VOC, Waivers, other ideas:

Presentation Outline

- Some VOC ideas
- Relative Volatility
- Various Methods of Determining VOC
- Using GC with corrections is most efficient?

VOC Categories versus Sliding Scale

Category Zero-VOC (I); less volatile than MePalm (or comparable standard like dibutyl phthalate) by dried film retention experiment @ 110 ºC

Category Near Zero-VOC (II); volatility about equal to less than glycerol but more than MePalm by dried film retention experiment @ 90 ºC

Category Low VOC (III); volatility less than Texanol but more than glycerol by dried film retention experiment @ 70 ºC

Category VOC (IV); materials obviously more volatile than Texanol by TGA, NBP, dried film or other experiment

*** The GC method would be used for an initial evaluation of a sample with the above criterion applied to waive certain molecules with "non-representative" GC Rt's**

**** Any material to be considered for Category I, II or III classification should have a demonstrated favorable HES profile (*e.g.*, LD50(rat) > 1000 mg/kg, *etc.*)**

***** Additive producers interested in an official value for an additive would need to have the test(s) carried out at a validated external lab**

Willing to define a threshold level of material of defined volatility as “Zero-VOC”

* full acknowledgement by footnote that said definition is a consensus agreement rather than an actual zero-VOC (as zero-VOC is a theoretical state that can’t be obtained

{(total amount of type II * 0.05) + (total amount of type III*0.1) + TOTAL amount of IV} < 0.1%

a. Type I content; any amount
b. Type II content; less than 2%
c. Type III content; less than 1%
d. Type IV content; less than 0.1%

* some other combination adhering to a limit formula

Waiver Testing

What is the best test?

Exact parameters of retention test still TBD:

1) Temperature of bake

“relative volatility as function of T”

2) Length of bake

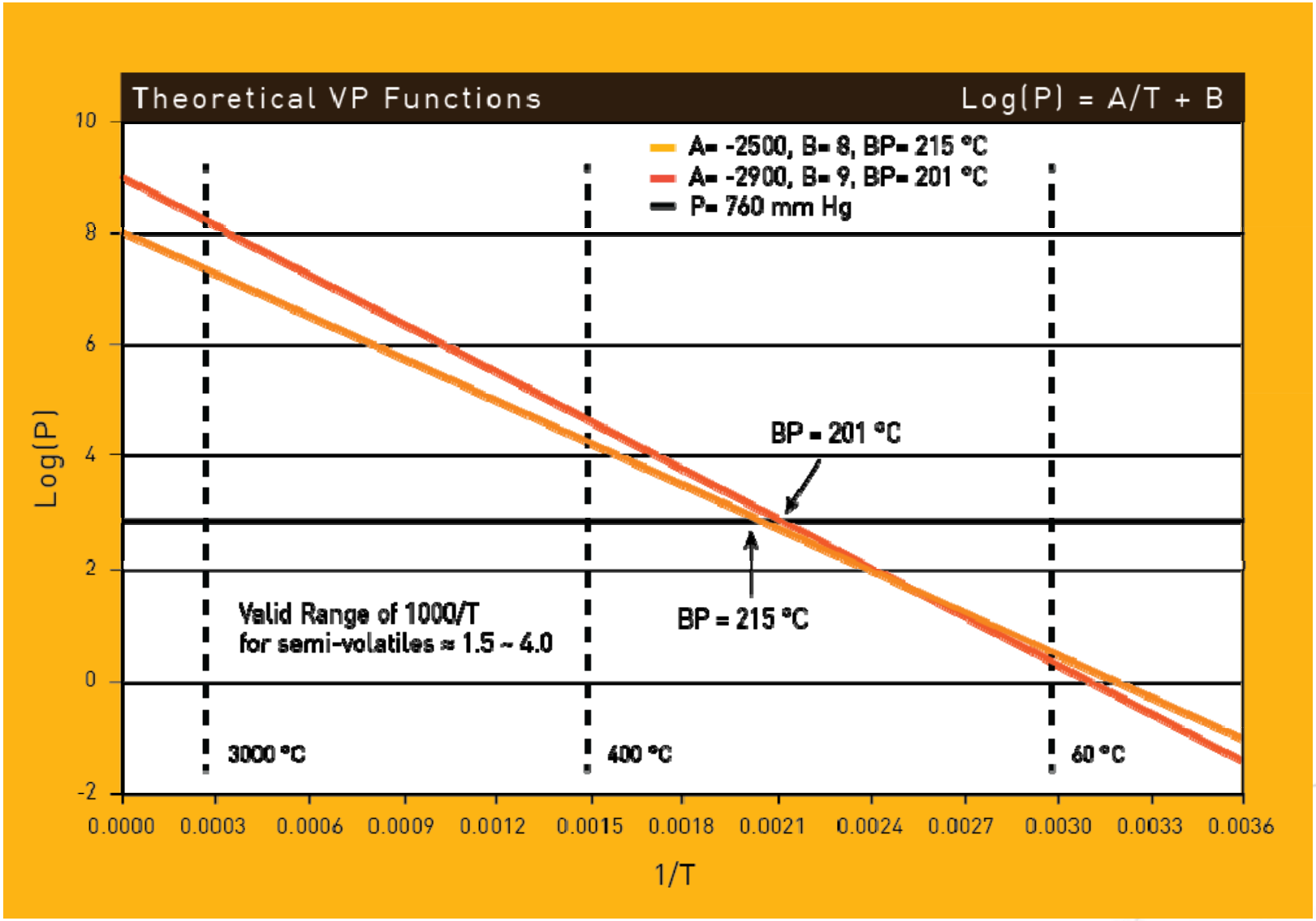
3) Type(s) of paint to use as matrix for testing additives

4) Consideration of possible incorporation of additive by covalent bonding (*e.g.*, ester formation) into resin/polymer.

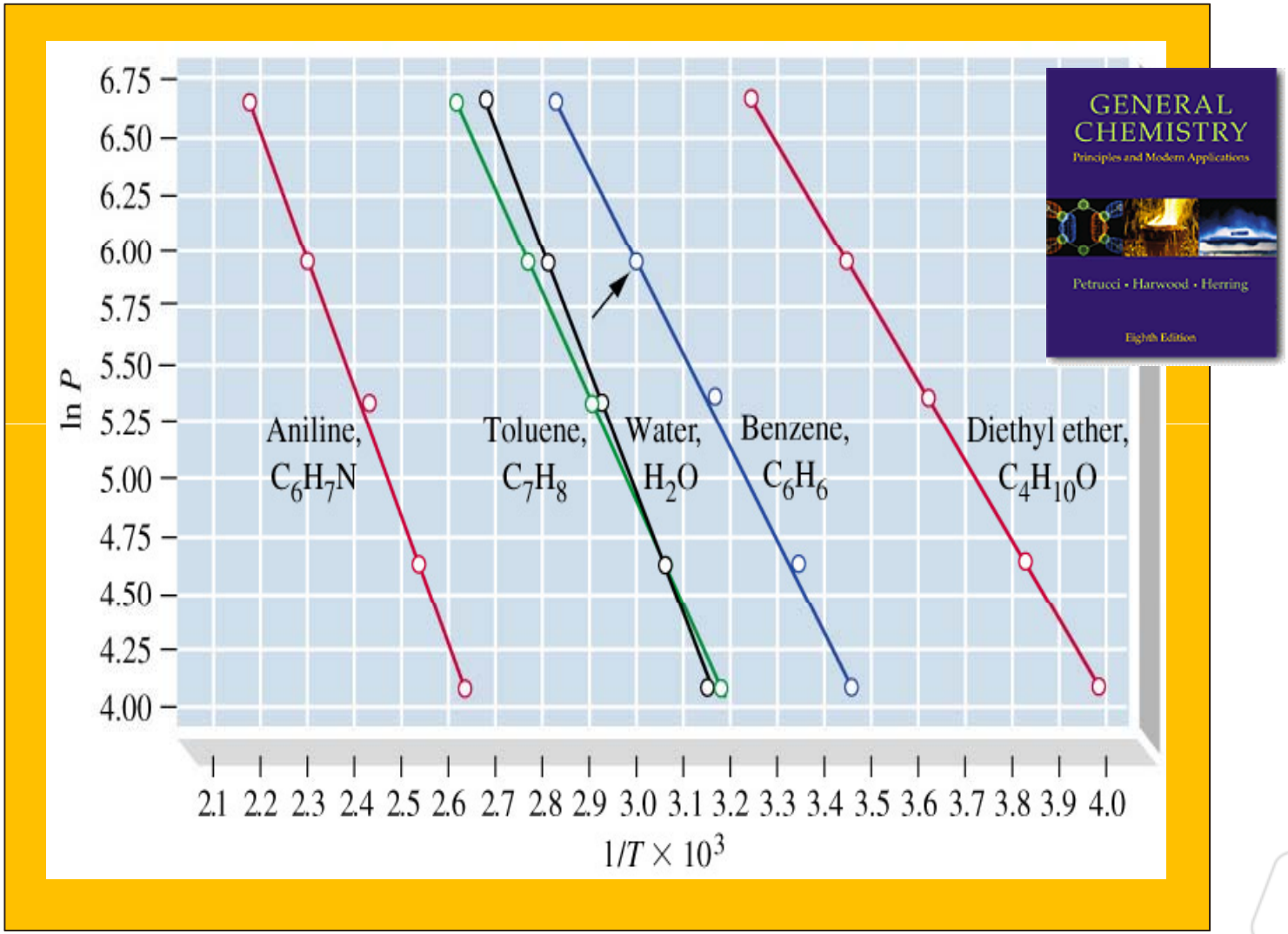
“consider if possible”

“Relative Volatility” Changes with Temperature

Theoretical VP Functions



VP Functions



VOC-or Not?

Surface Coatings International 1997 (10)

VOC – or Not?
Determination of an Important Environmental Parameter

C Nielsen, B Hogh and E Walistrom

$$T = \frac{\Delta\Delta H}{R\ln\left(\frac{P_2}{P_1}\right) + \Delta\Delta S} = \frac{\Delta A}{\ln\left(\frac{P_2}{P_1}\right) + \Delta B}$$

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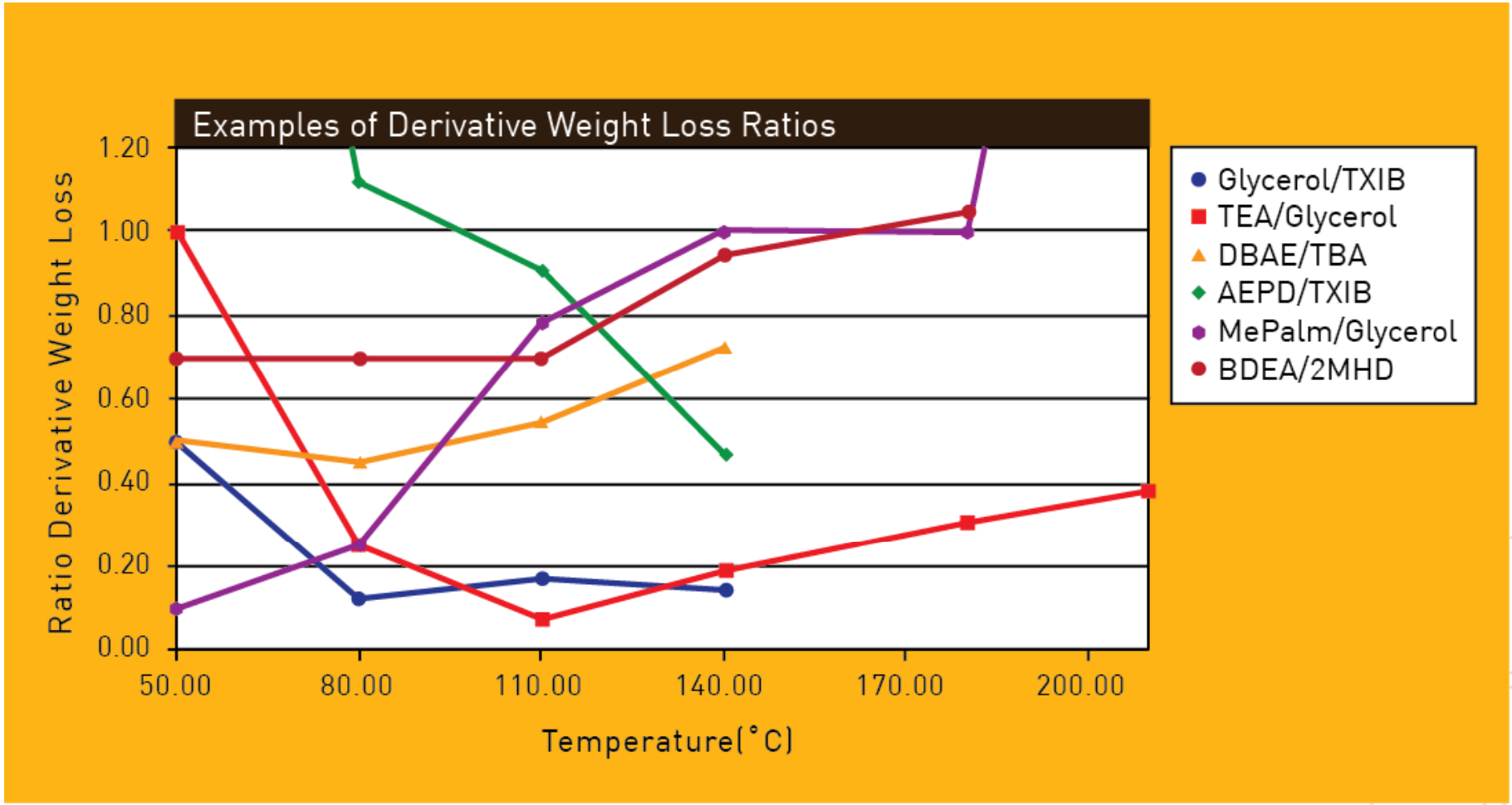
VOC or not: boiling point limits

A screening of the literature for experimental values of the boiling point temperatures and vapor pressures at 23°C gave the following:

- no organic solvents boiling below 170°C have a vapor pressure below 10 Pa at 23°C
- all solvents boiling above 260°C have a vapor pressure which is below 10 Pa at 23°C
- only three solvents, two ethers and a chlorinated compound, were found to have a vapor pressure above 10 Pa in the boiling point range 235-260°C
- for common organic solvents such as linear hydrocarbons, alcohols and polyols the boiling point is below 220°C before the solvents become a VOC according to their vapor pressure at room temperature.

ΔΔH (J/mol)	ΔΔS (J/mol-K)	VP Ratio (P_2/P_1)	T(°C)
1000	3	1.1	180
1000	3	1.0	60
1000	3	$(1.1)^{-1}$	-116
4000	10	1.3	238
4000	10	1.0	127
4000	10	$(1.3)^{-1}$	55

Examples of Derivative Weight Loss Ratios



ASTM E1868-10

(81°C, 110 minutes)

AAA	VOC (g/l)	% Evaporated	Normal BP (C)
DCHA	911 g/l	99.7%	256
BAE	883 g/l	98.9%	199
DBAE	860 g/l	99.8%	230
3-amino-4-octanol	620 g/l	78.2%	218
≈50% MDEA (aq)	197 g/l	68.3%	-
MDEA	**171 g/l**	**16.5%**	**247**
HBHEBA	151 g/l	18.1%	≈295
≈50% BDEA (aq)	**87 g/l**	**58.4%**	**-**
BDEA	69 g/l	7.5%	285
ODEA	<10 g/l (considered zero VOC)	0%	≈350

Loss-On-Drying by Thermogravimetry ASTME1868-10

LOD, Loss-On-Drying 110 min @ 81° CASTME1868-10	58.4%
Volatile Material Content ASTME1868-10	588.6g/L
VOC, Volatile Organic Compounds Content ASTME 1868-10	16.5%
Density @ 15C ASTM(D4052)	1.0075 g/ml
Water by Karl Fischer (ASTME D6304)	49.780 wt%
LOC, Loss-On-Drying 110 min @81° CASTME1868-10	16.5%
Volatile Material Content ASTME1868-10	171.8g/L
VOC, Volatile Organic Compounds Content ASTME1868-10	171.4g/L
Density @ 15oC (ASTM D4052)	1.0428 g/ml
Water by Karl Fischer (ASTM D6304)	0.040wt%

GC1/Rt and Volatility

GC 1/Rt does not strongly correlate to volatility

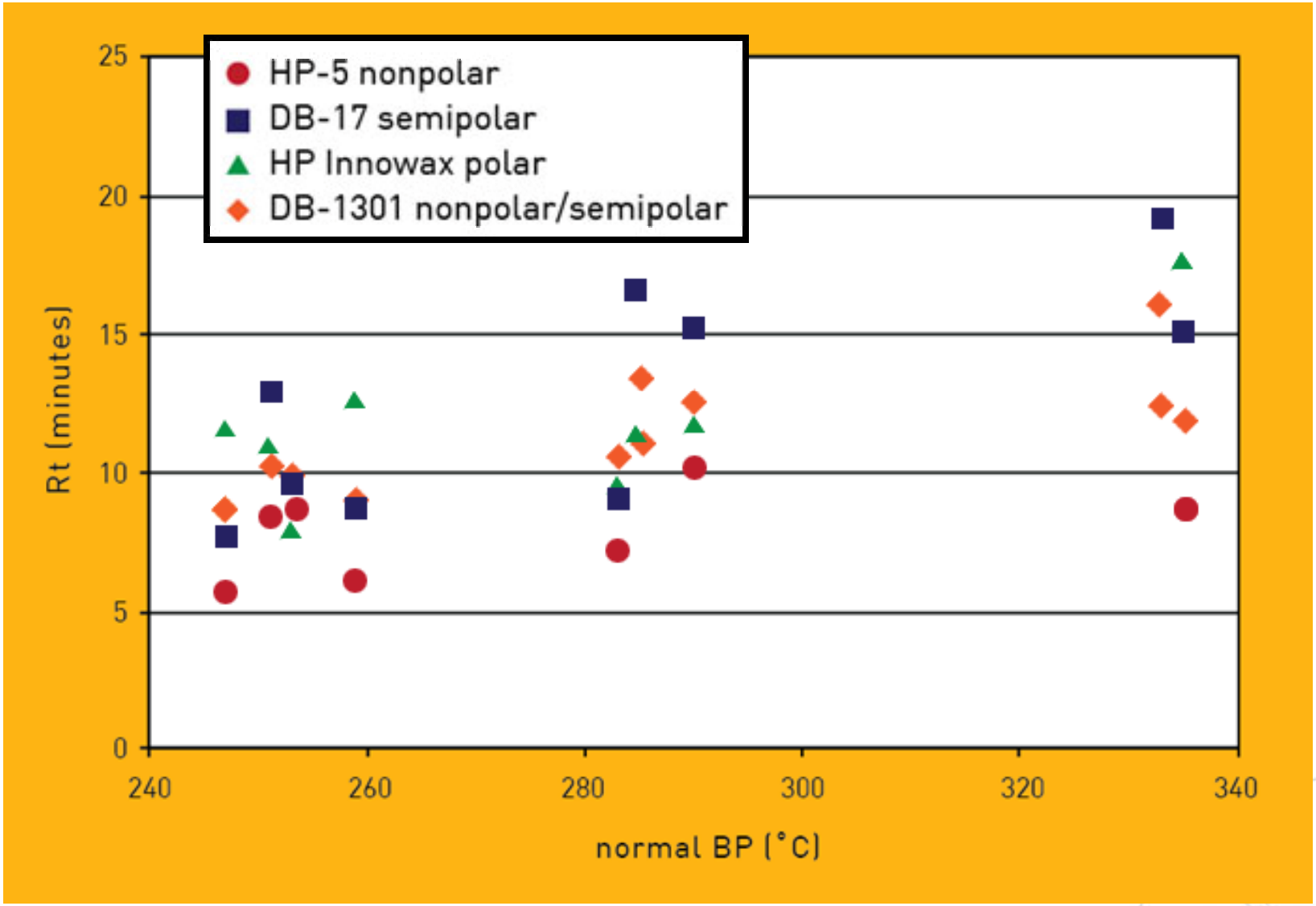
HP-5 (apolar)		
Compound	**Boiling point °C**	**RT min**
Methyldiethanolarnine	247	5.70
2-amino 2-ethyl 1, 3 propaandiol	259	6.20
Butyldiethanolarnine	283	7.30
Diethyladipate	**251**	**8.50**
Tetradecane	**253**	**8.53**
Triethanolarnine	335	8.60
BisDMAPA-PO	290	10.30
Tris-DMAPA	285	11.10

DB-1301 (apolar)		
Compound	**Boiling point °C**	**RT min**
Methyldiethanolarnine	247	8.58
2-amino 2-ethyl 1, 3 propaandiol	259	9.04
Tetradecane	**253**	**10.00**
Diethyladipate	**251**	**10.40**
Butyldiethanolarnine	**283**	**10.52**
Triethanolarnine	335	11.91
BisDMAPA-PO	290	12.55
Tris-DMAPA	285	13.42
Methylpalmitate	333	16.10

HP-Innowax (polar)		
Compound	**Boiling point °C**	**RT min**
Tretradecane	**253**	**7.94**
Butyldiethanolarnine	283	9.45
Diethyladipate	**251**	**11.05**
Tris-DMAPA	285	11.35
Methyldiethanolarnine	247	11.50
BisDMAPA-PO	290	11.70
2-amino 2-ethyl 1, 3 propaandiol	259	12.5
Triethanolarnine	335	17.70

DB-17 (semi-polar)		
Compound	**Boiling point °C**	**RT min**
Methyldiethanolarnine	247	**7.80**
2-amino 2-ethyl 1, 3 propaandiol	259	8.65
Butyldiethanolarnine	**283**	**9.05**
Tetradecane	**253**	**9.55**
Diethyladipate	**251**	**12.95**
Triethanolarnine	335	15.15
BisDMAPA-PO	290	15.25
Tris-DMAPA	285	15.50

Comparisons



Rating Volatility:

1) TGA
2) DSC
3) **Additive Retention**
4) Chamber Tests
5) Boiling Point by Ebuliometry
6) GC Rt

* Additive retention is complement of chamber and/or vapor space testing