Asphalt Component Compatibility
An Overview

RAP ETG Meeting

October 29, 2008

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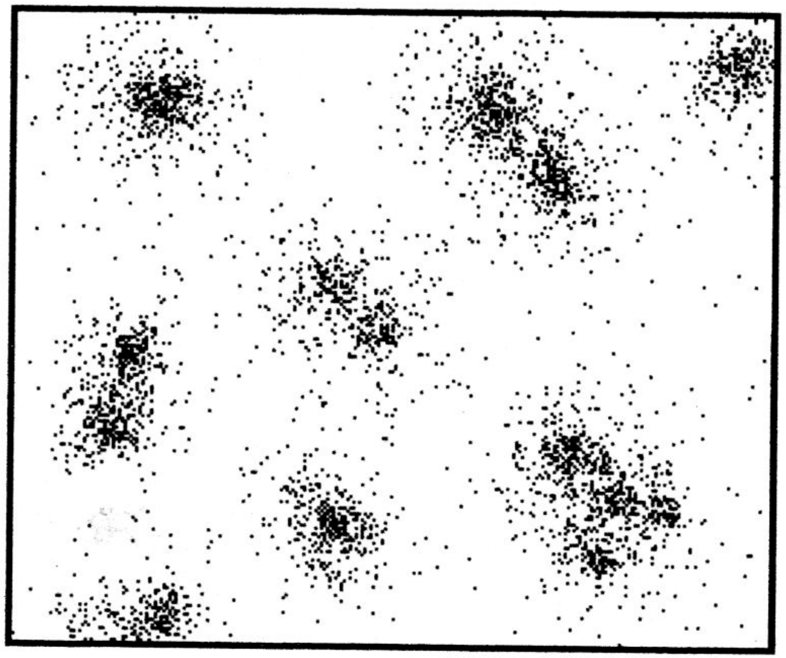
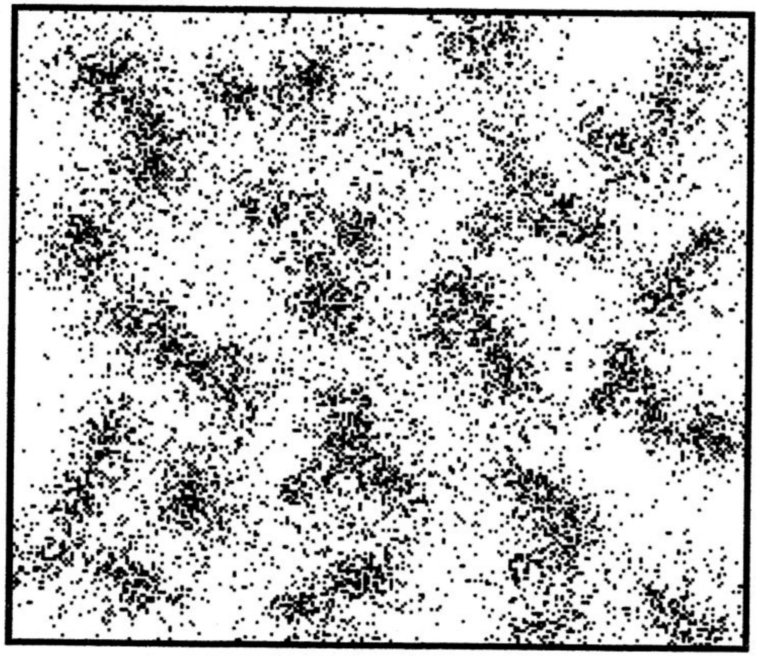
MICROSTRUCTURAL MODEL OF ASPHALT

WELL DISPERSED



GOOD COMPONENT COMPATIBILITY

POORLY DISPERSED



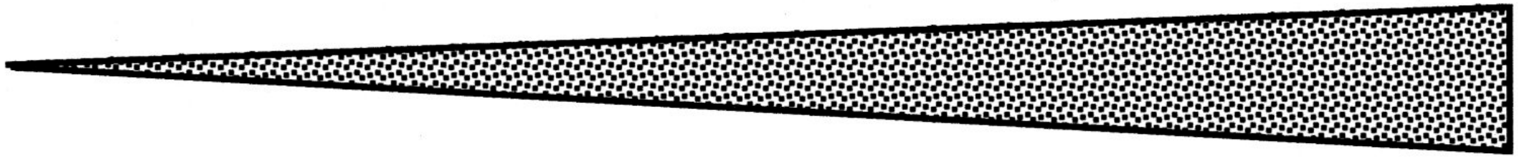
POOR COMPONENT COMPATIBILITY

ROSTLER	CORBETT	FUNCTION
PARAFFINS	SATURATES	GEL
2ND ACIDAFFINS	NAPHTHENE AROMATICS	FLUIDITY
1ST ACIDAFFINS		SOLVENT
NITROGEN BASES	POLAR AROMATICS	DISPERSANT
ASPHALTENES	ASPHALTENES	THICKENER

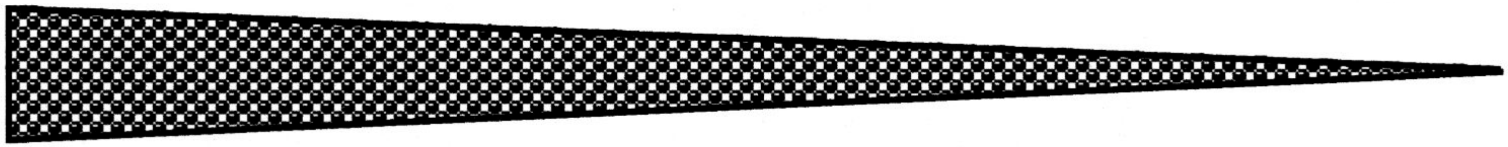
COMPOSITION *VS* PHYSICOCHEMICAL PROPERTIES

SATURATES → NAPHTHENE AROMATICS → POLAR AROMATICS

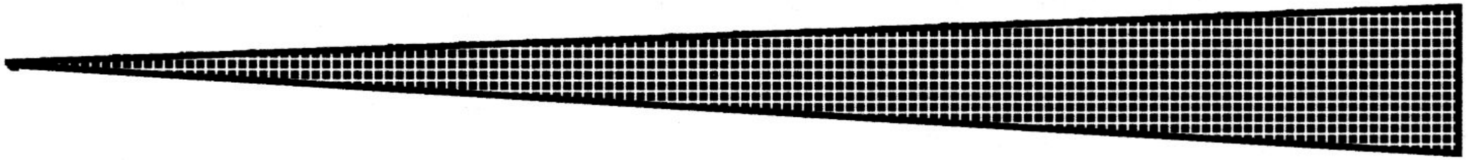
DEGREE OF MOLECULAR ASSOCIATION (EFFECTIVE MW)



CONCENTRATION OF SULFOXIDE PRECURSORS (SULFIDES)

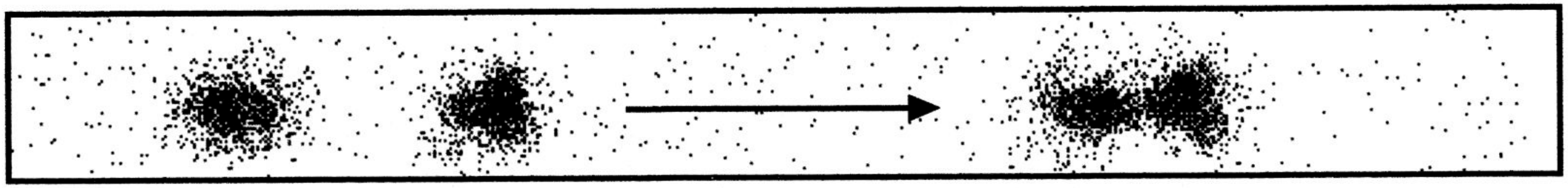


CONCENTRATION OF KETONE PRECURSORS (BENZYL CARBON)



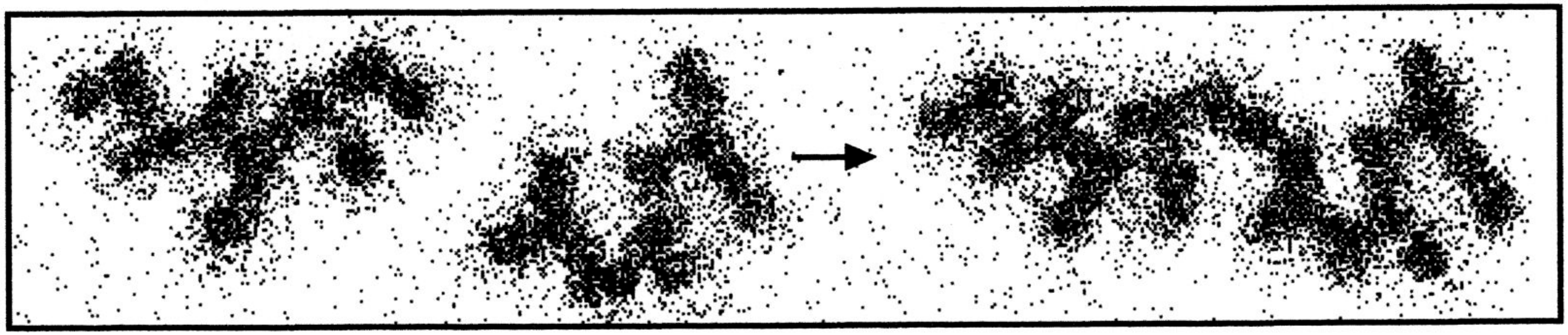
ASSOCIATION *VS* EFFECTIVE MOLECULAR WEIGHT

DISPERSED POLAR WITH DISPERSED POLAR

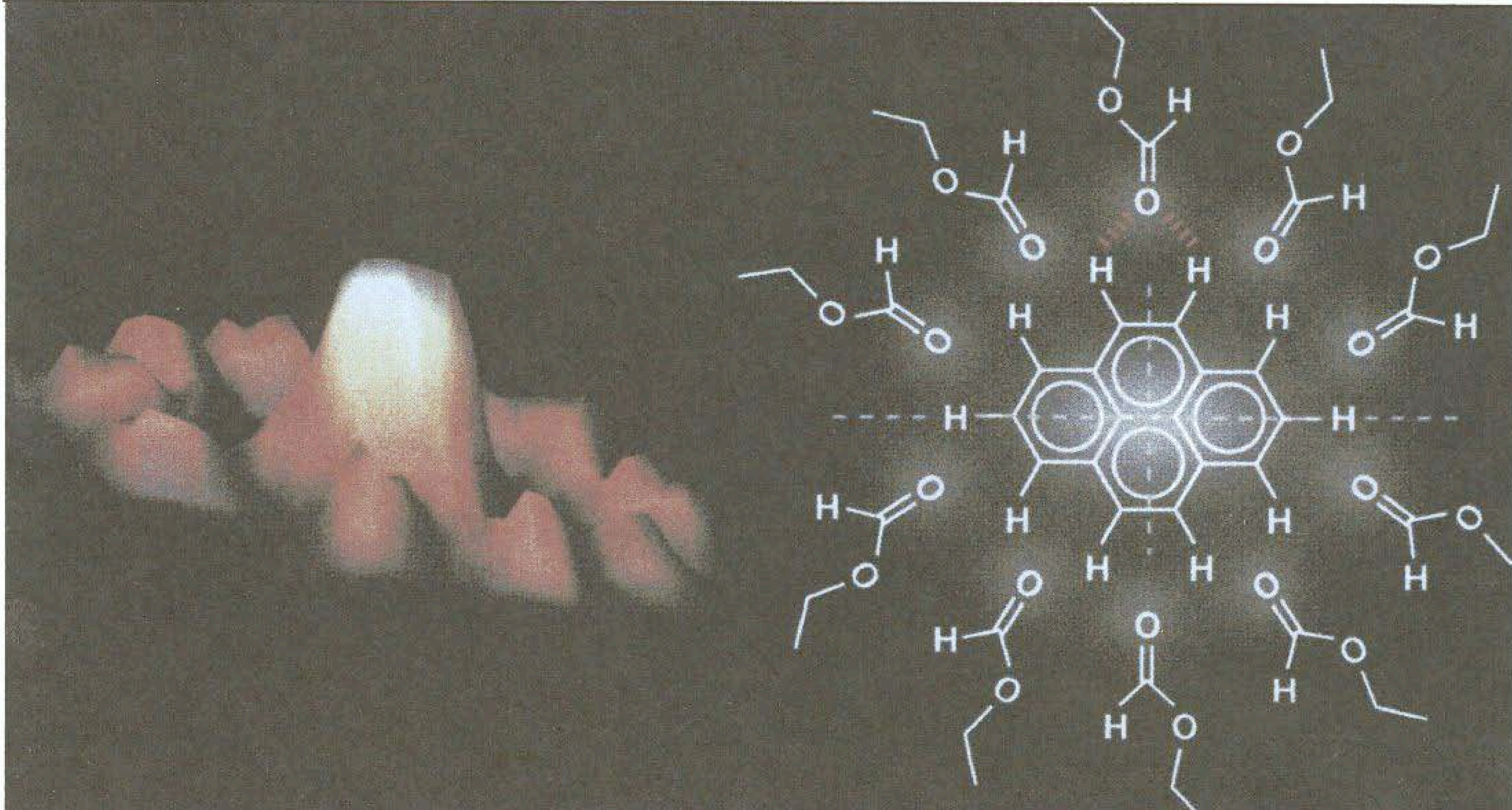


DISPERSED POLAR WITH ASSOCIATED POLAR

ASSOCIATED POLAR WITH ASSOCIATED POLAR



PROPOSED H-BONDING COMPLEX BETWEEN PYRENE AND ETHYL FORMATE BASED ON SMI* IMAGE



*Scanning Tunneling Microscopy

Reference: Prof. Peter McBreen and group at Laval University, Quebec as reported in the October 16, 2006 issue of Chemical and Engineering News, p. 51.

JCP 10/17/06

EFFECT OF MOLECULAR TYPE ON VISCOSITY OF FRACTIONS FROM MOLECULAR DISTILLATION CUT

FRACTION	*APPARENT MOLECULAR WEIGHT*	*VISCOSITY (POISES)*
SATURATES	500	100
AROMATICS	500	10,000
RESINS	500	1,000,000

cf: GRIFFIN AND COWORKERS,
J. CHEM. ENG. DATA, 4, 249, (1959)

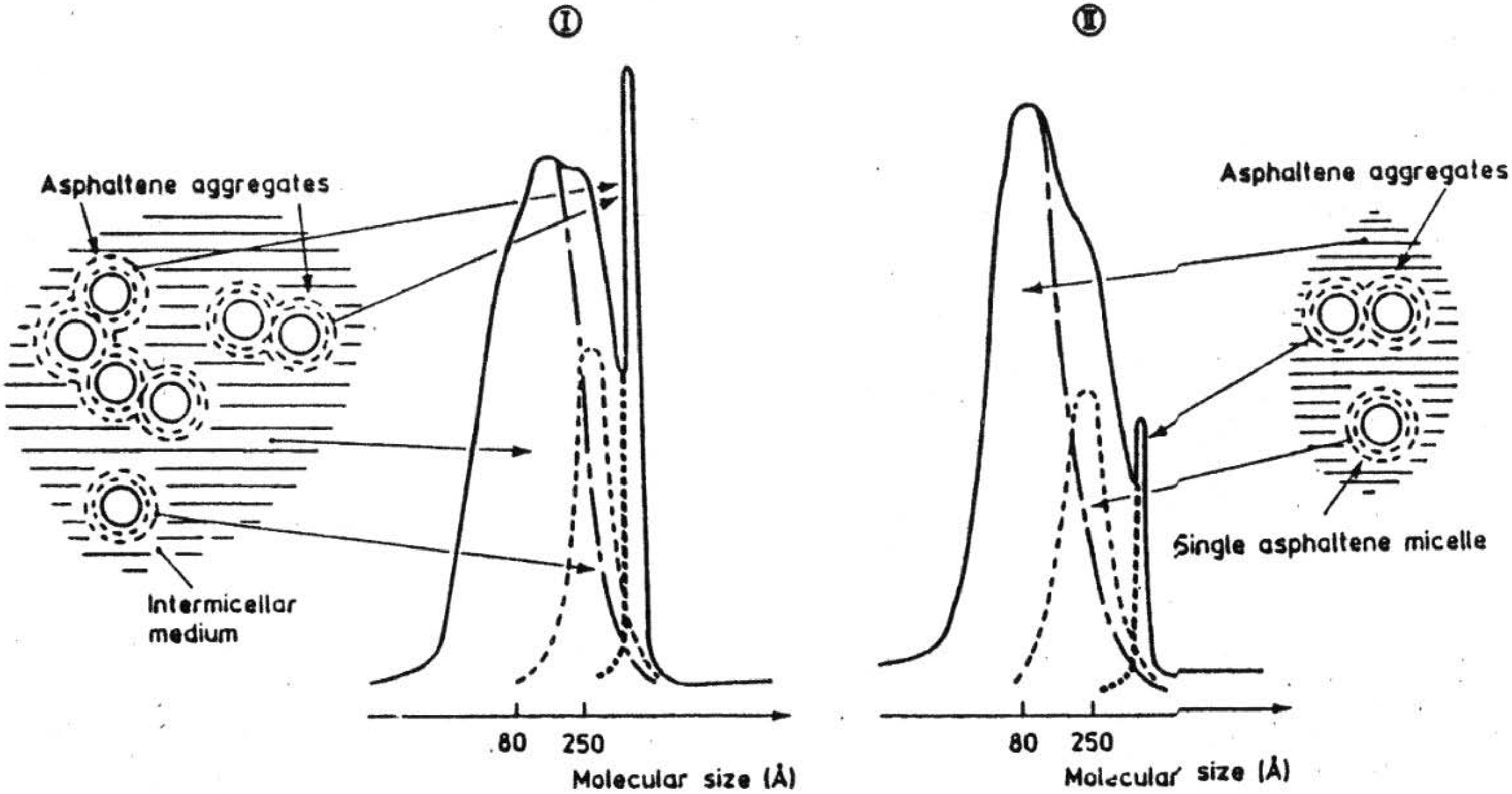


Fig. 16 - GPC chromatograms and colloidal structure of road asphalt cements :
I , blown asphalt cement ; II , straight-run asphalt cement
the chromatograms have been broken down into three populations :

—·— *intermicellar medium (saturated oils and aromatics)*
----- *asphaltene and resin micelles*
••••• *resin-peptized asphaltene aggregates*

FAST HPLC/SEC OF AGED AND UNAGED AAA-1 AND AAG-1

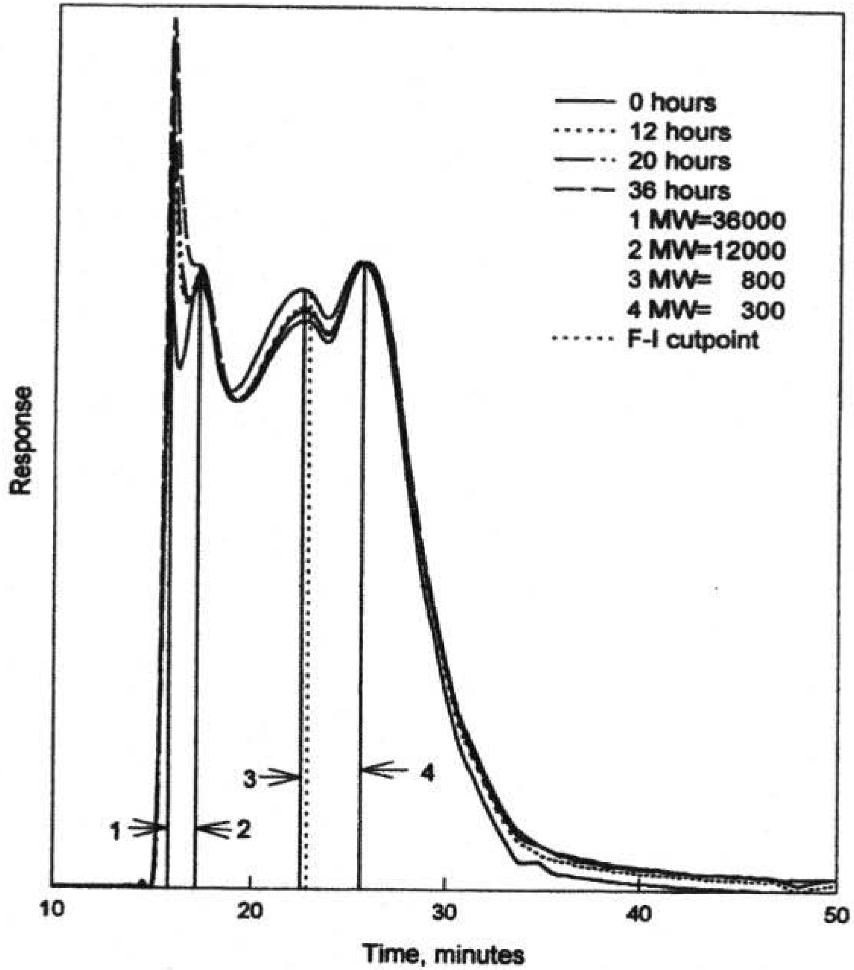


Figure O-6. HPLC/SEC of asphalt AAA-1 RTFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 22.84 min.

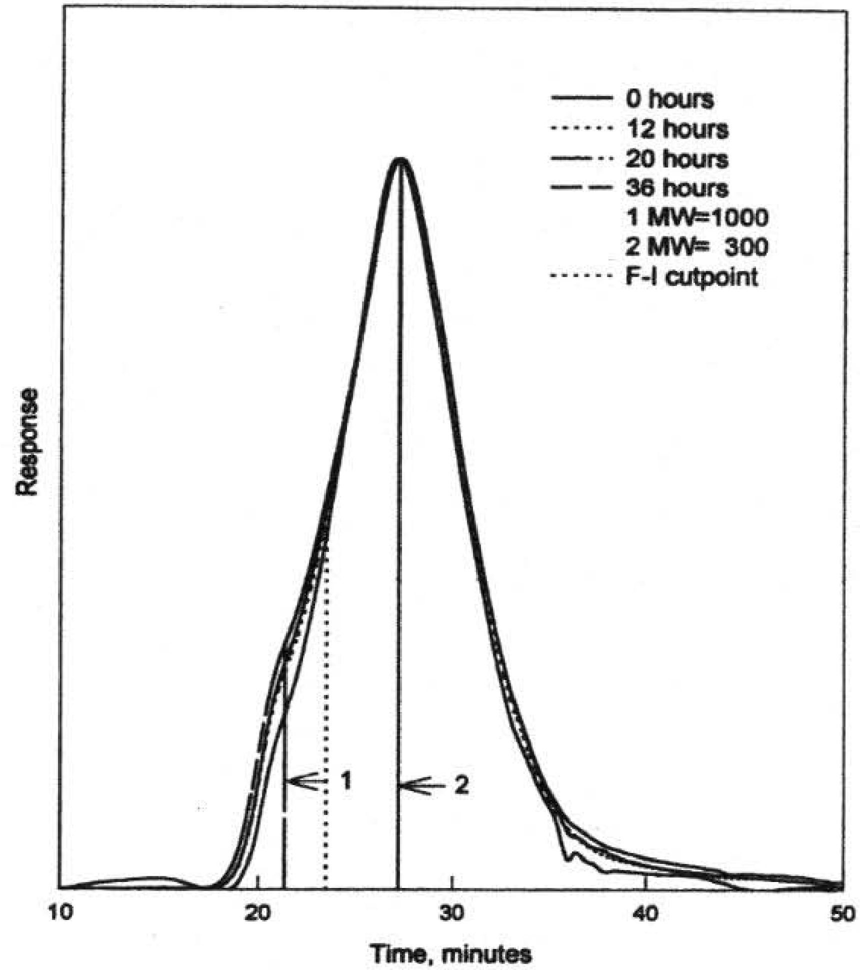


Figure O-11. HPLC/SEC of asphalt AAG-1 RTFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 23.47 min.

Source: WRI Semi-Annual Technical Report --- Fundamental Properties of Asphalts and Modified Asphalts, November 1, 1996, pp. 196-217.

METHODS FOR ESTIMATION OF COMPATIBILITY

- ◇ Asphaltene dispersibility index
- ◇ Asphaltene filtering rate
- ◇ Heithaus parameters
- ◇ Asphaltene compatibility index (Branthaver)
- ◇ Relative viscosity (V. asphalt/ V. maltenes)
- ◇ Reduced specific viscosity
- ◇ Asphaltene settling test (Plancher)
- ◇ Ratios of fractions (Corbett, Roster, Schweyer, Traxler)

COMPOSITION AND COMPONENT COMPATIBILITY

HEITHAUS

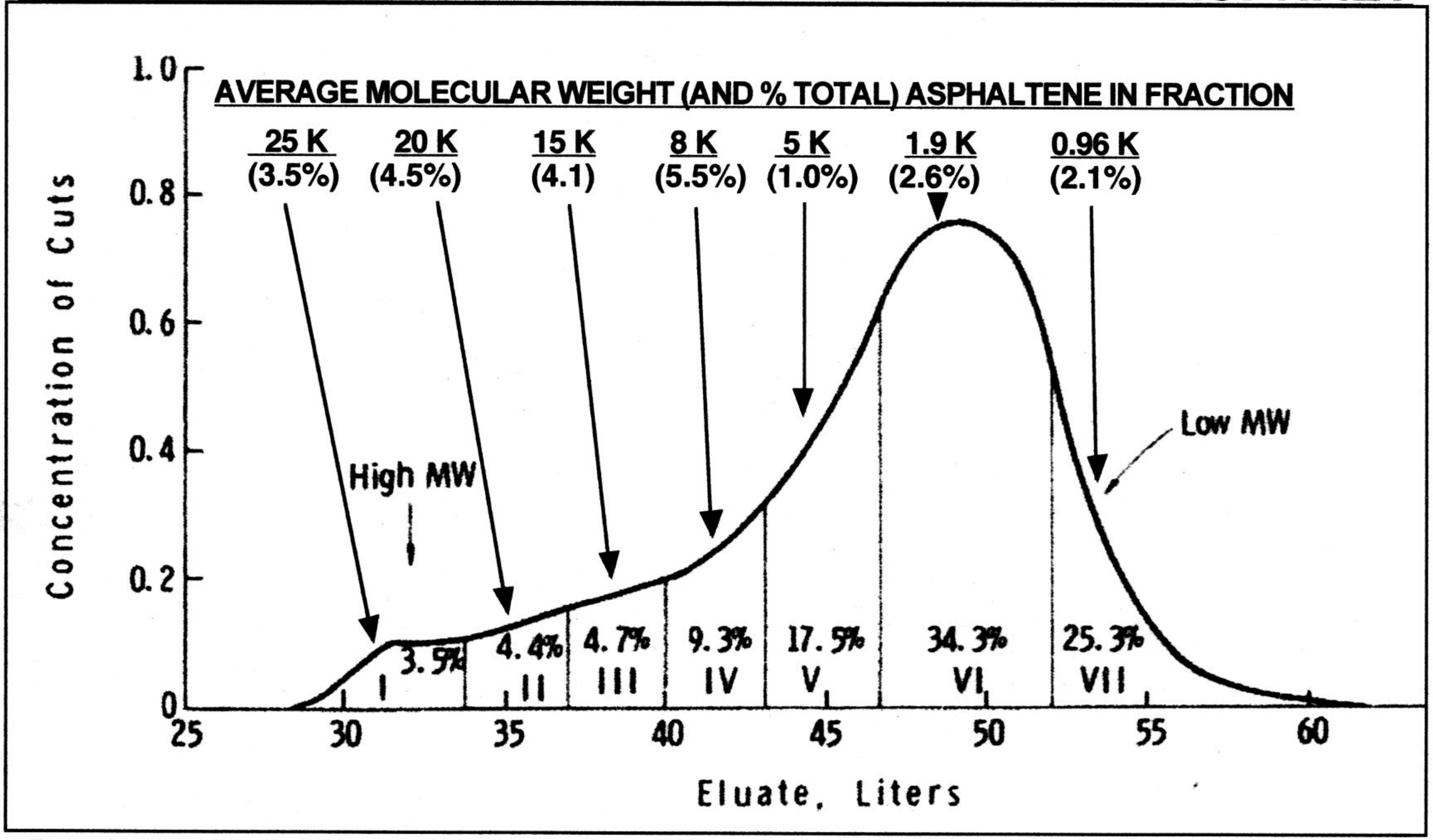
MUST MATCH -

- SOLVENT POWER OF PETROLENES
- DISPERSIBILITY OF ASPHALTENES

ALTGELT AND HARLE -

- "THICKENING POWER" OF ASPHALTENES RELATED TO DEGREE OF ASSOCIATION
- DEGREE OF ASSOCIATION OF ASPHALTENES CONTROLLED BY SOLVENT POWER OF PETROLENES

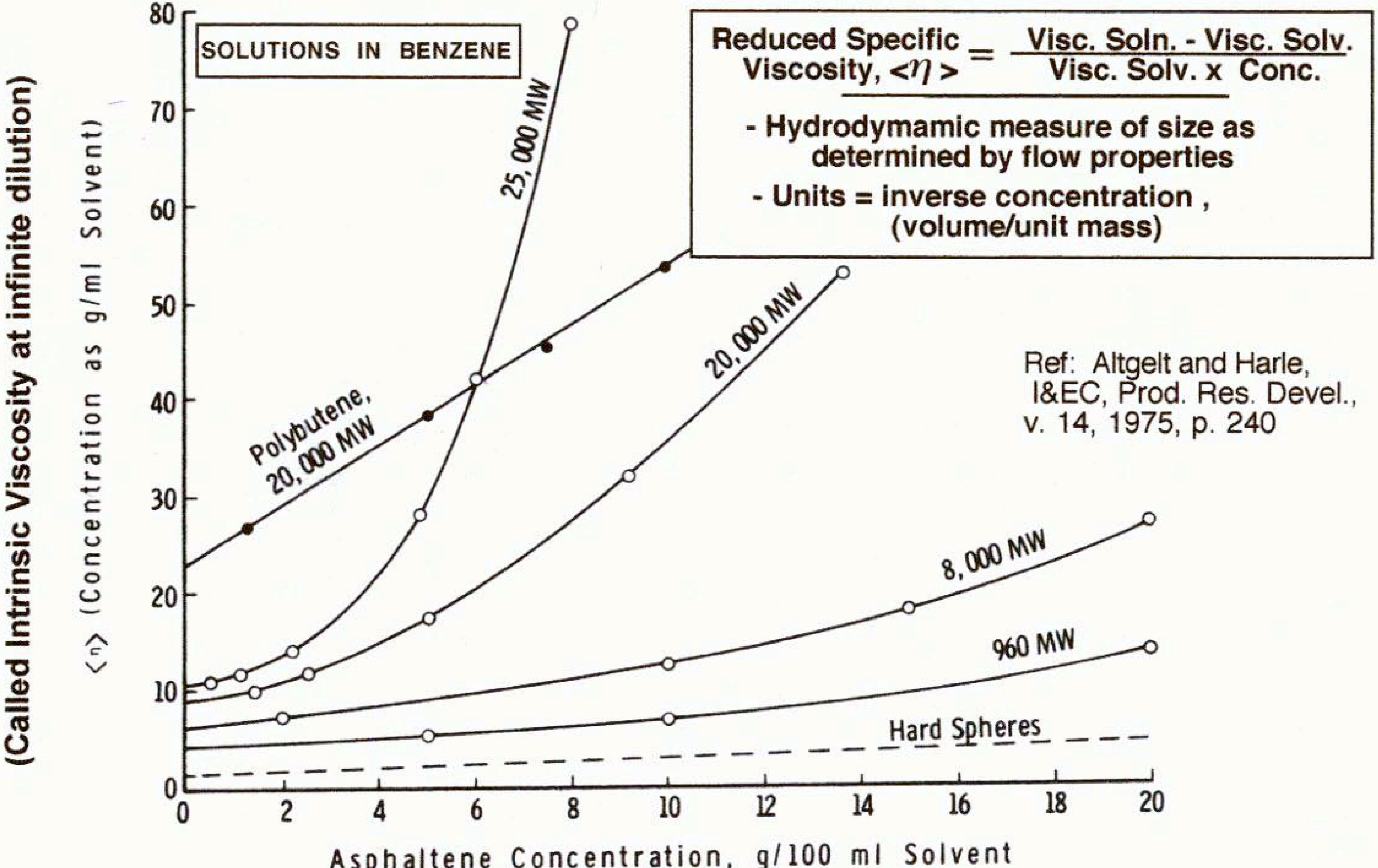
ALTGELT'S GPC SEPARATION OF BOSCAN ASPHALT



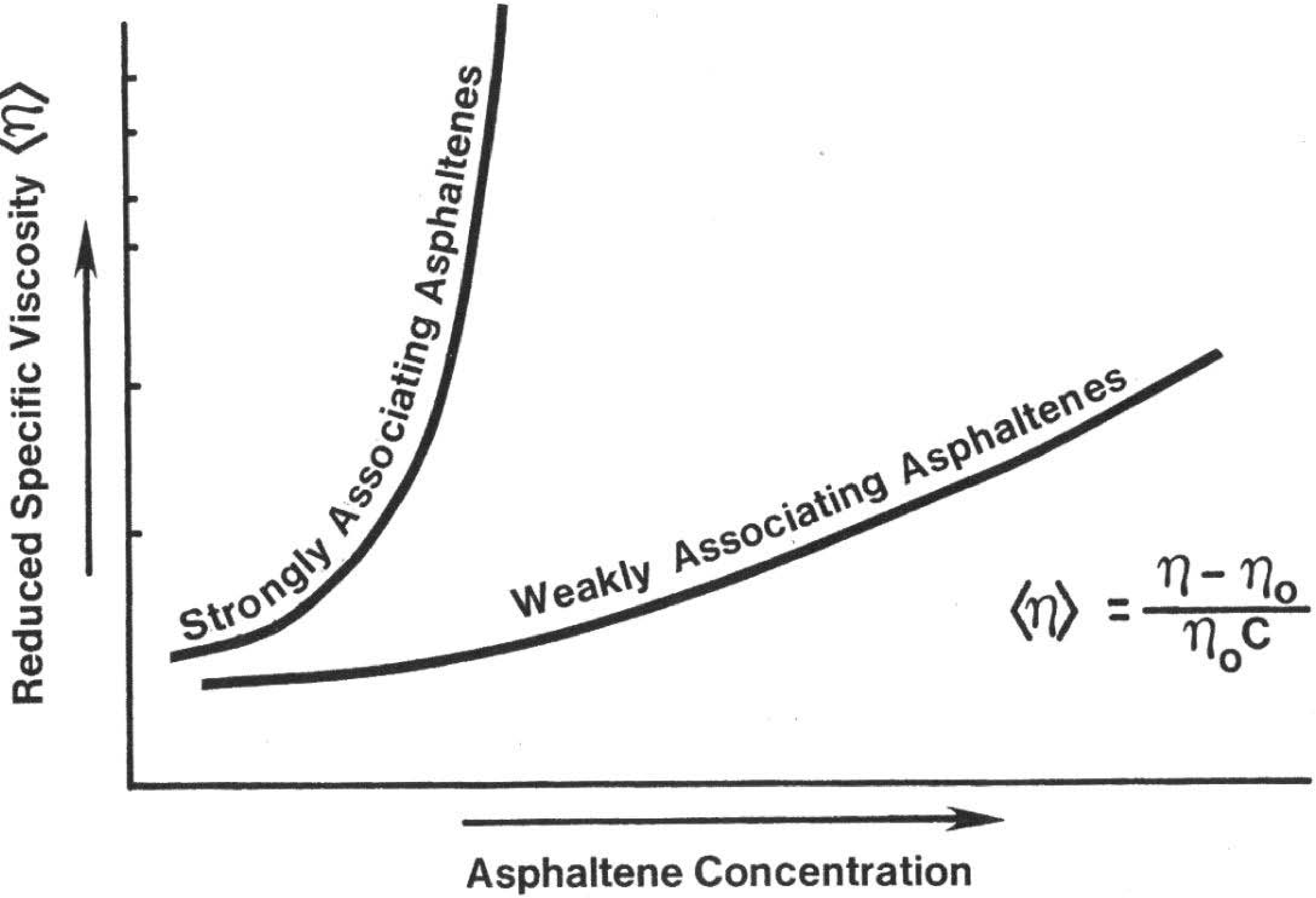
Data from: Altgelt, K.H. and O.L. Harle. "The Effect of Asphaltenes on Asphalt Viscosity, *I&EC, Prod. Res. Devel., v. 14,* **1975,** pp. 240-246.

JCP 09/08

EFFECT OF ASPHALTENE APPARENT MW ON REDUCED SPECIFIC VISCOSITY

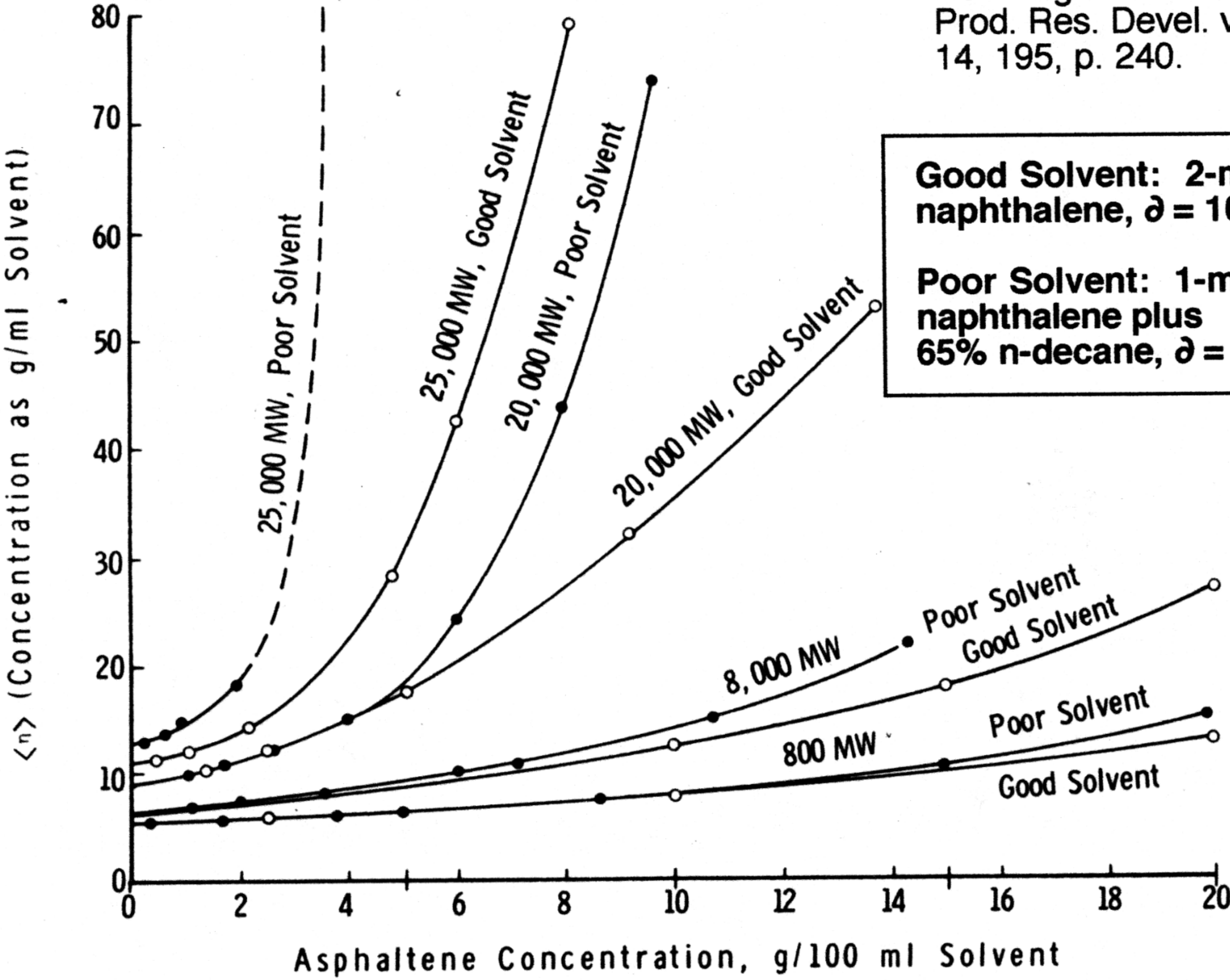


Effect of Association of Asphaltenes on reduced Specific Viscosity



EFFECT OF SOLVENT AND MW ON REDUCED SPECIFIC VISCOSITY

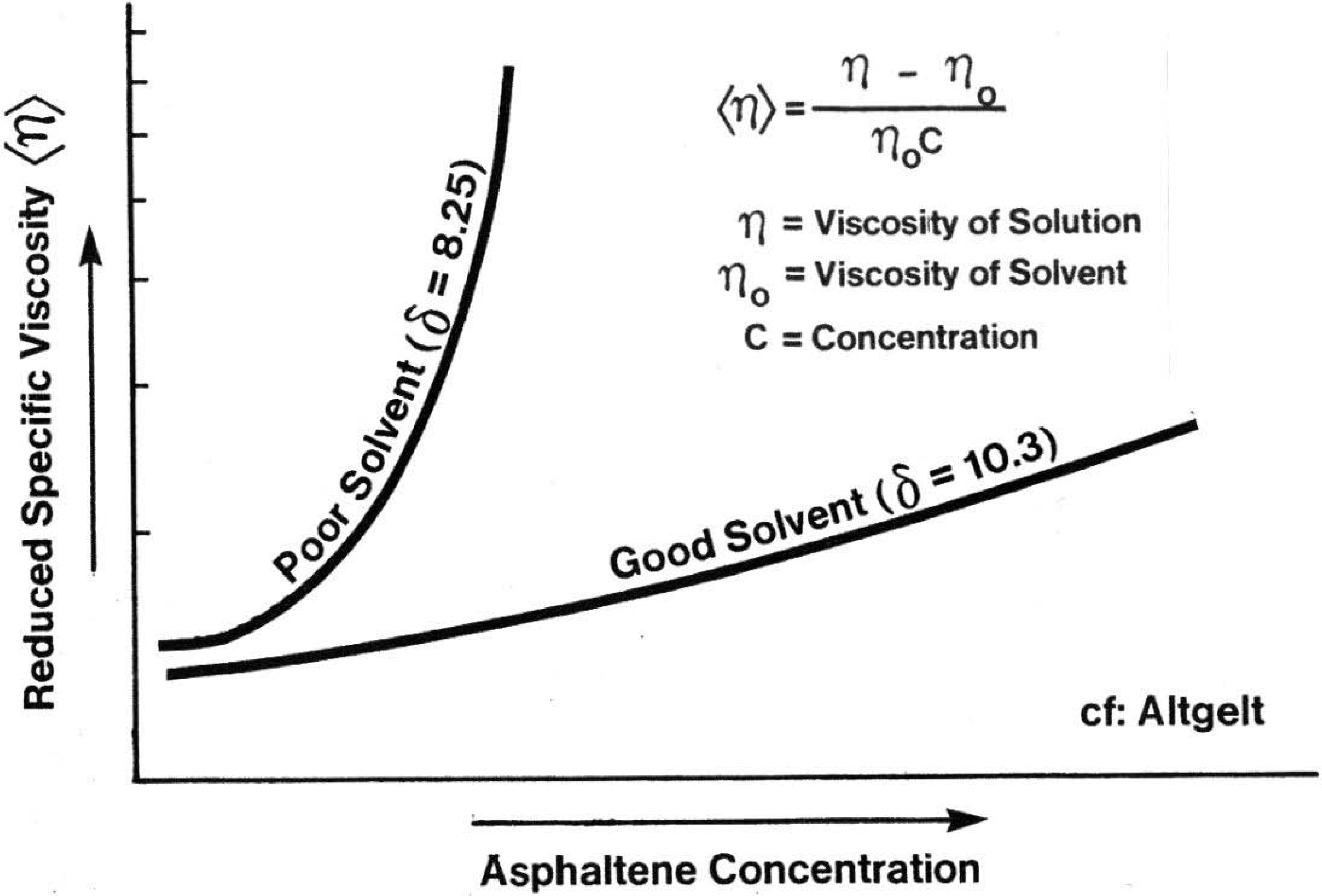
Ref: Altgelt and Harle, Prod. Res. Devel. v. 14, 195, p. 240.



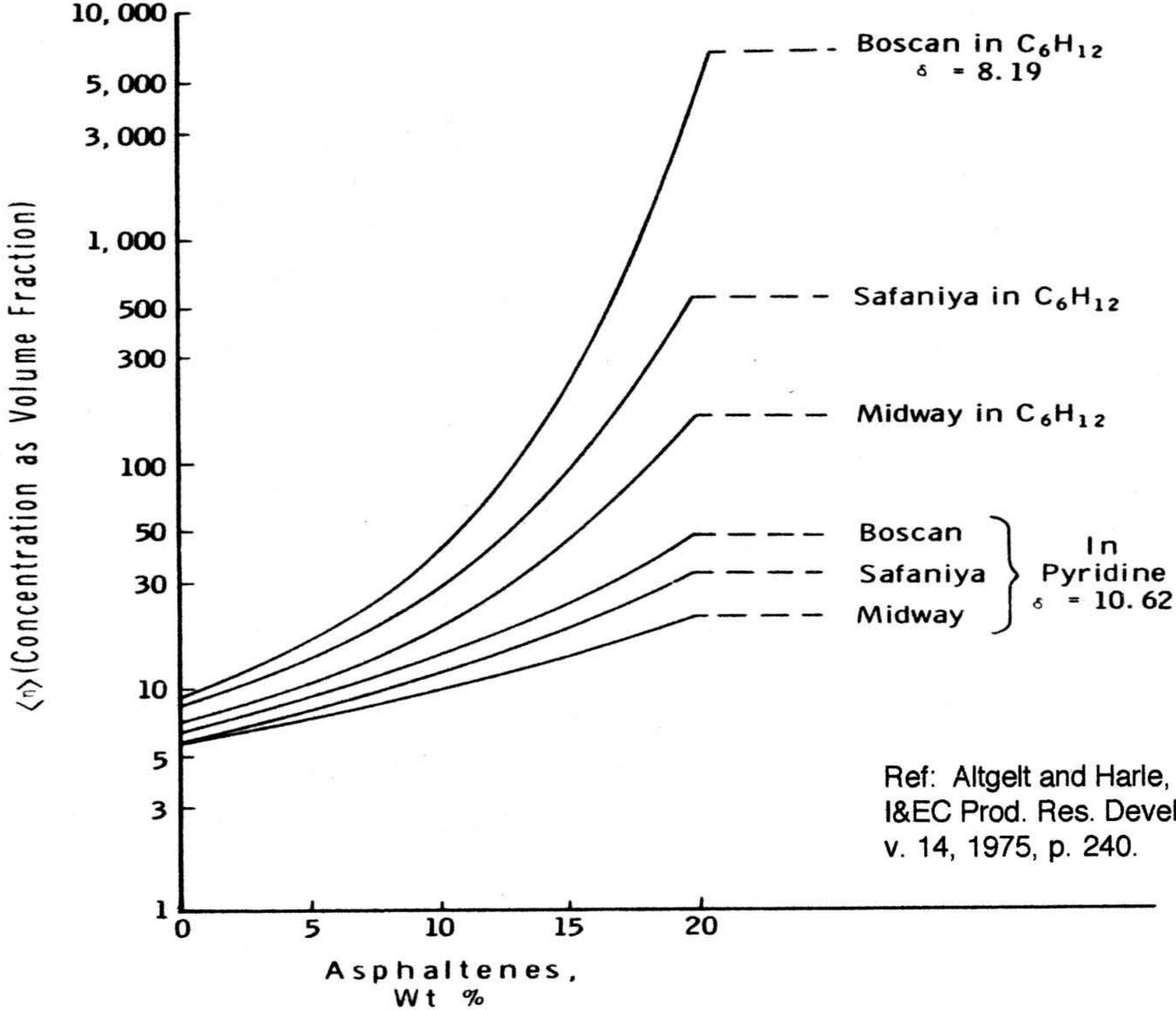
Good Solvent: 2-methyl naphthalene, ∂ = 10.3

Poor Solvent: 1-methyl naphthalene plus 65% n-decane, ∂ = 8.6

Effect of Solvent Power on Reduced Specific Viscosity of Asphaltenes

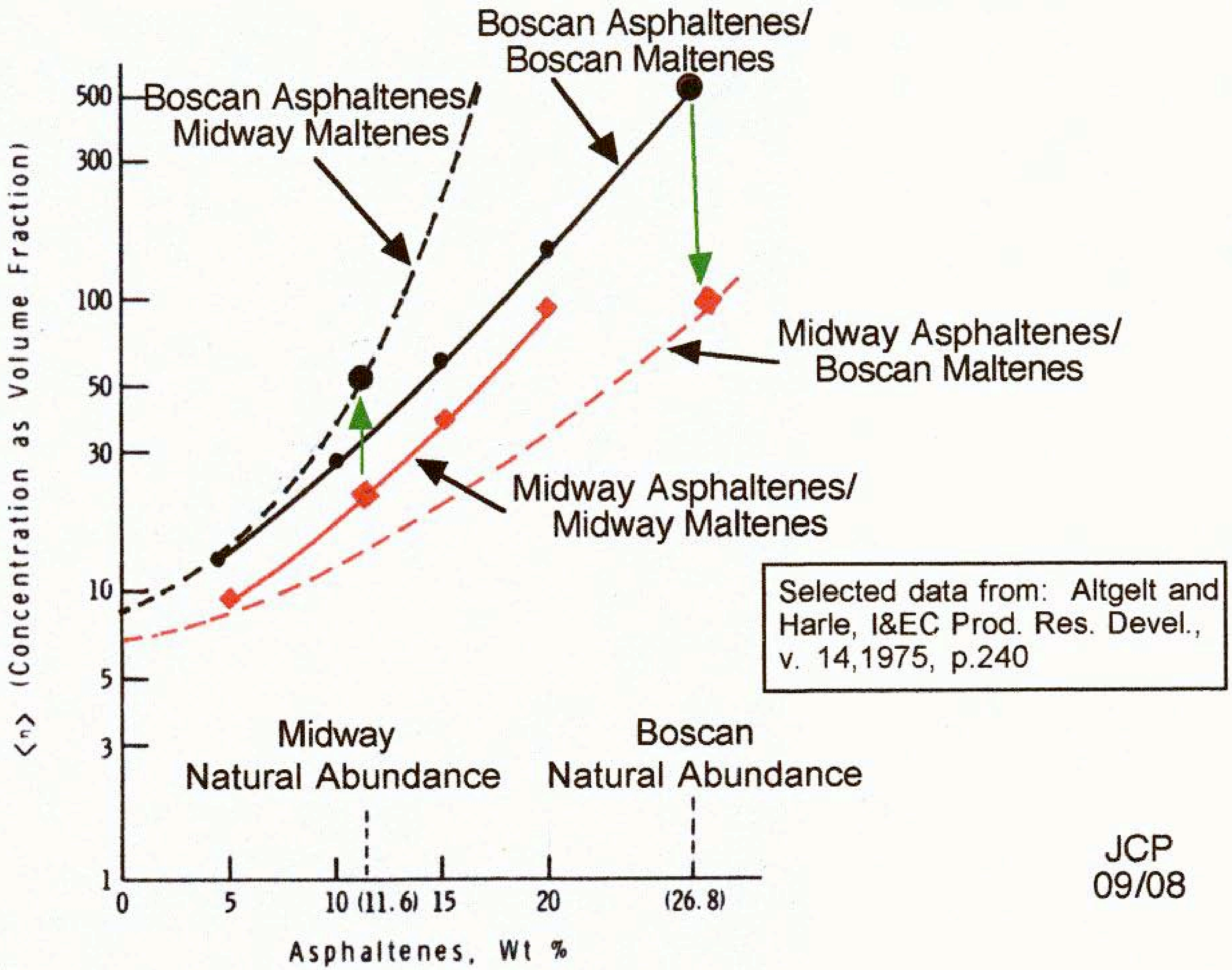


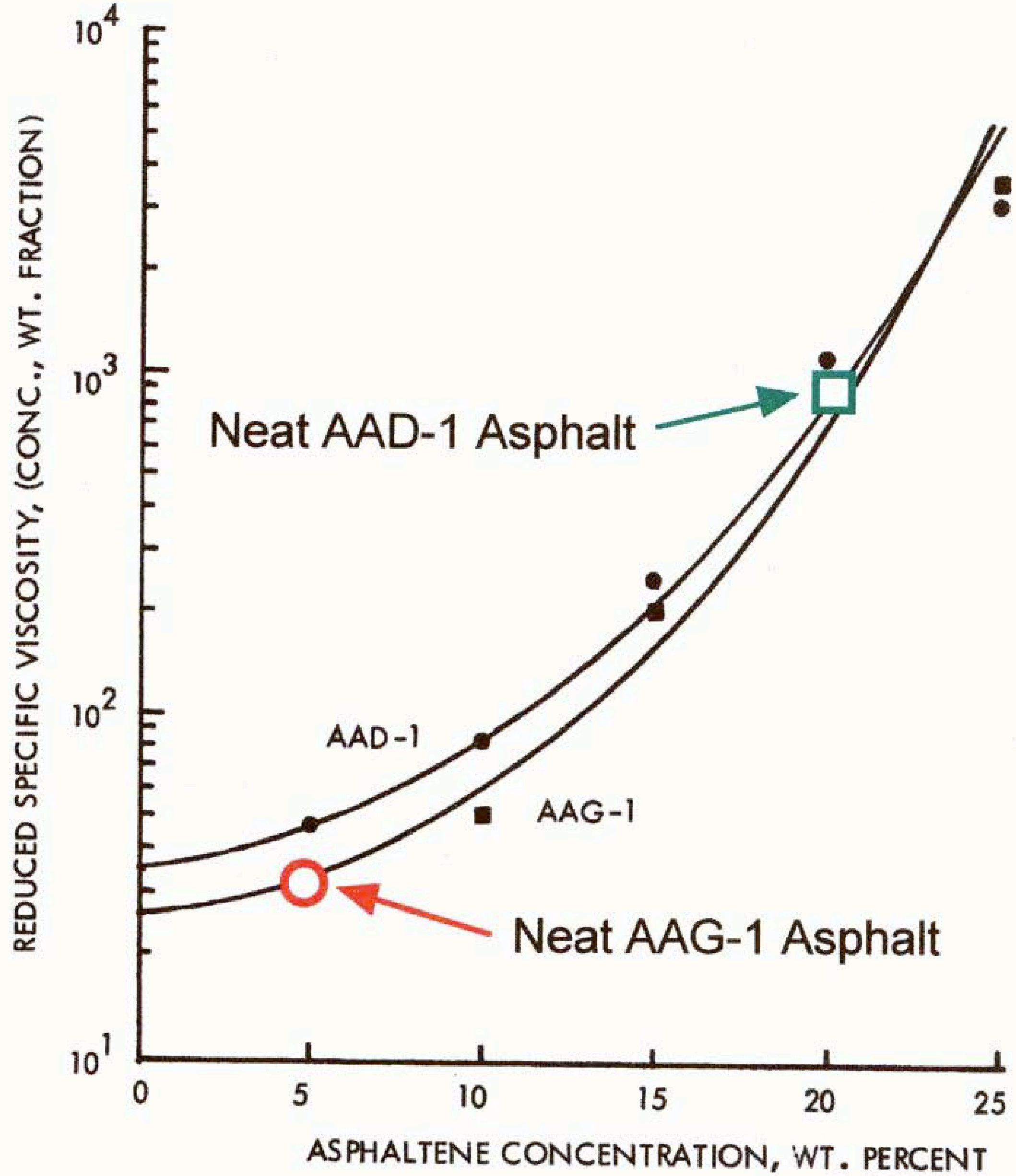
EFFECT OF SOLVENT AND ASPHALT SOURCE ON REDUCED SPECIFIC VISCOSITY



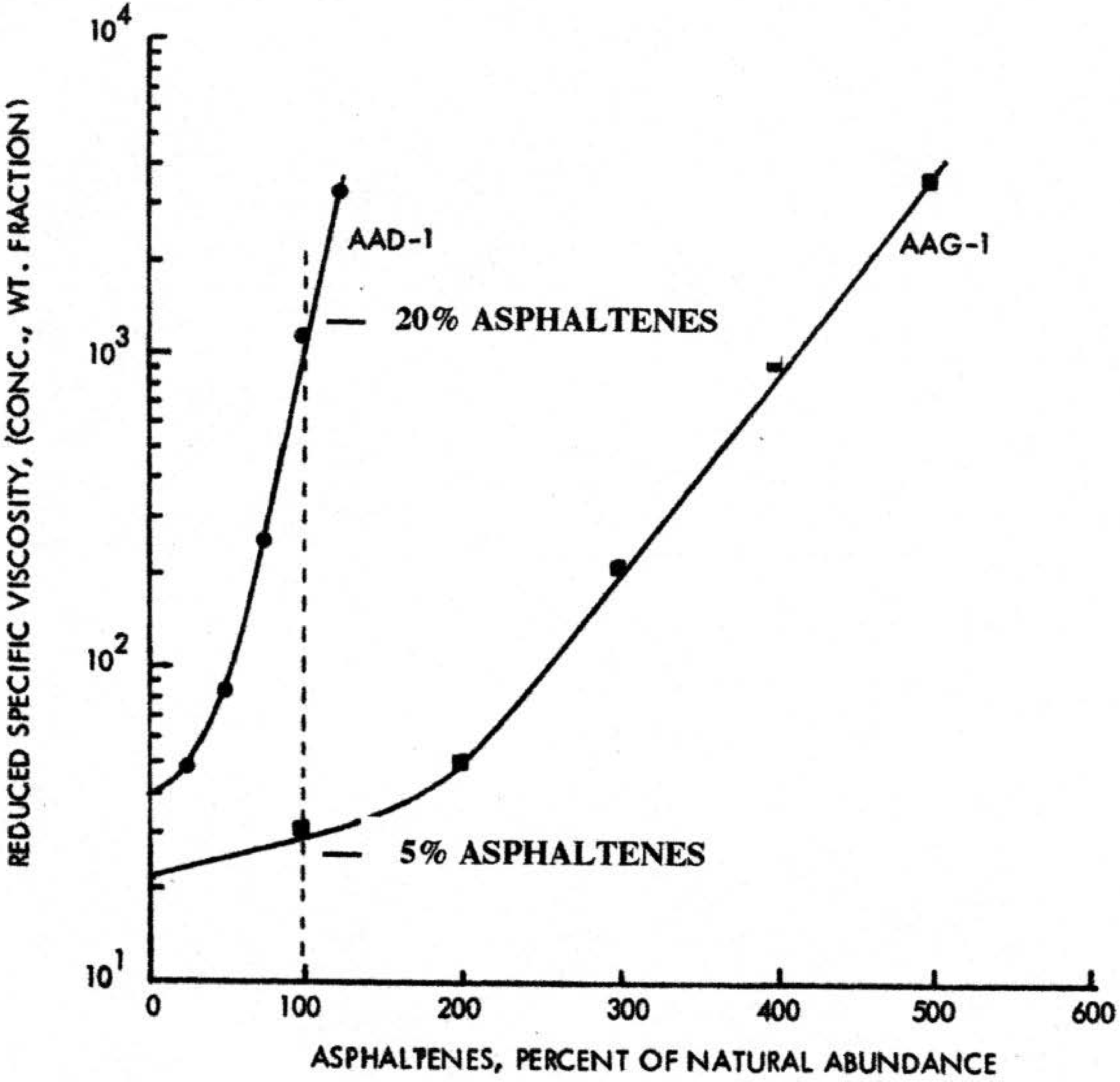
Ref: Altgelt and Harle, I&EC Prod. Res. Devel., v. 14, 1975, p. 240.

EFFECT OF COMPATIBILITY ON MOLECULAR SIZE OF MICROSTRUCTURE



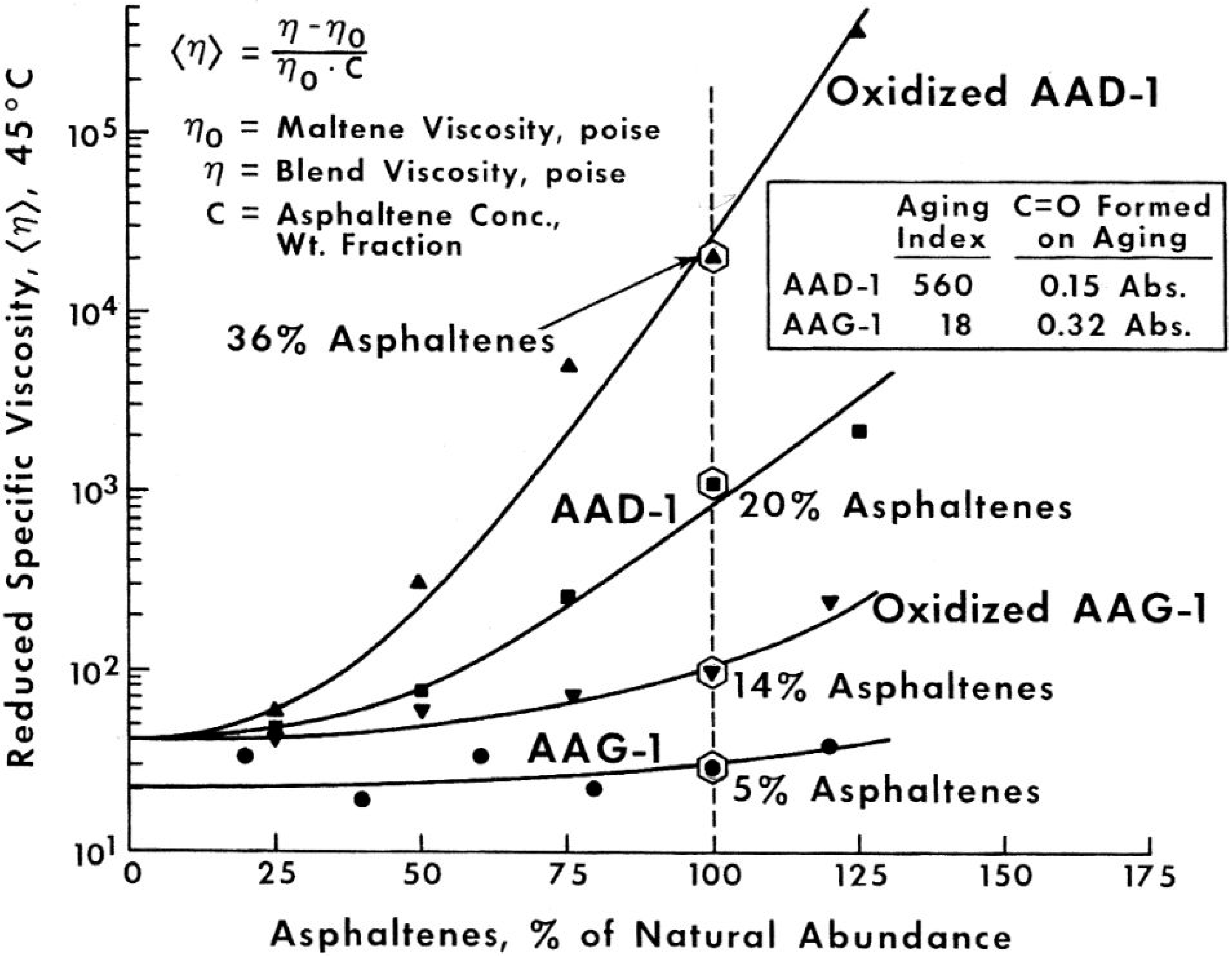


10^4
10^3
10^2
10^1
REDUCED SPECIFIC VISCOSITY, (CONC., WT. FRACTION)
0
5
10
15
20
25
ASPHALTENE CONCENTRATION, WT. PERCENT
AAD-1
AAG-1
Neat AAD-1 Asphalt
Neat AAG-1 Asphalt



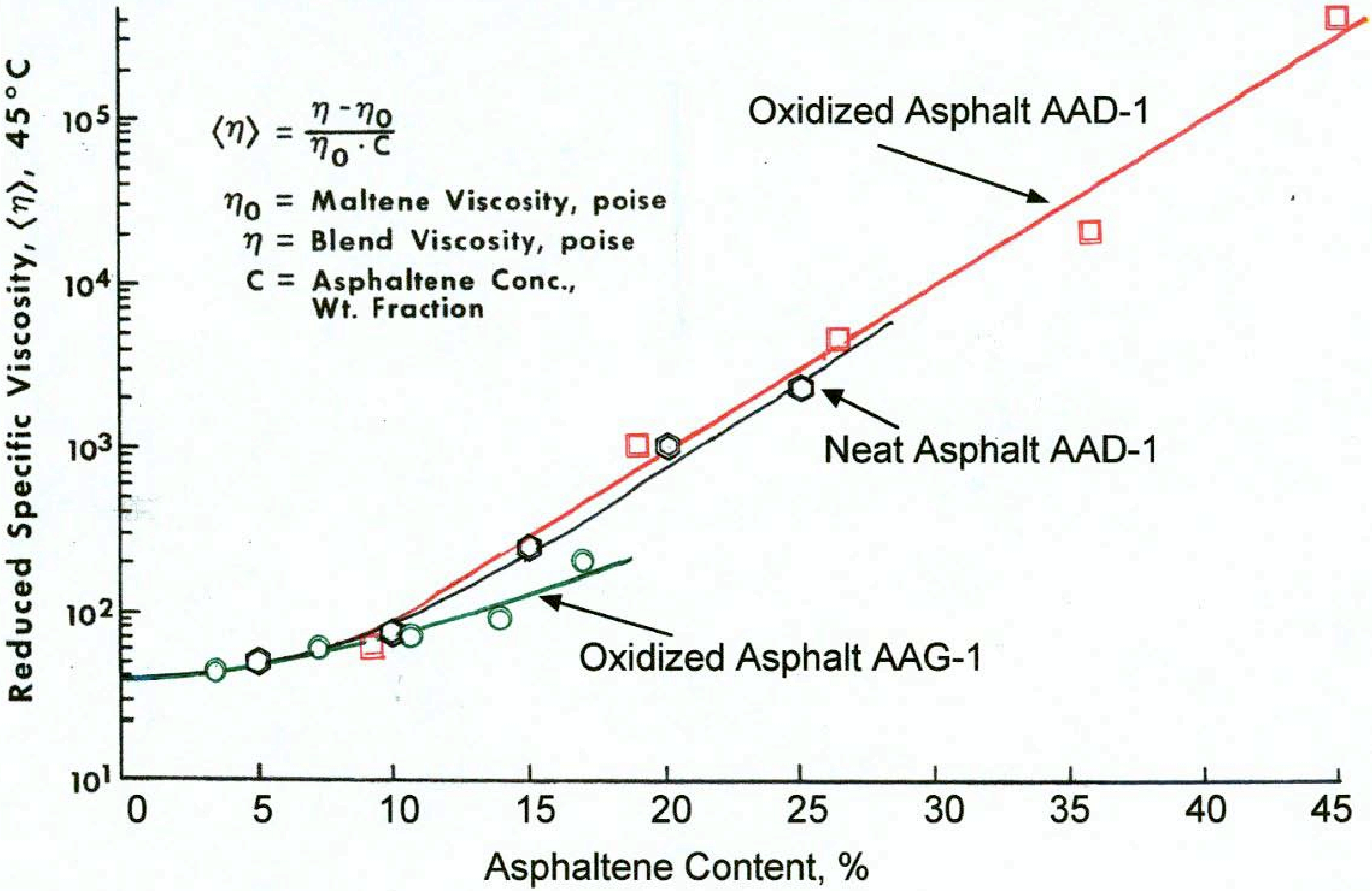
10^4
10^3
10^2
10^1
REDUCED SPECIFIC VISCOSITY, (CONC., WT. FRACTION)
AAD-1
AAG-1
20% ASPHALTENES
5% ASPHALTENES
0
100
200
300
400
500
600
ASPHALTENES, PERCENT OF NATURAL ABUNDANCE

EFFECTS OF MICELLAR ASSOCIATION ON CHEMICAL AND PHYSICAL PROPERTY CHANGES ON AGING



	Aging Index	C=O Formed on Aging
AAD-1	560	0.15 Abs.
AAG-1	18	0.32 Abs.

RELATIVE SIZE OF ASPHALTENE AGGLOMERATE (RED. SPEC. VISC.) VERSUS ASPHALTENE CONTENT



EFFECTS OF CROSSBLENDING MALTENES AND ASPHALTENES

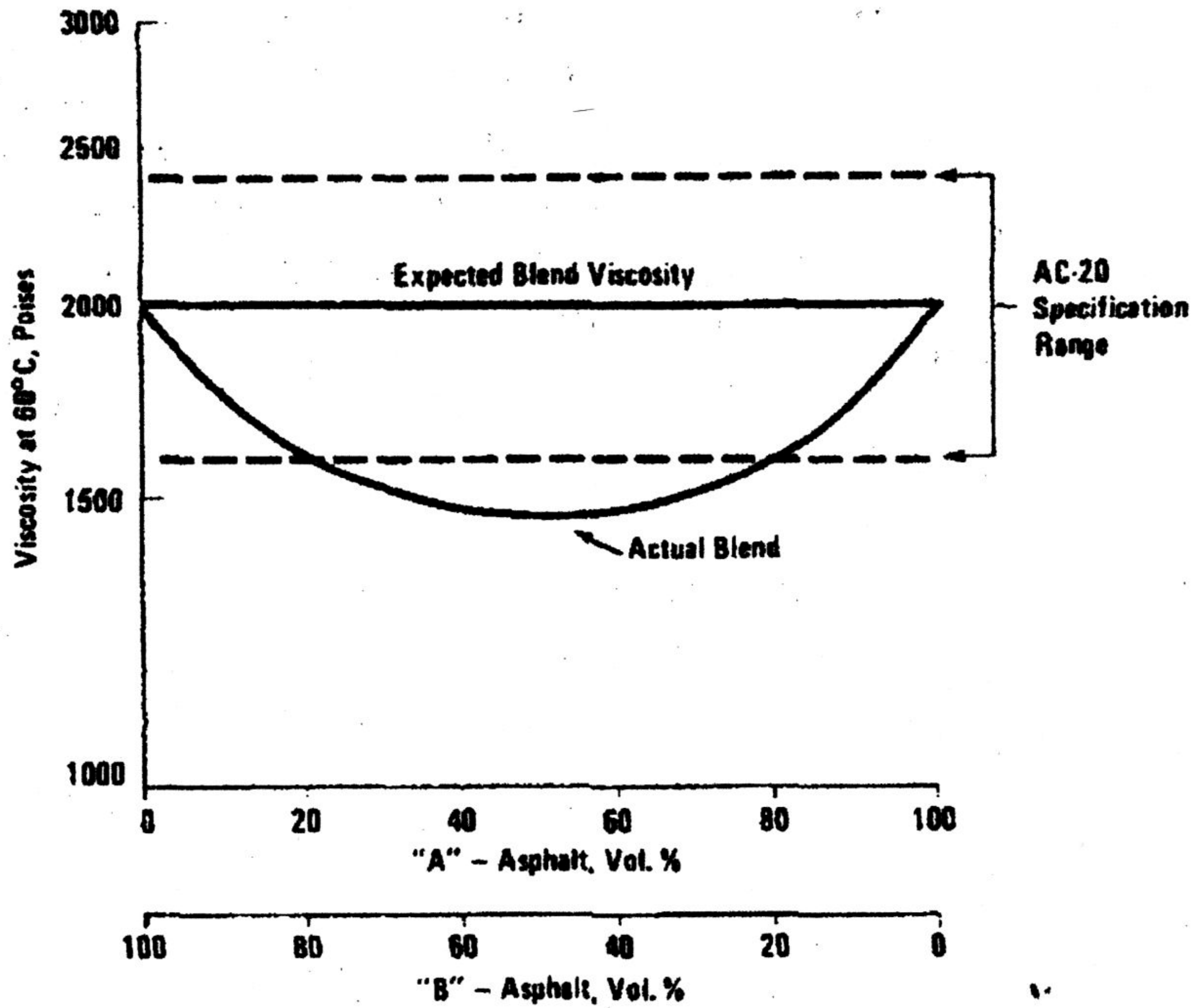
Mix #	Components of Mixture	Neat: Vis., Pa•s 25°C, 1 r/s	Neat: Tan ∂ 25°C, 1 r/s	Neat: R. S. Visc. 25°C, 1 r/s	TFOT + PAV, 60°C, 144 hours: Vis., Pa•s 25°C, 1 r/s	TFOT + PAV, 60°C, 144 hours: Tan ∂ 25°C, 1 r/s	TFOT + PAV, 60°C, 144 hours: Aging Index 60°C, 1 r/s
I (A)	AAD Maltenes (79%) AAD Asphaltenes (21%)	49,011	3.2	705	550,650	1.5	15.4
VII (B)	AAG Maltenes (94%) AAG Asphaltenes (6%)	389,100	6.3	64	1,086,400	1.6	4.2
Cross Blends							
V (C)	AAG Maltenes (79%) AAD Asphaltenes (21%)	4,970,900	1.5	287 (?)*	20,662,000	0.8	15.5
III (A) (C)	AAD Maltenes (79%) AAG Asphaltenes (21%)	62, 908	3.7	906	552,310	1.8	9.0
II (D)	AAD Maltenes (94%) AAG Asphaltenes (6%)	1,023	>10	35	7,108	<10	3.7
VI (B) (D)	AAG Maltenes (94%) AAD Asphaltenes (6%)	337,190	6.0	54	2,125,400	2.3	5.3

Data from: "Fundamental Properties of Asphalts and Modified Asphalts", Vol. 1: Interpretive Report FHWA-RD-99-212, Oct. 2001.

(JCP, 09/08)

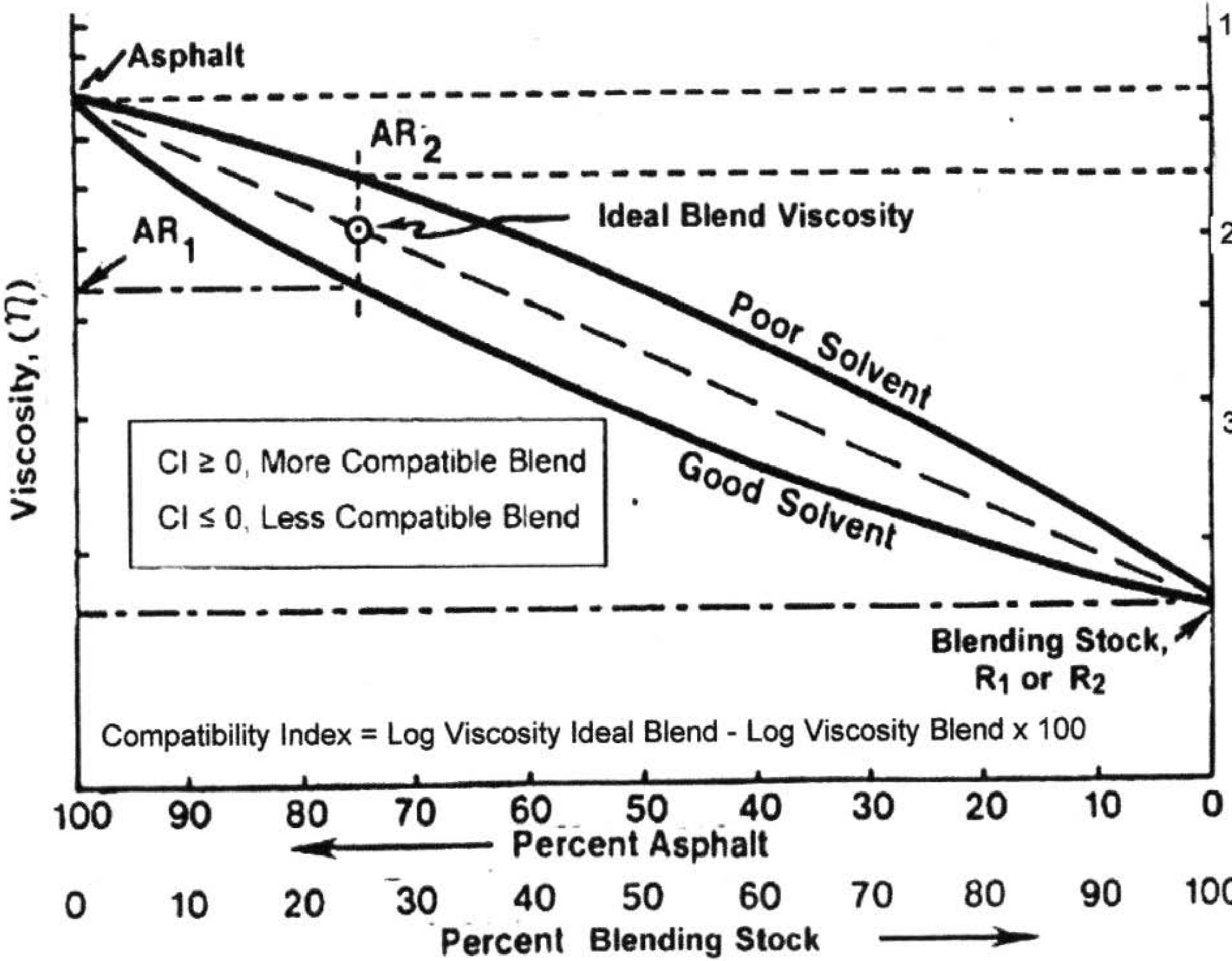
*Value is suspect. Reduced specific viscosity at 60°C is reported as 393.

EFFECT OF BLENDING ON ASPHALT VISCOSITY



Reference: W. J. Kari. "Effects of Construction Practices on the Asphalt Properties in the Mix", *Proc. Canadian Tech. Asphalt Assn.*, vol. XXVII (1982), pp. 321-334. (cited in AAPT, Anderson, Petersen and Christensen, v. 55 (1986), pp. 250-268.

Method for Estimating Component Compatibility of Asphalt with Blending Stock



Assumptions

1. Viscosity will be reduced most by the most effective asphaltene dispersant
2. System with the best dispersion of asphaltenes will be most compatible
3. Increased Compatibility gives Increased Durability

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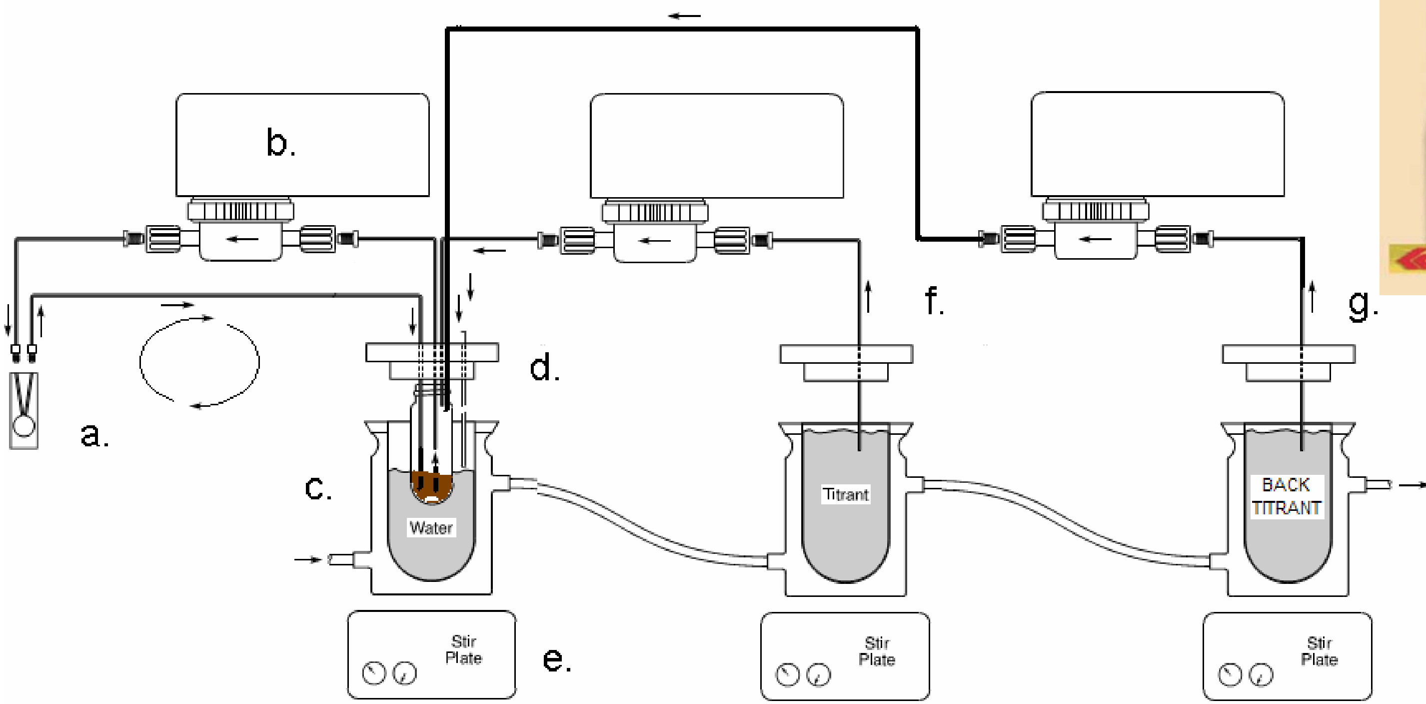
JCP 10/04/04

NCHRP 9-43 EXPERIMENTAL APPROACH COMPATIBILITY

- Samples of SHRP asphalt AAA-1 and AAD-1 were RTFO/PAV aged at 100°C/20 hr and 60°C/144 hr (homemade-RAP)
- SHRP asphalts AAB-1, AAG-1, and field asphalt YNP(Yellowstone National Park), were mixed with Fischer-Tropes hard wax, Sasobit® (1.5% by mass) (@130°C, 60-min, lab mixer in oven)
- SHRP asphalts AAB-1, AAG-1, and field asphalt YNP WMA samples were mixed with homemade-RAP at different mass concentrations (@130°C for an additional 60-min)
- Compatibility Testing of RAP-WAM mixtures employing the Automated Flocculation Titrimeter
- Estimates/measurements of maltene viscosity and asphaltene content were made to conduct mixture calculations

Koehler Instruments brand Automated Flocculation Titrimeter (AFT)
Schematic of a reversible AFT apparatus; a. sample circulation loop,
flow cell housed in a UV visible spectrometer [ASTM D6703, 2008, Heithaus, 1962],
b. metering pump, c. reaction chamber, sample vial and cap, e. stir plate,
f. titrant dispersion assembly, back-titrant dispersion assembly .

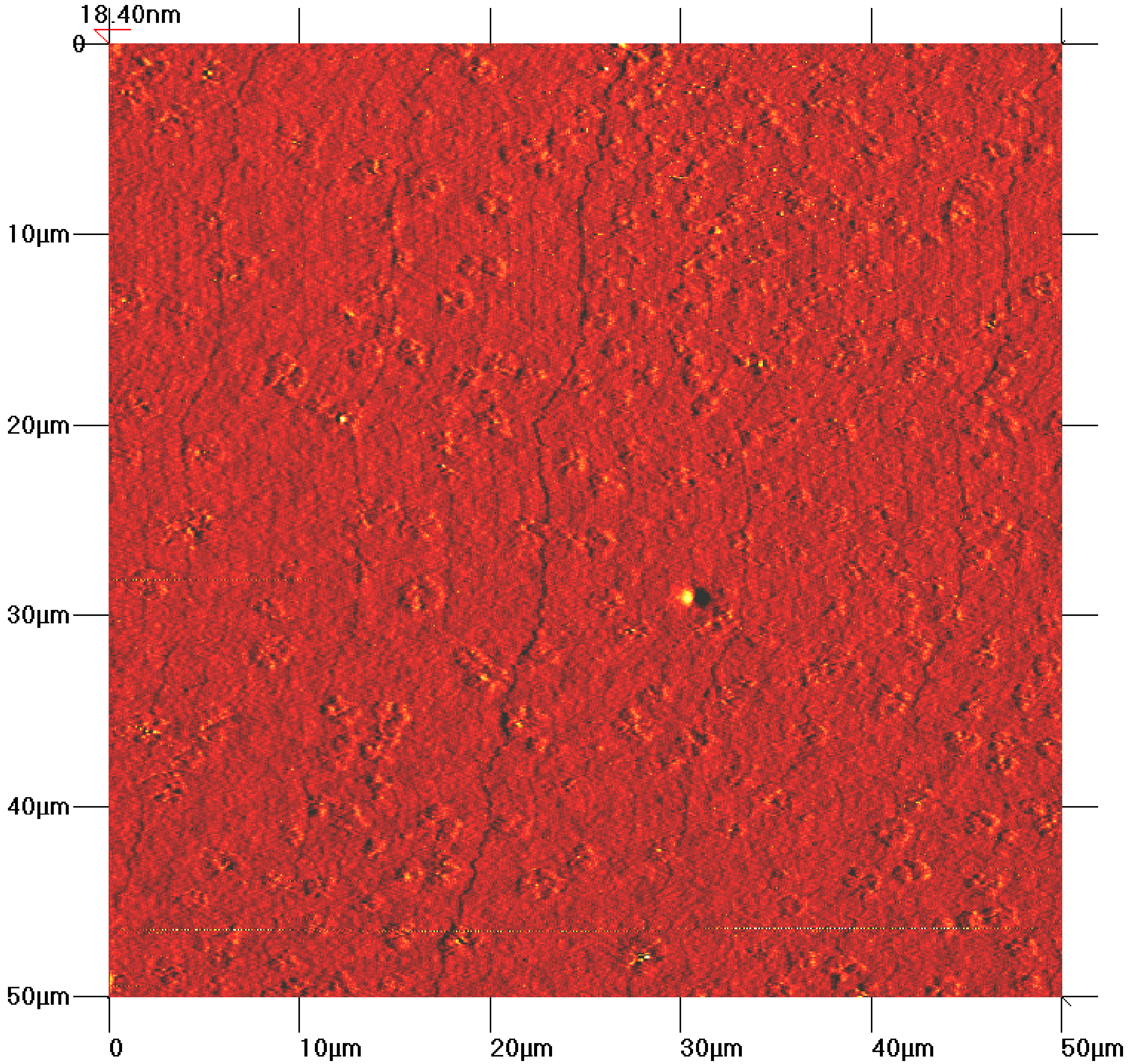


HEITHAUS COMPATIBILITY PARAMETERS

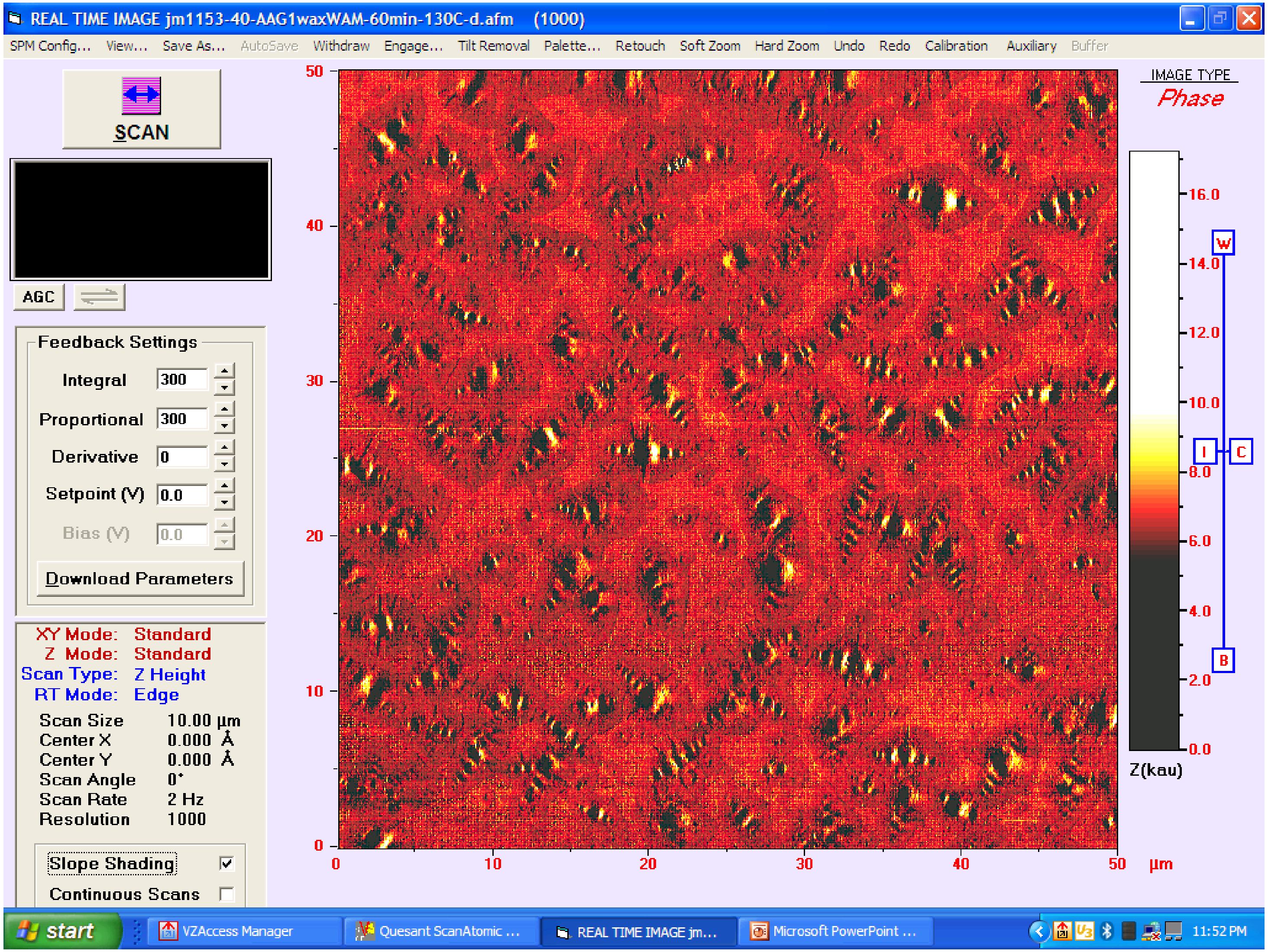
Sample	% "RAP"	p_a	p_o	P
AAB-1 Neat	0	0.42	3.75	6.44
AAB-1 + 5% Wax	0	0.57	2.30	5.39
AAB-1 + 5% Wax	5	0.55	2.01	4.48
AAB-1 + 5% Wax	15	0.47	2.71	5.13
AAB-1 + 5% Wax	25	0.45	2.85	5.22
AAB-1 + 5% Wax	50	0.42	2.99	5.17
RTFO/PAV AAA-1	100	0.43	2.68	4.71

"RAP" is Asphalt AAA-1 RTFO/PAV aged , 100°C for 20 hrs

AFM topography image of a thin film of SHRP asphalt AAG-1 (thermally annealed).



AFM profile topography scan of a WMA spin-cast thin-film coating, AAG-1/WMA(wax) spin cast onto a glass microscope slide, which was thermally annealed 20-min, 130°C.

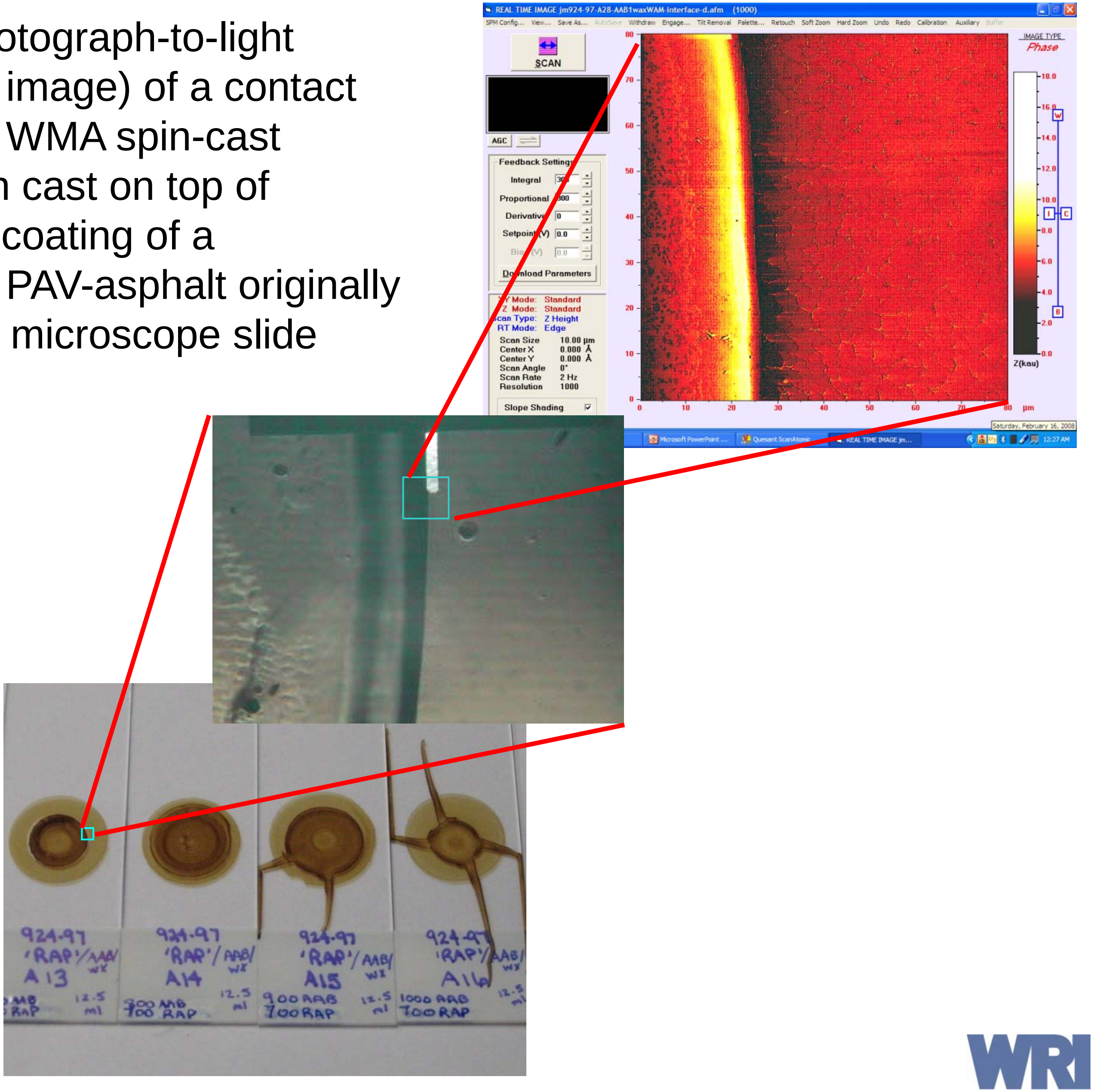


EXPERIMENTAL APPROACH WETTING

- SHRP asphalt AAD-1, RTFO aged at 60°C for 144hr (homemade-RAP) was prepared in solution (toluene, 1g/10mL) and spin-cast as a thin-film (1.0 μm) on microscope slides (Borosilicate glass)
- SHRP asphalts AAB-1, AAG-1, and field asphalt YNP prepared as WMA samples were prepared in cyclohexane(1g/10mL) then spin-cast onto RAP films. (i.e., a film-on-film system)
- Film-on-Film systems were imaged using atomic force microscopy
- In certain cases, films were heated in a 130°C oven for 20-30-min then re-imaged to observe changes in the film morphology

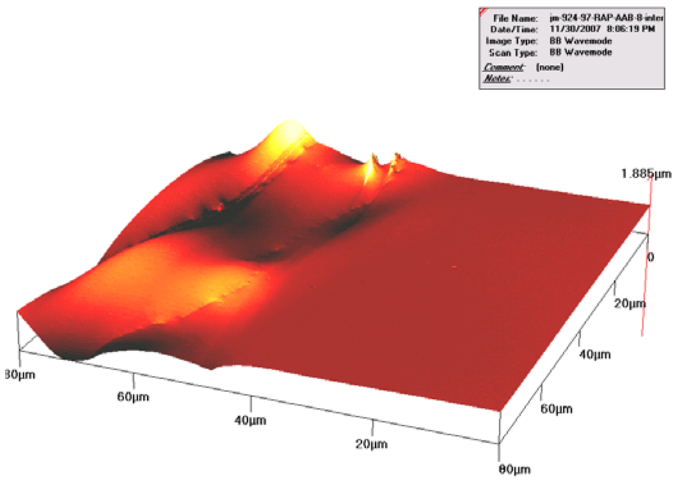
WRI

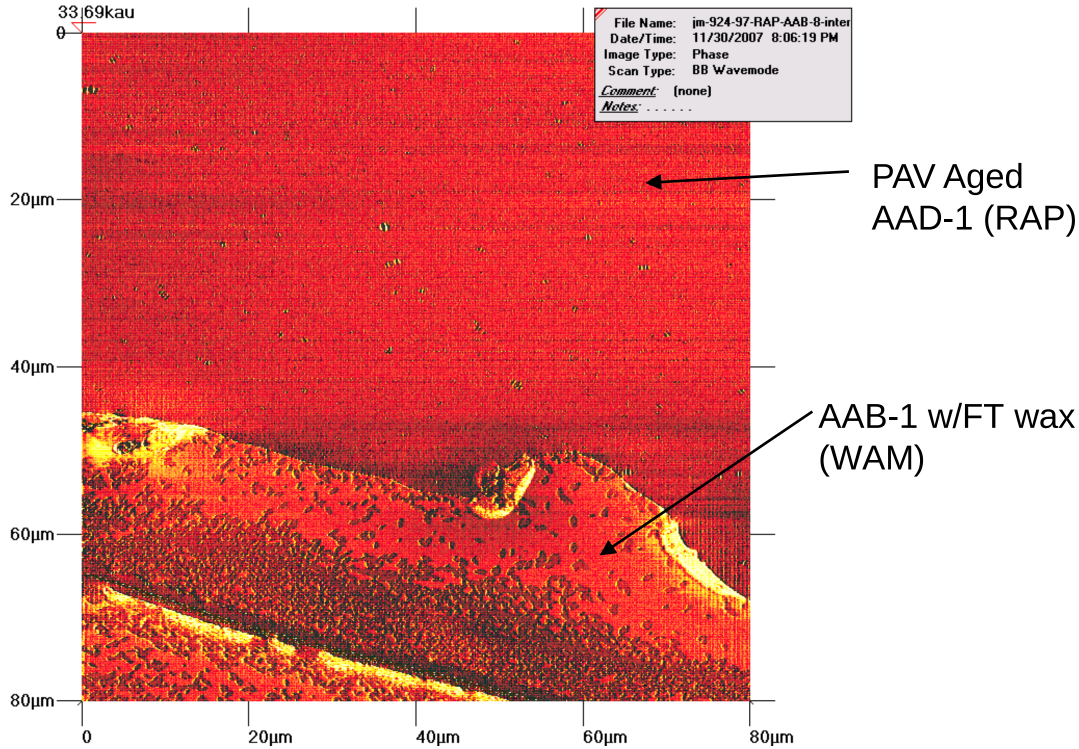
Projected views (photograph-to-light microscope-to-AFM image) of a contact interface between a WMA spin-cast thin-film coating spin cast on top of a spin-cast thin-film coating of a RAP-representative PAV-asphalt originally spin-cast on a glass microscope slide



WRI

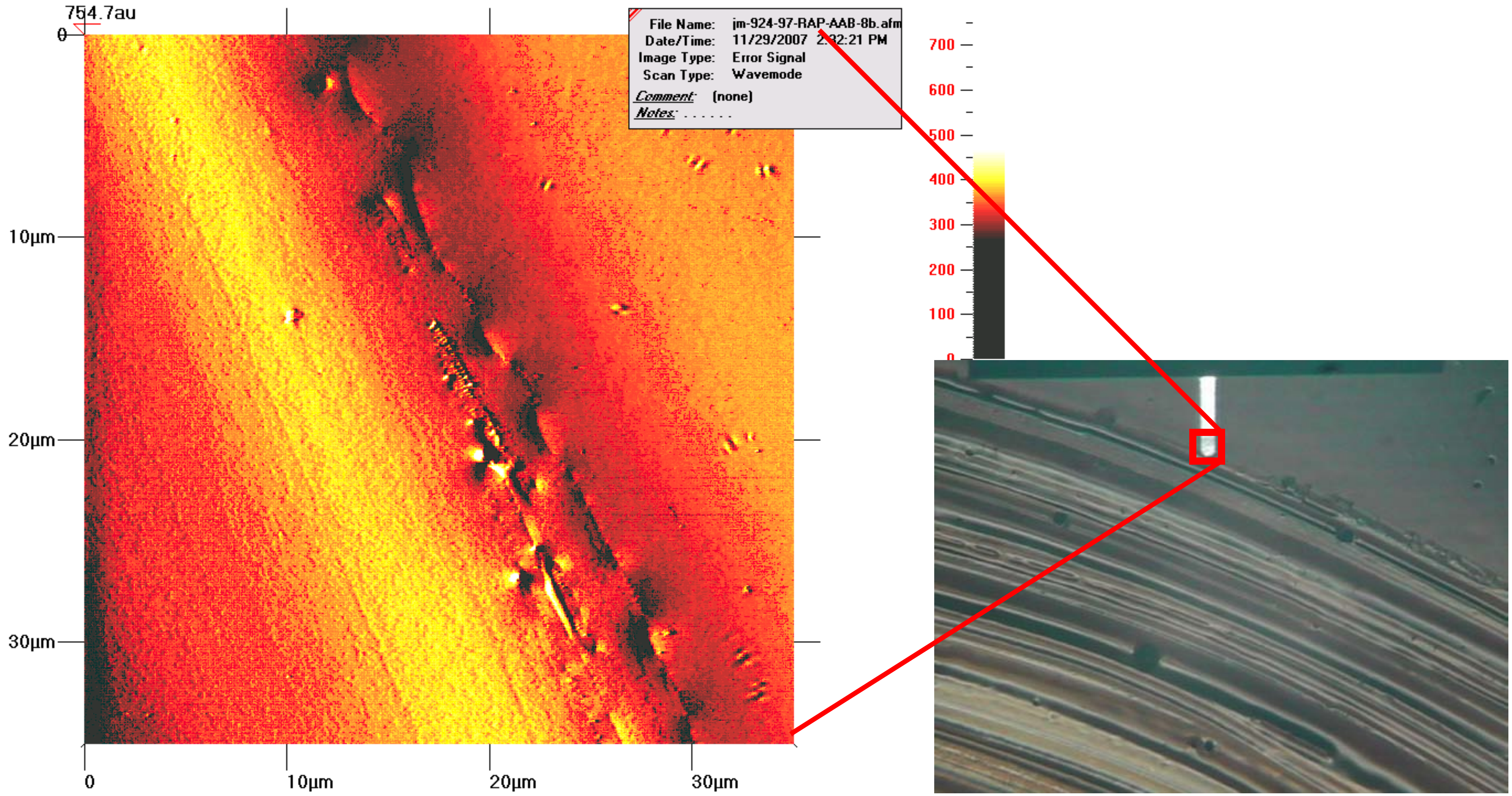
AFM profile topography (left) and phase-contrast (right) scans of an interfacial contact line between a WMA spin-cast thin-film coating spin cast onto the top of a spin-cast thin-film coating RAP-representative PAV-asphalt



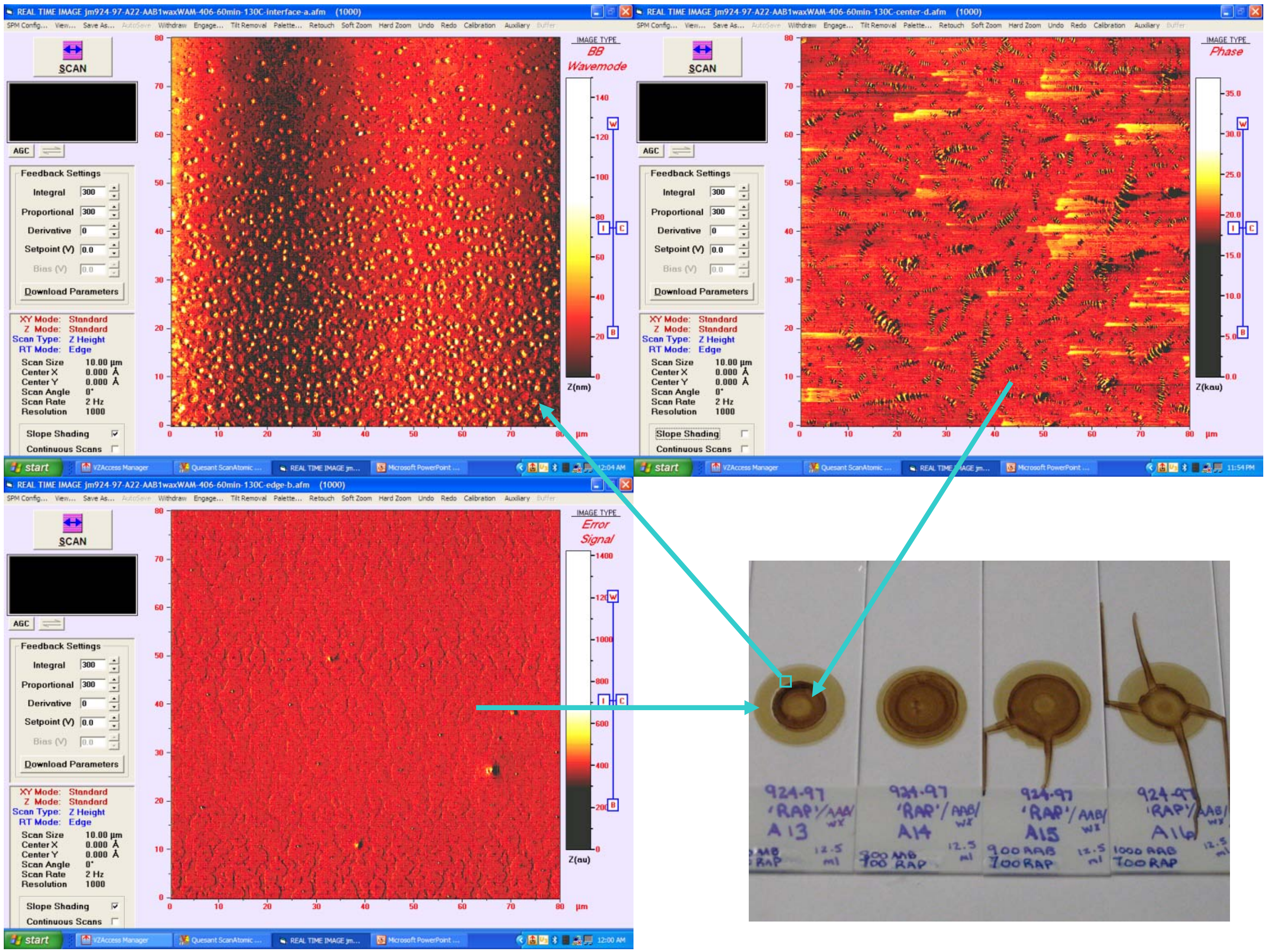


WRI

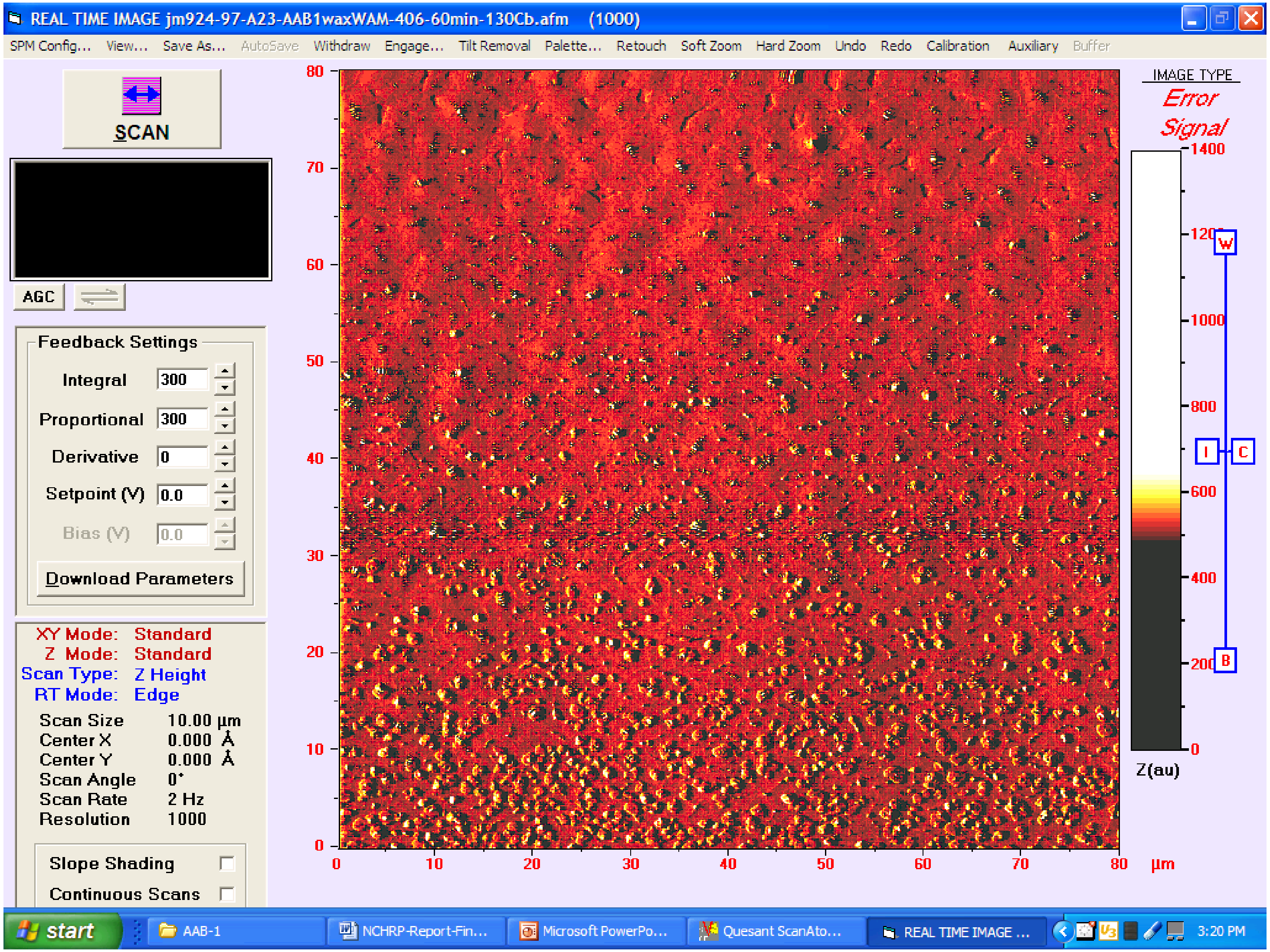
AFM profile topography (left) , and microscopic photograph view (right) depicting the interfacial contact line between a WMA spin-cast thin-film coating (AAB-1/wax) spin cast onto the top of a spin-cast thin-film coating RAP-representative PAV-asphalt (AAD-1).



AFM scans at the interfacial contact line (upper-left), at the WMA surface toward the center of the top film (upper-right), and the RAP film toward the edge (lower-left) for WMA spin-cast thin-film coating spin cast onto the top of a spin-cast thin-film coating RAP-representative PAV-asphalt after annealing films in a 130°C oven for 60 minutes .

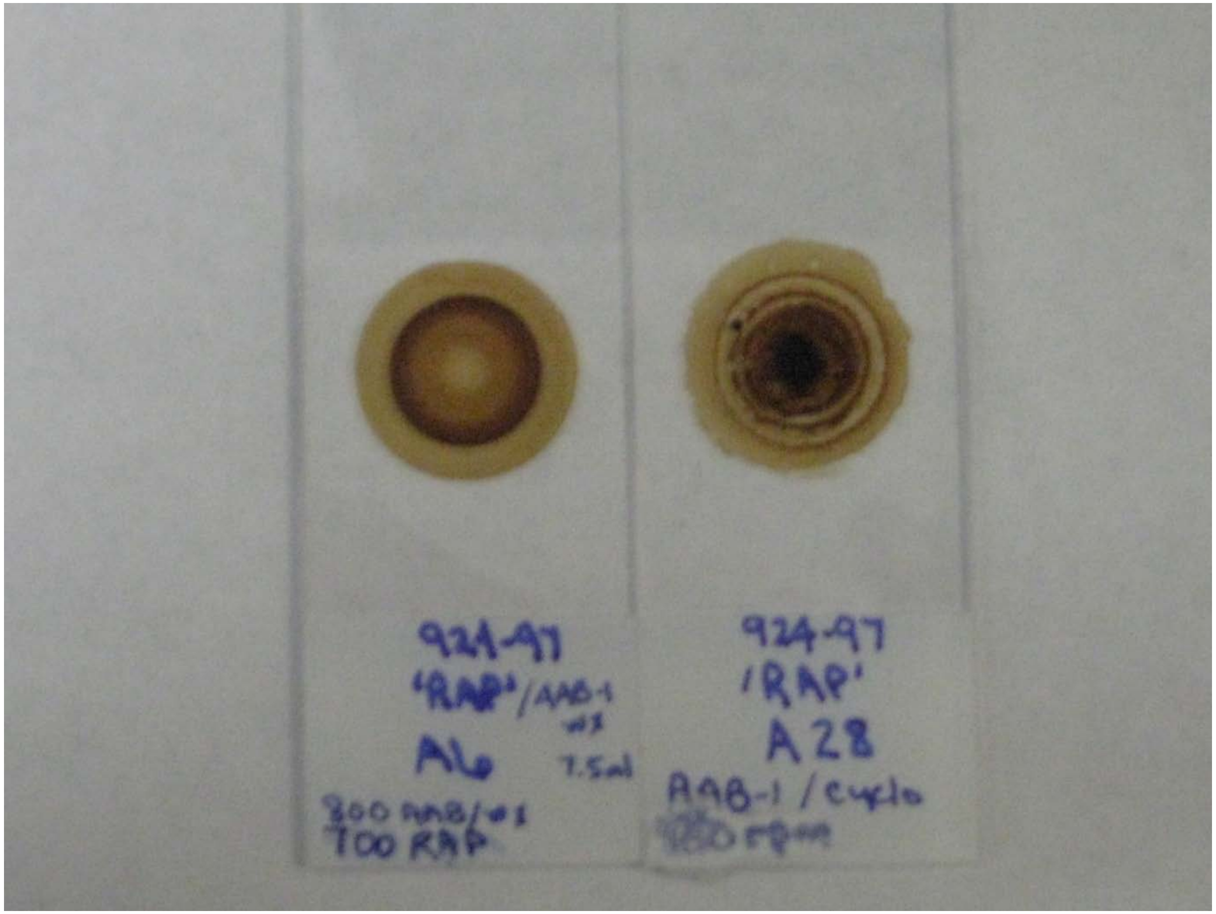


AFM scan at the interfacial contact line, between the WAM film and the RAP film, imaged after annealing the film in a 130°C oven for 60 minutes.



WRI

Photograph image of two “WMA film-on-RAP film”
AAB-1/WMA(wax) on RTFO/PAV-aged AAD-1
samples spin cast onto glass microscope slides, (left, prior to thermal annealing), (right, thermally annealed for 60 min @ 130°C).



WRI

THOUGHTS

- New and RAP asphalts mix --- Degree?
- Is compatibility of new and RAP an issue?
  - Depends
  - Compatibility decreases
  - Combined binder rheology will be a function of compatibility
- Better understanding of compatibility is needed
- If crude prices remain high, asphalt properties will probably change.
- Are RAP stockpiles checked for additives?