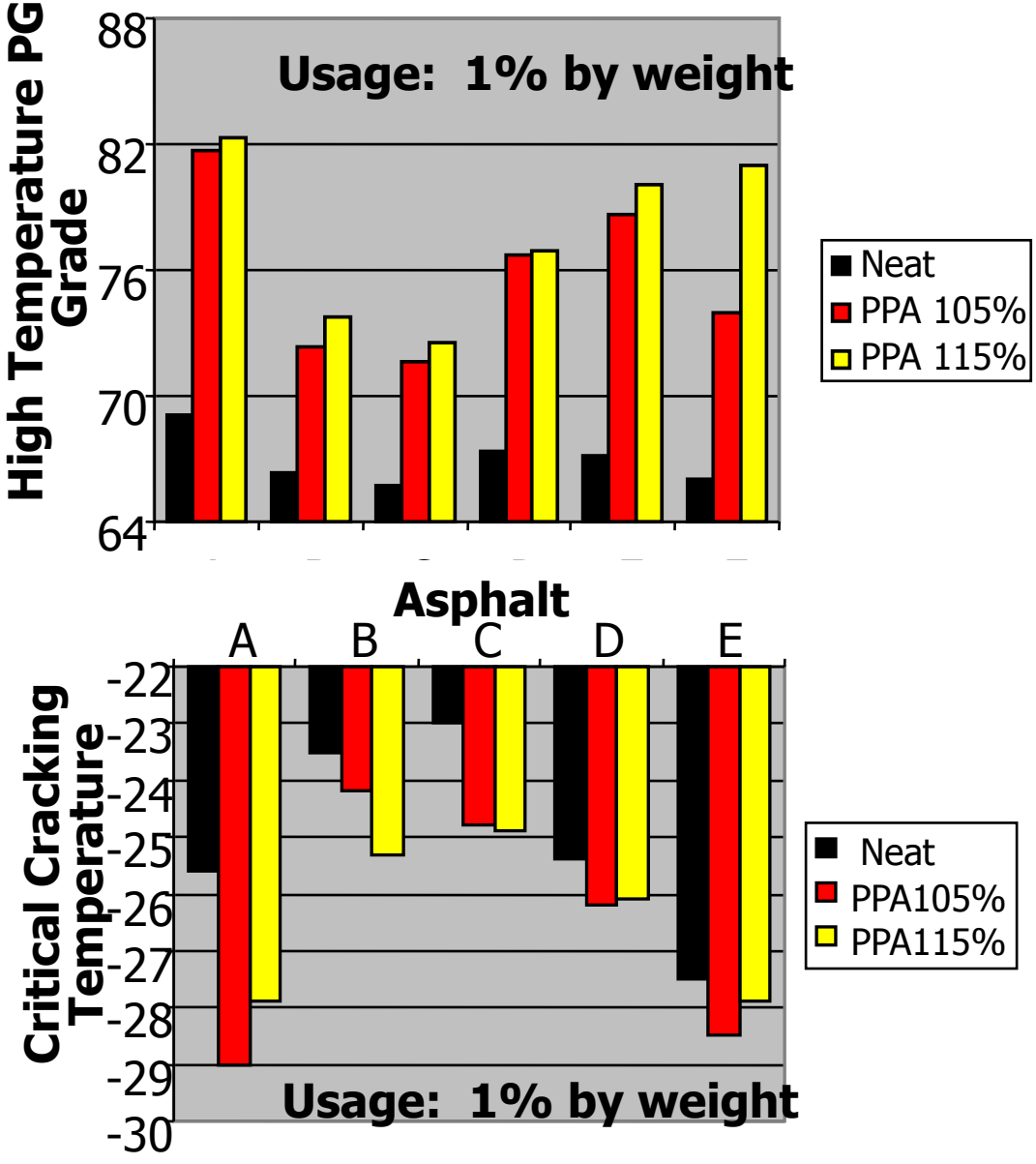
Dr. Alexander - 1973

- Condensed Derivatives of Phosphoric Acid (Polyphosphoric Acid, “PPA”) used to modify to non air-blown Paving Grade Asphalt
  - Provided Increase Viscosity e.g. AC30 Modified to AC40 with little to no effect on Penetration Values (Improved PG or wider Useful Temperature Interval, UTI)

- **Effect of PPA Modification is Crude Dependent Based on Asphalt Chemical Composition**

- **Increases "Useful Temperature Interval" or PG True-grade by Improving Both Upper and Lower PG Limits**

- **PPA Modification Does Not Oxidize Asphalt or Promote Brittleness**



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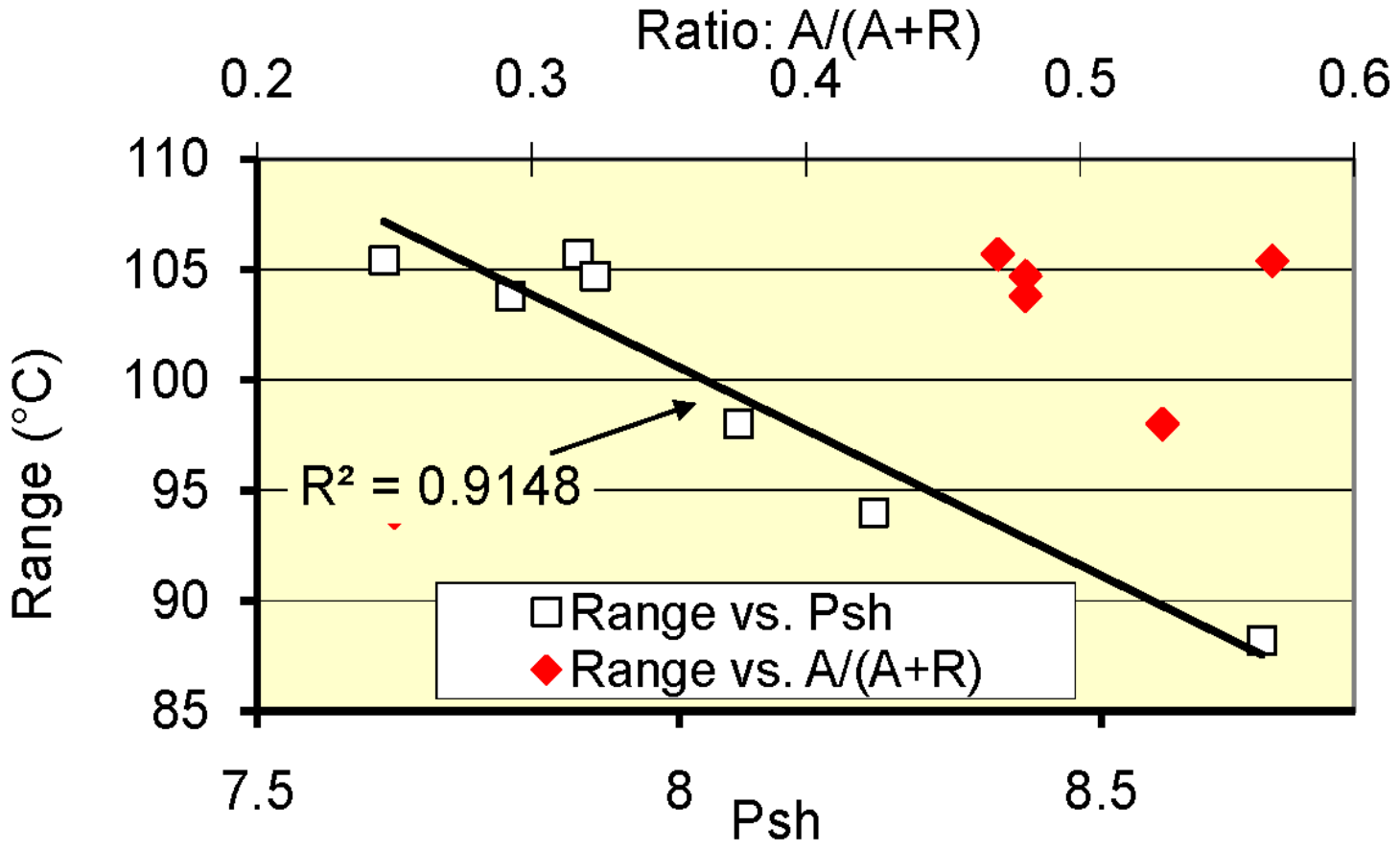
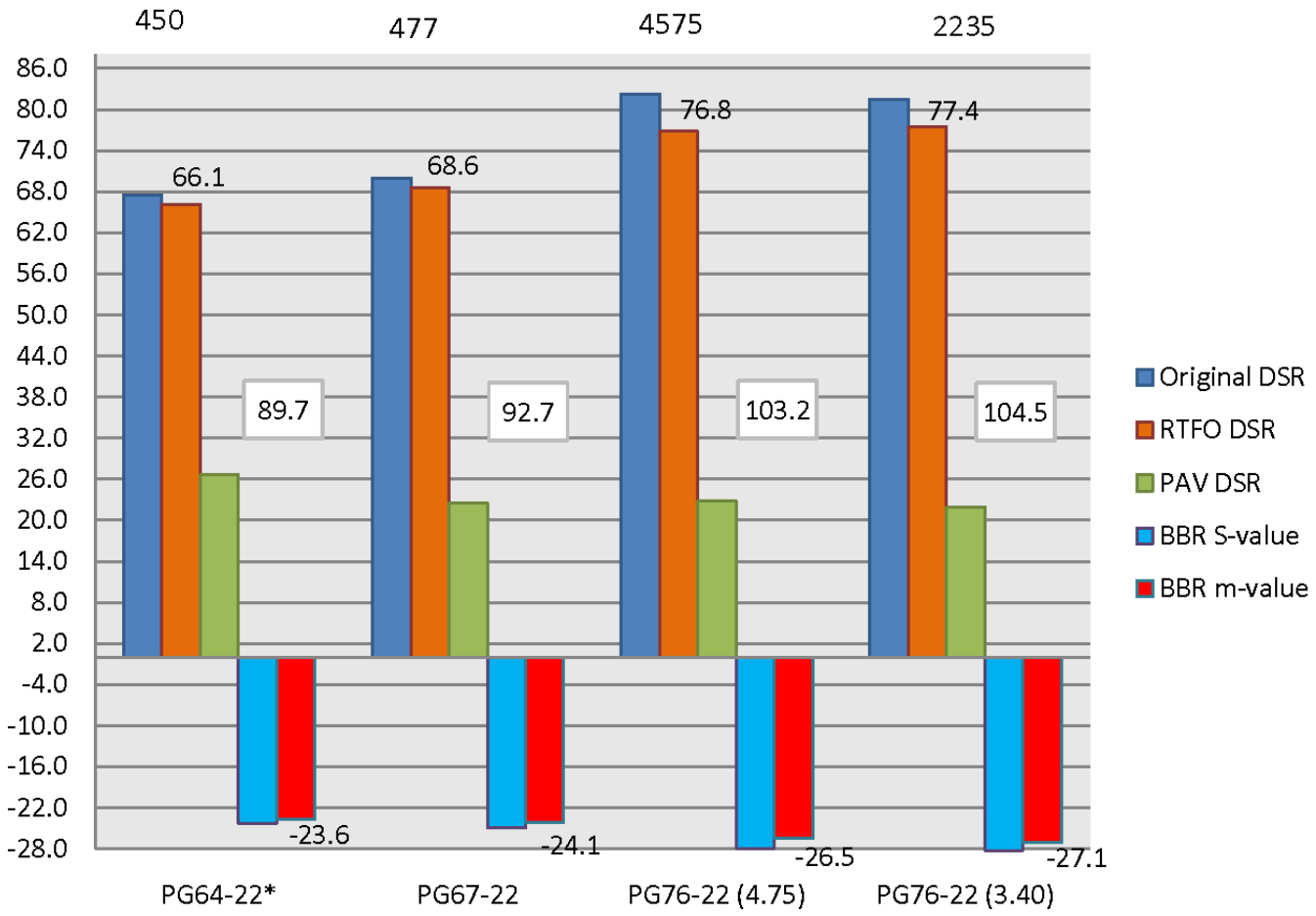



450
477
4575
2235
86.0
80.0
74.0
68.0
62.0
56.0
50.0
44.0
38.0
32.0
26.0
20.0
14.0
8.0
2.0
-4.0
-10.0
-16.0
-22.0
-28.0
66.1
68.6
76.8
77.4
89.7
92.7
103.2
104.5
-23.6
-24.1
-26.5
-27.1
PG64-22*
PG67-22
PG76-22 (4.75)
PG76-22 (3.40)
Original DSR
RTFO DSR
PAV DSR
BBR S-value
BBR m-value

PG76-22 from Saudi Asphalt

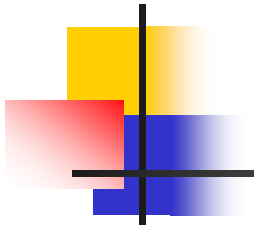
PG Grade Achieved	76-22	76-22	76-22	76-22
PPA %	0	0.2	0.4	0.6
Polymer %	4.75%	4.10%	3.75%	3.40%
Brookfield Vis.@ 135	2950	3870	3290	2230
ODSR	1.606	1.532	1.561	1.534
Phase Angle	67.1	64.5	66.2	69.2
Wt. Loss	-0.105	0.21	-0.053	-0.034
RDSR	2.378	2.613	2.569	3.03
PDSR	1198	1126	1422	1276
BBR S Value	125	142	148	143
BBR M Value	0.325	0.335	0.332	0.327
Elastic Recovery	87.50%	86.70%	85.00%	85.00%

PG76-22 from Venezuelan Asp

PG Grade Achieved	76-22	76-22	76-22	76-22
PPA %	0	0.2	0.4	0.6
Polymer %	4.25	3.75	2.9	2.6
Brookfield Vis.@ 135	2350	2030	1510	1360
ODSR	1.557	1.524	1.366	1.42
Phase Angle	68.7	68.6	78.3	79.4
Wt. Loss	0.012	-0.024	0.23	0.008
RDSR	2.472	2.802	2.281	2.58
PDSR	1424	2038	1804	1934
BBR S Value	138	150	163	172
BBR M Value	0.32	0.31	0.311	0.306
Elastic Recovery	80.00%	77.50%	69.00%	64.00%

PG76-16 from CA Valley

PG Grade Achieve	76-16	76-16	76-16	76-10
PPA %	0	0.2	0.4	0.6
Polymer %	5.5	4.4	3.8	3.25
Brookfield Vis.@ 135	2060	1450	1310	1140
ODSR	2.092	1.595	1.414	1.253
Phase Angle	55.8	61.5	67.3	72.2
Wt. Loss	0.11	0.24	0.127	0.049
RDSR	2.327	2.521	2.335	2.296
PDSR	1959	2203	2782	1719
BBR S Value	211	286	291	115
BBR M Value	0.337	0.317	0.312	0.425
Elastic Recovery	85.00%	87.50%	85.00%	82.50%



Phosphorous Magnetic Resonance of PPA Modified Asphalt

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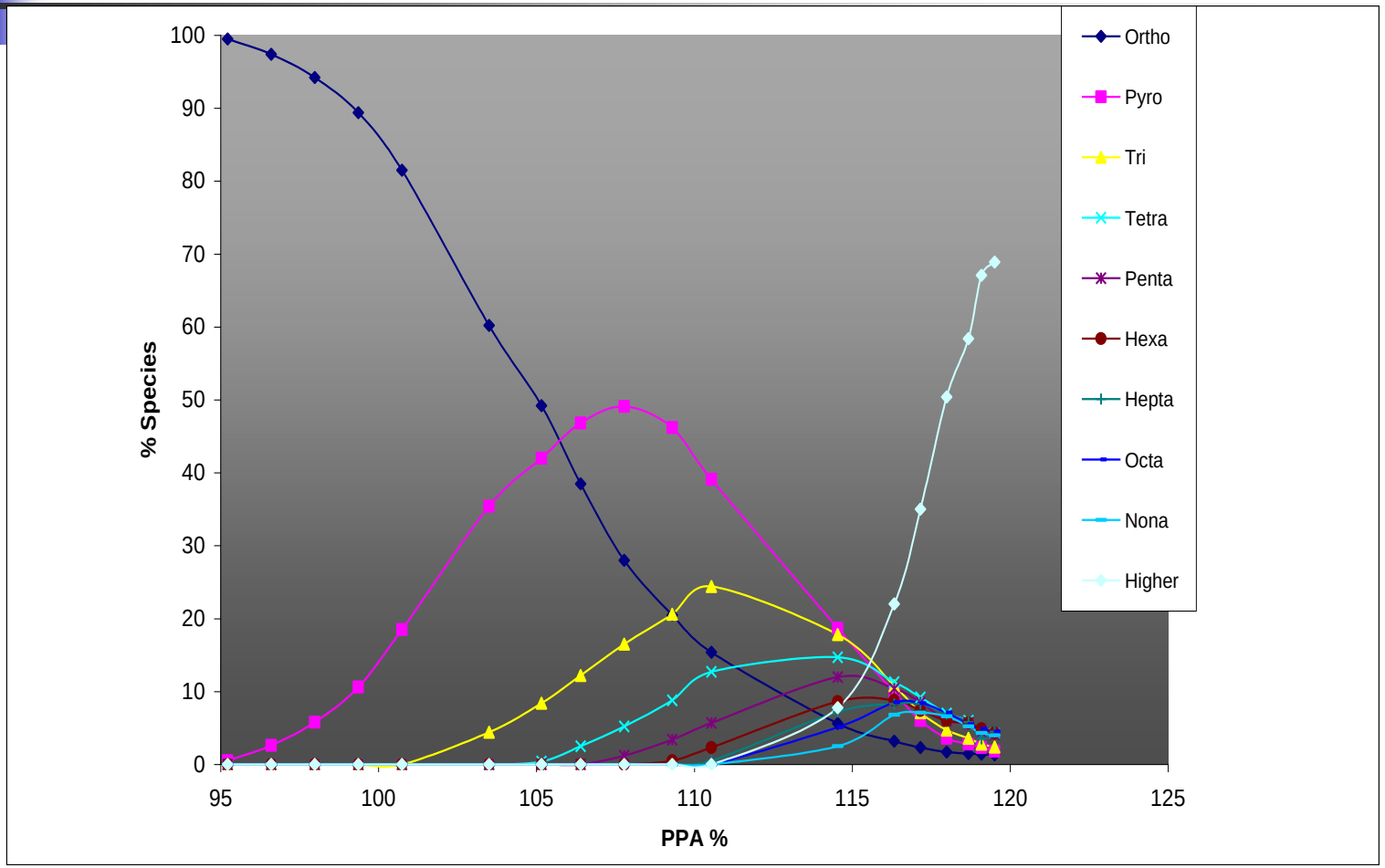
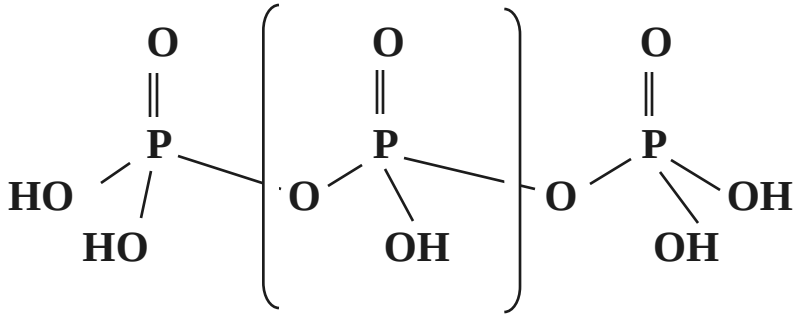
Polyphosphoric Acid Complex Composition : many chain lengths exist and are proportioned depending on concentration



Martin 2005

Polyphosphoric Acid

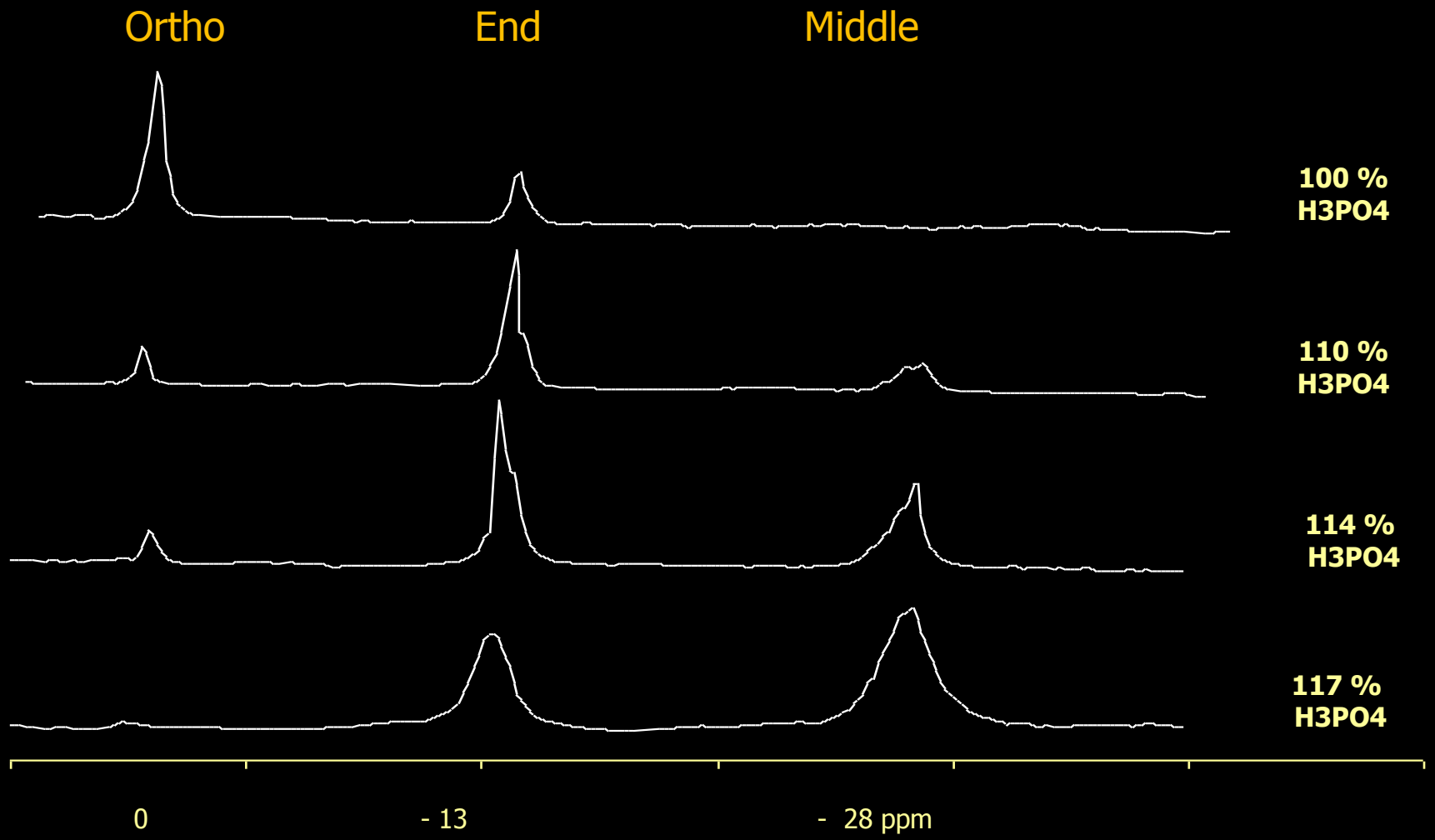


H_3PO_4

#P atoms	1	2	3	4	5	6	7	8
105%	53.9	40.7	4.86	0.46				
115%	7.32	23.0	19.3	15.9	12.3	8.21	5.73	3.89

Miknis 2008

NMR Spectra of Polyphosphoric Acids*



Nuclear Magnetic Resonance Method for Analysis of Polyphosphoric Acids
Guffy, J. C., and G. R. Miller, *Anal. Chem.*, (1959), 31, 1895-1897

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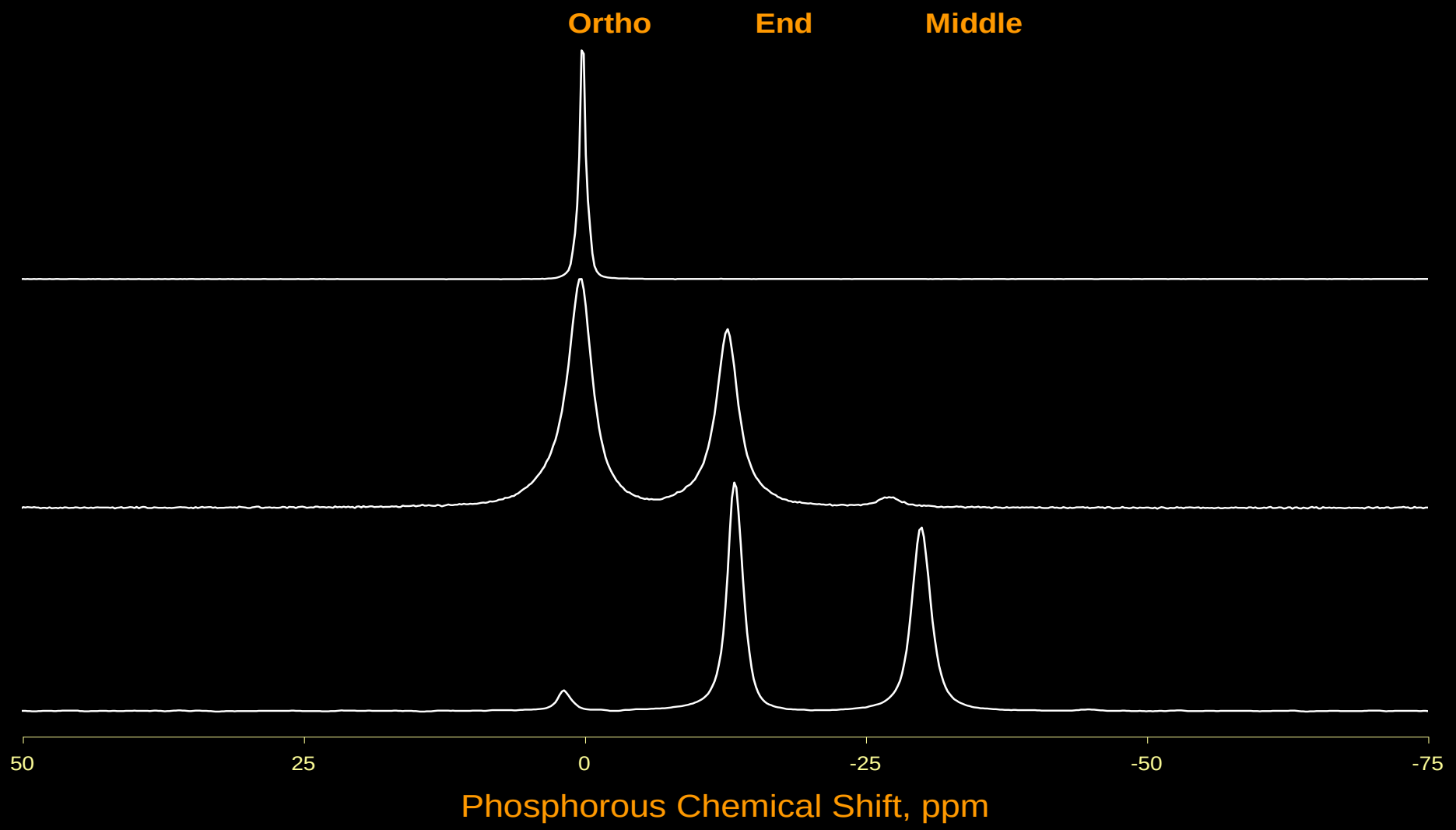
Phosphoric Acids



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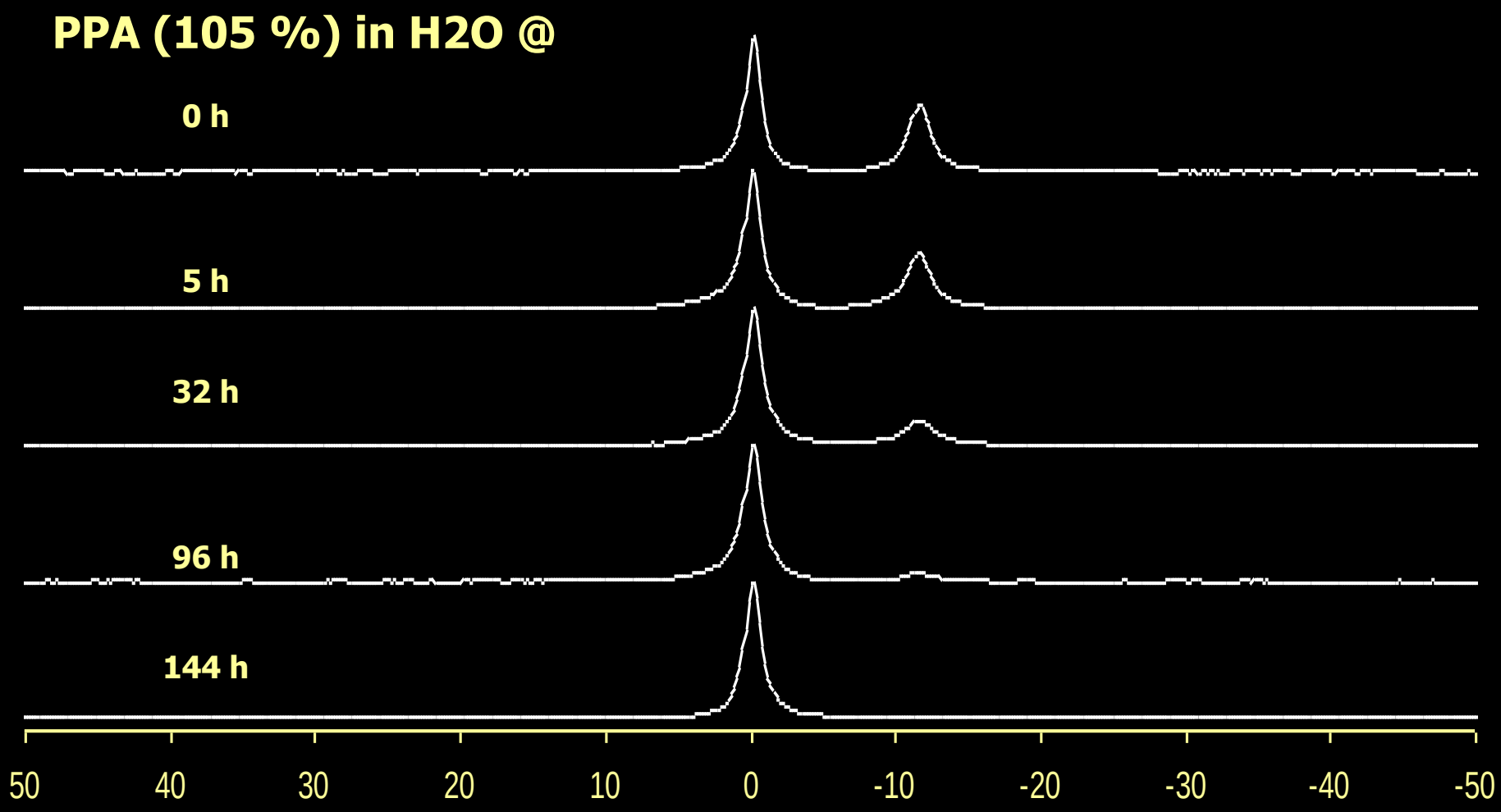
About Polyphosphoric Acid

…..Polyphosphoric acid is highly hygroscopic and rapidly absorbs moisture when exposed to air. Besides making accurate weighing of a sample difficult, the absorbed moisture begins the hydrolysis process.

When water is added to the sample, the hydrolysis process is free to proceed to completion. Quantitative data on rate of hydrolysis is scarce. At room temperature the rate is slow. …..*

* http://www.innophos.com/brochures/Plphsphrccdss/page1.asp

105 % PPA in Water



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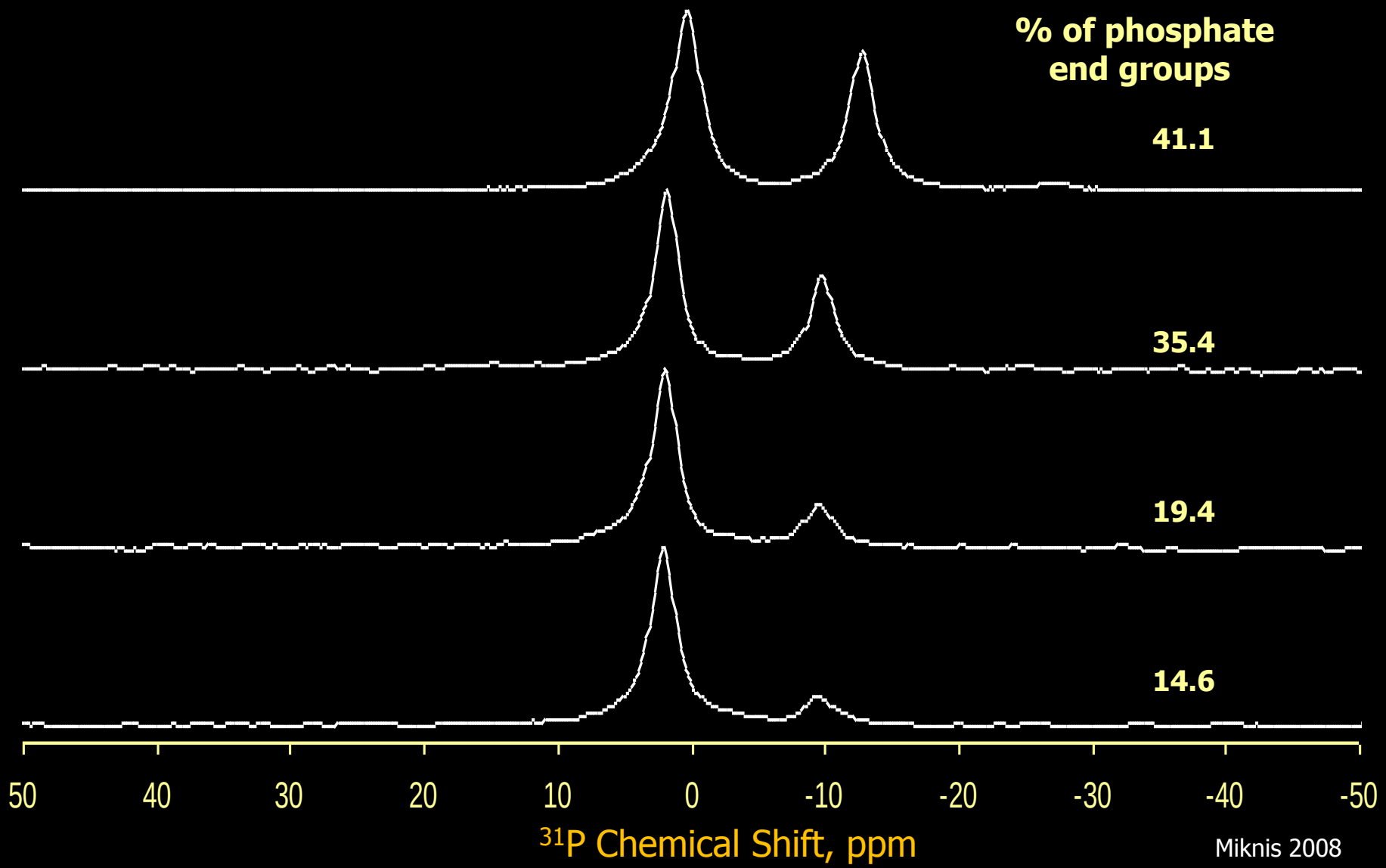
1.5 % PPA in Asphalt



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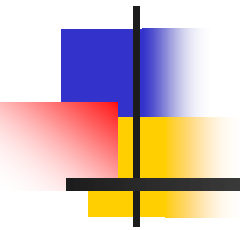
Closing Comment

Common Opinion is that Polyphosphoric Acid Chemically ages or Accelerates Oxidative Aging of Asphalt. Results Reported in Patents Cited Indicate that Polyphosphoric Acid Actually has Anti-Oxidative Characteristics in the Asphalts Studied.

Conclusions

- The Effects of Asphalt Modification with Polyphosphoric Acid is Asphalt and Crude Source Dependent.
- Polyphosphoric Acid is a valuable tool to binder suppliers necessary to provide binders that meet current specifications and provide performance desired.
- It is the Formulators Responsibility to Investigate Performance Characteristics, Good or Bad



Thank You!