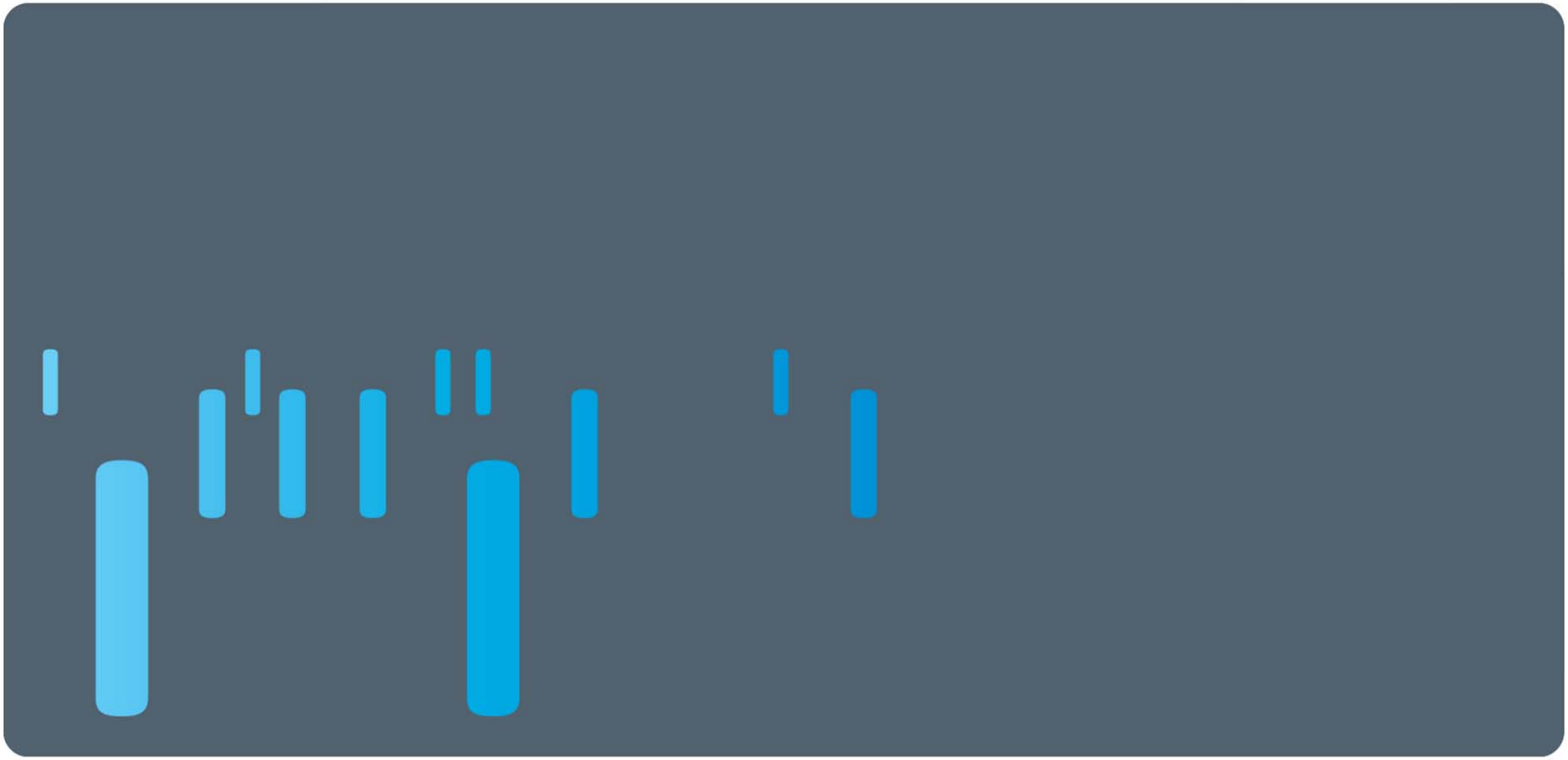
Tert-Butyl Acetate: VOC-Exempt Solvent for Coatings



Outline

- Solvent Use in Coatings
- Solvent Regulations
- Tert-Butyl Acetate as a VOC replacement
  - TBAC properties
  - Formulating compliant products with TBAC
    - Lacquers
    - Urethanes
    - Epoxies
    - Alkyds
- Conclusions

Solvent Uses in Coatings and Adhesives

- Resin Synthesis
  - Acrylics, alkyds
- Formulation
  - Resin solubilization
  - Pigment grinding
- Surface Preparation
  - Parts degreasing
- Application
  - Viscosity reduction
  - Surface wetting
  - Flow and leveling
  - Hardness development and curing
- Cleanup
  - Spray gun cleanup

Solvent Regulations Multiply…

- International Regulations
  - Montreal protocol on ozone depleting substances (ODS)
- National Regulations
  - Control of Volatile Organic Compounds (VOCs)
  - Control of Hazardous Air Pollutants (HAPs)
- State and local regulations
- Grass roots initiatives

Grass Roots: Green Building Initiatives

- EPA lacks jurisdiction to regulate indoor air quality
- Health and environmental concerns:
  - Indoor air quality (VOCs, HAPs, ozone, PM, mold, pollen, etc…)
  - Materials safety (lead, asbestos, phthalates)
  - Efficient use of resources (energy and materials)
  - Environmental impact of products (global warming, pollution, ozone depletion)
- Leading to new product certification requirements:
  - Leadership in Energy and Environmental Design (LEED rating)
  - Green Seal product standards:
    - Commercial Adhesives (GS-36)
    - Paints and Coatings (GS-11)
    - Stains and Finishes (GS-47)

Benefits of “Greener” Solvents

- Protect the environment, worker and consumer
- Reduce product liability
- Avoid impact of regulations
- Extend product life
- Expand markets and sales
- Promote a positive company image

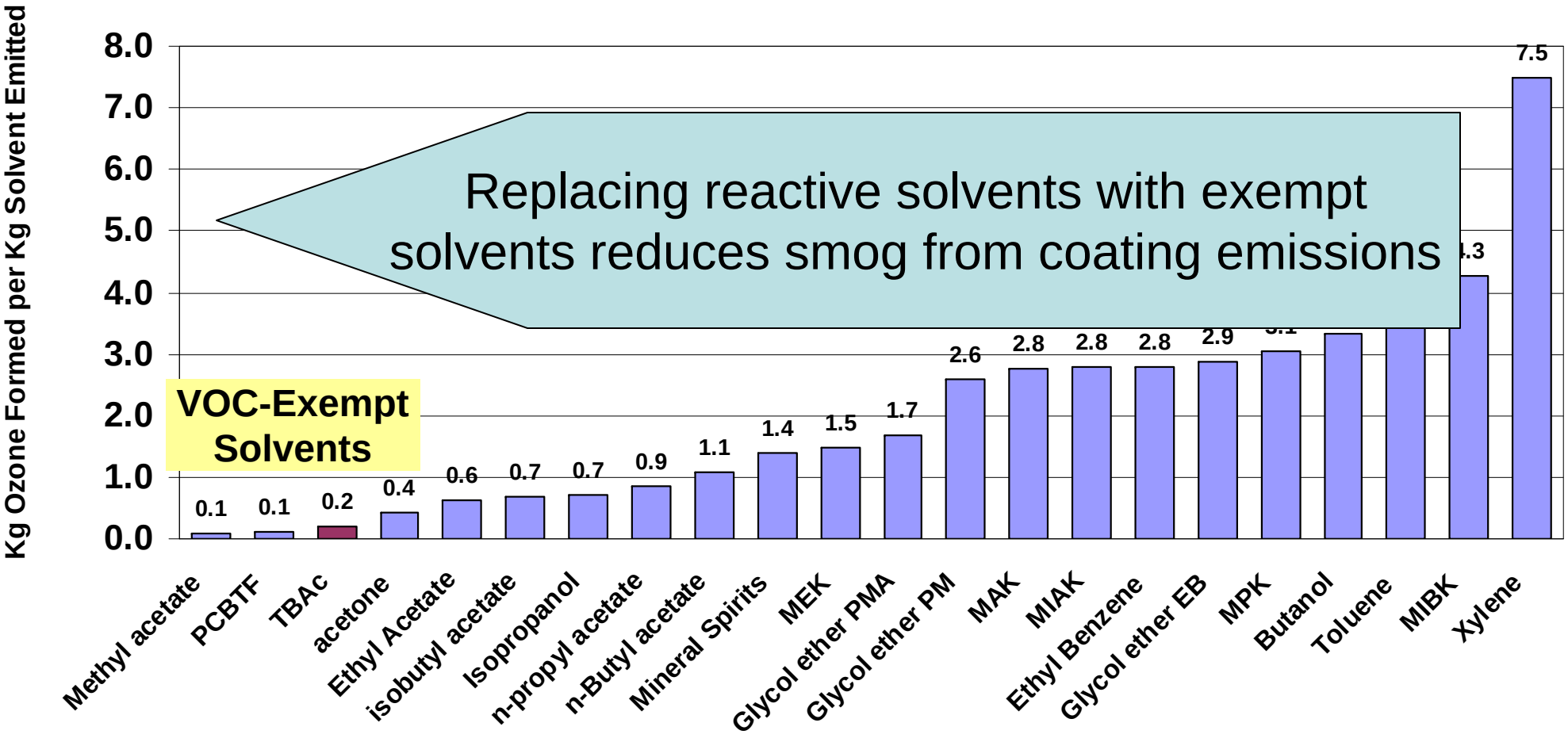
Why Regulate VOCs in Coatings?

- Volatile Organic Compounds (VOCs) contribute to ground level ozone (smog) formation
- Ozone is a lung irritant and criteria pollutant
- Major sources (biogenic, cars and truck) are difficult to reduce
- Coating operations are a minor but visible source of VOCs
- Low-VOC coating technologies exist
  - Water-based
  - Energy curable (UV and powder)
  - High solids
  - Exempt solvents

VOC Regulations in the US and Canada

- US lowers ozone standard to 75 ppb in 2008
- Effective 9/30/09, TBAC is VOC-exempt in Canada for architectural and automotive coatings
- US and Canadian Regulations based on photochemical reactivity
  - Only photochemically reactive compounds are regulated
  - Negligibly reactive compounds are exempt:
    - Acetone, methyl acetate, TBAC, many halogenated solvents.
    - Many halogenated compounds are regulated under the Montreal protocol because they deplete stratospheric ozone.

Reactivity of Solvents Varies Greatly



Based on Dr. William Carter's SAPRC-99 model
http://pah.cert.ucr.edu/~carter/reactdat.htm

Formulating with TBAC

- TBAC is a medium-fast evaporating solvent (2.8 times n-BuAc)
- Solvent blend must contain ~30% slow solvent for optimum flow, leveling and appearance (e.g. MAK, EEP, PMA, xylene)
- TBAC blush resistance superior to acetone and methyl acetate
- Slow solvents should be used for pigment grinding
- TBAC can be used with isocyanates and amido curatives
- TBAC is stable in acid-catalyzed varnishes
- Coating properties are unaffected because TBAC evaporates first

Resins Soluble in TBAC

- Acrylics and styrene acrylics
- Urethanes and isocyanates
- Alkyds and polyesters
- Modified alkyds (silicone, oil-modified urethanes, acrylic and phenolic)
- Nitrocellulose and other cellulosic resins
- Some chlorinated resins (not PVC)
- Epoxies and their amino and amido-amine curatives
- Melamine and urea-formaldehyde
- Phenolic and styrenated
- Silicones and silanes

Coating Applications

- Coatings – Solvent-based
  - Automotive refinish clearcoats
  - Industrial maintenance coatings
  - Wood lacquers and enamels
  - Aerospace coatings
  - Metal coatings
  - Concrete coatings
  - Traffic paints
- Resin solvent: alkyds, acrylic resins
- Spray equipment cleanup, thinners, degreasers

Wood Lacquer Reformulations

Components	Conventional Formulation	TBAc/n-BuAc Formulation	**TBAc/PMAc Formulation**
RS 1/2 Nitrocellulose	14.3	14.3	**14.3**
Beckosol 12-035	11.7	11.7	**11.7**
Diisononyl phthalate	3.0	3.0	**3.0**
xylene	30.5	0.0	**0.0**
MEK	10.7	0.0	**0.0**
n-butyl acetate	22.7	13.9	**0.0**
n-butanol	7.1	7.1	**7.1**
PM Acetate	0.0	0.0	**13.9**
TBAc Solvent	0.0	50.0	**50.0**
Total lbs	100.0	100.0	**100.0**
lbs VOC/lb solids*	**3.99**		**1.50**
lbs HAP/lb solids	**2.29**		**0.23**
Viscosity, cps	146	185	**102**
Dry Time, min	20	10	**10**
20 degree gloss	42	47	**49**
60 degree gloss	86	87	**89**
Whiteness index	65	67	**67**
Yellowness index	6.0	5.4	**5.4**

Lower HAPs & VOCs

Replaced xylene, MEK, and BuAc with TBAC and PMA

Dry time is reduced/ coating properties unchanged

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2K Urethane Clearcoat Formulations

Components	Conventional	TBAC-Based	Conventional High-solids	TBAC-Based
G-Cure 105 P70	100.0	100.0	50.0	50.0
JONCRYL 920	0.0	0.0	50.0	50.0
T-12 (1% in toluene)	1.9	1.9	0.3	0.3
FC 430 (10% in toluene)	0.3	0.3	0.3	0.3
HDI Trimer	28.3	28.3	33.9	25.4
IPDI Trimer	0.0	0.0	0.0	15.6
MAK	25.0	25.0	24.0	24.0
n-Butyl acetate	25.0	0.0	24.0	0.0
TBAc Solvent	0.0	25.0	0.0	24.0
Total lbs	205.5	205.5	206.5	213.6
% solids	46%	46%	51%	51%
lbs VOC/gal*	4.40	3.28	3.96	2.86

- Significant VOC reductions are possible

2K Urethane Clearcoat Properties

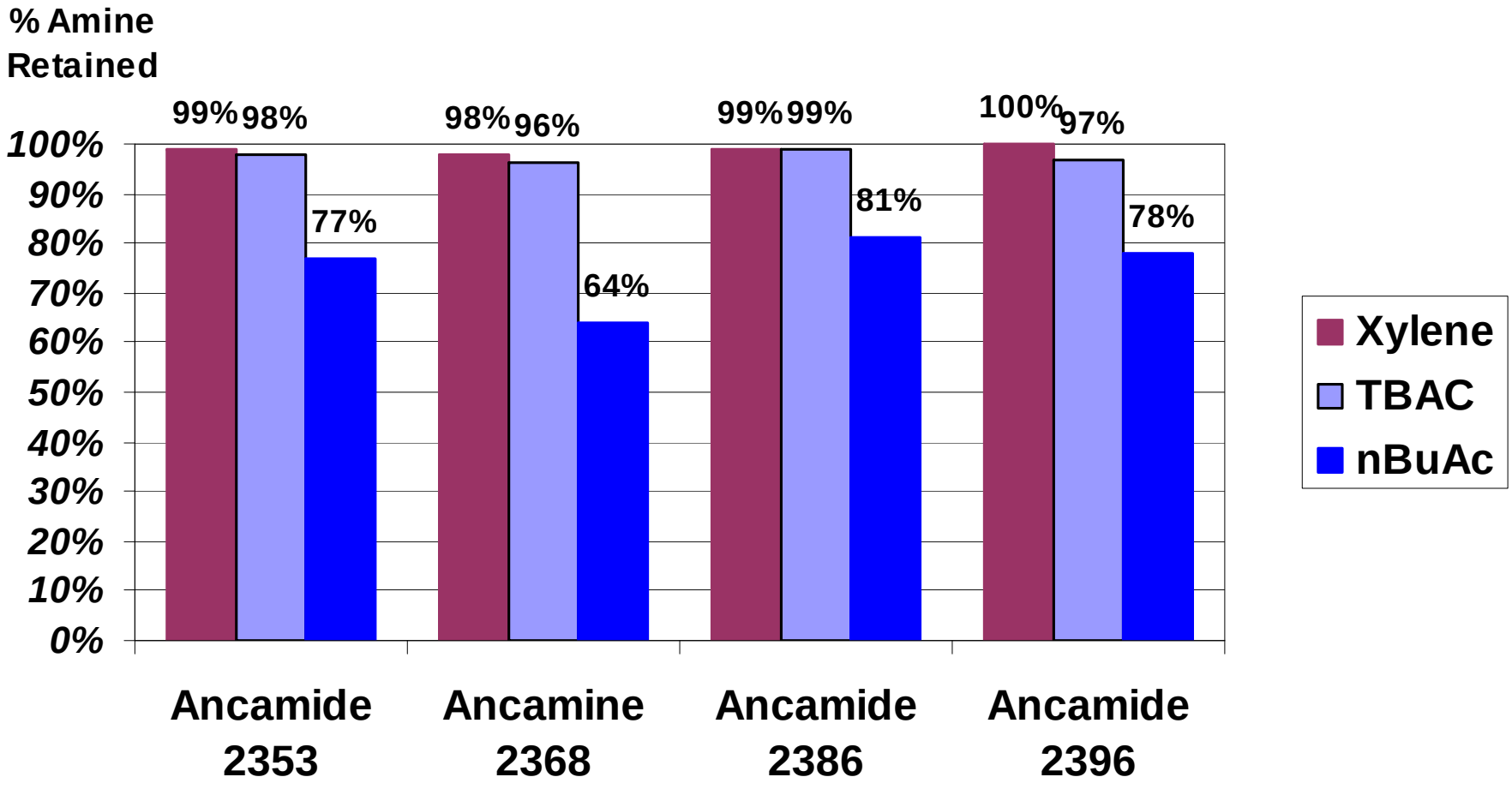
Properties	Conventional	TBAC-Based	High-solids	TBAC-Based
lbs VOC/gal*	4.40	3.28	3.96	2.86
Viscosity, sec #2 Zahn	21.2	21.1	20.9	20.8
Dry Time, hours	3.2	3.5	7	4
20 degree gloss	88	88	90	90
60 degree gloss	95	95	95	95
DOI	90	90	90	90
Reverse Impact, lbs	160	160	160	160
Direct Impact, lbs	160	160	160	160
Cross hatch adhesion, %	100%	100%	100%	100%
10% acid resistance (30 min)	pass	pass	pass	pass
100 MEK double rubs	pass	pass	pass	pass

- No change in coating performance

TBAC: Not Your Typical Ester Solvent

- Other esters react with amino and amido epoxy curatives
- Studied four types of amine and amido curatives
- Compared stability in xylene, TBAC, n-Butyl acetate
- Accelerated aging at 60°C for 30 days
  - Equivalent to one year at ambient temperature
- Measured residual amine using ASTM D2896

Storage Stability of Amine and Amido Curatives



- Xylene and TBAC show similar stability

Ancamide and Ancamine are trademarks of Air Products & Chemicals.

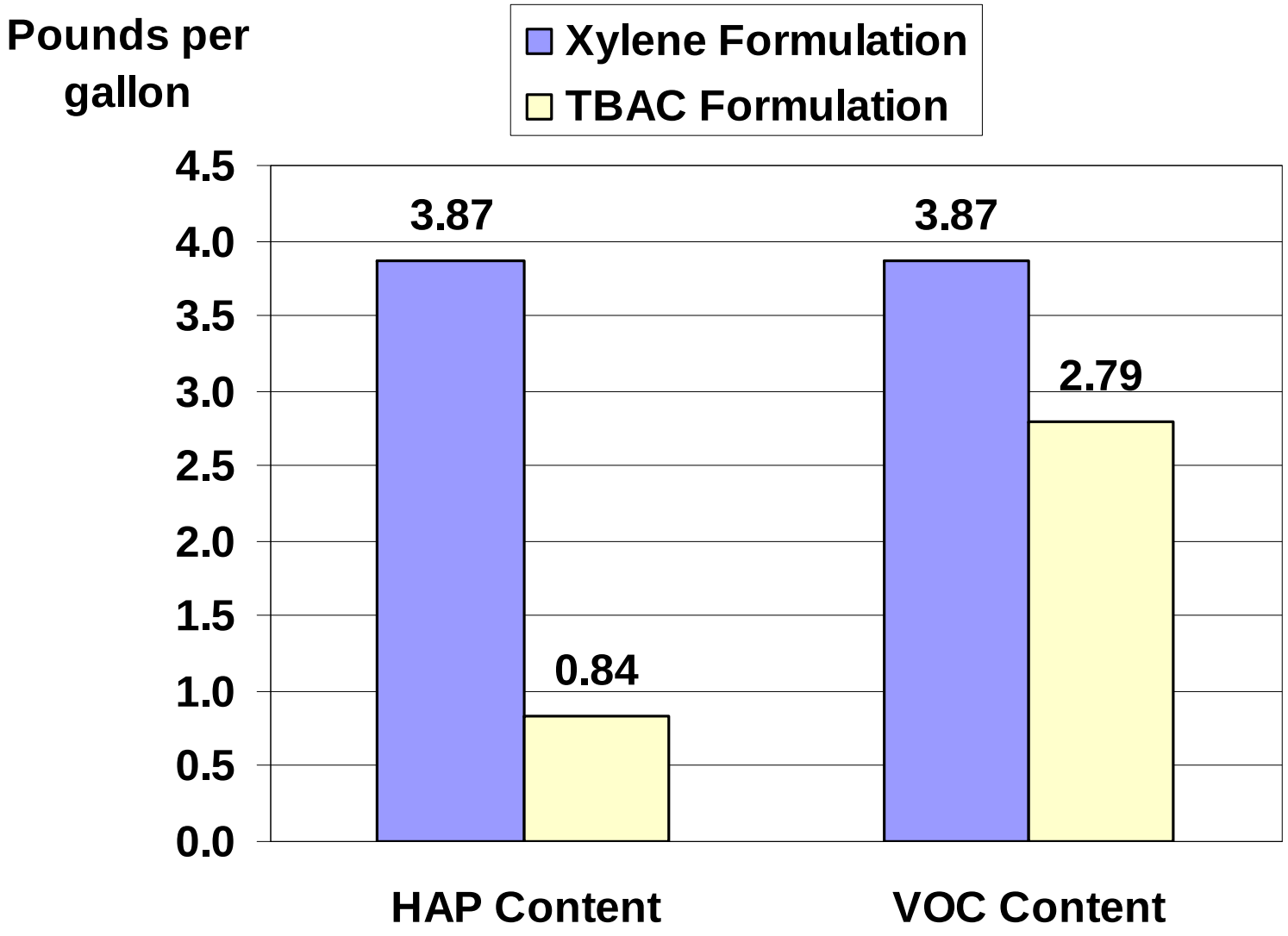
2K Epoxy Reformulation

	Xylene Formulation	TBAC Formulation
Part A		
Epon 1001X75	301	301
Pigment & fillers	260	260
Beetle 216-8	12	12
Xylene	221	
Aromatic 100		30
ARCOSOLV PM		76
TBAc Solvent		115
MAK		15
Part B		
Epicure 3115	131	131
Xylene	70	
Aromatic 100		15
TBAc Solvent		55
Formulation constants		
Volume Ratio A/B	75/25	75/25
Wt % Solids mixed	62	62

Non-HAP Solvents

Non-HAP Solvents

Effect on HAP and VOC Contents



Epoxy Coating Properties

	Xylene Formulation	TBAC Formulation
Film Properties after 7 days		
Thickness, mils	**1.93**	**1.94**
Direct Impact, in.lb	**160**	**160**
Reverse Impact, in.lb	**160**	**160**
Crosshatch adhesion	**100%**	**100%**
1/8 Mandrel bend	**pass**	**pass**
800 hours Salt Spray	**<1 mm creep**	**<1 mm creep**
ASTM B117	**7 VF blisters**	**7 VF blisters**

Cure speed & film properties were identical

Other Coating Uses for TBAC

- **Alkyd coatings for general industrial and decorative coatings**
- **Conversion varnishes for wood**
- **Resin suppliers now offering alkyd resins in TBAC:**
  - **Reichhold, CCP, Hexion, Nuplex**
- **Acrylic polyols in TBAC also available from:**
  - **CCP, Cognis, Rohm & Haas, BASF (Johnson Polymer)**

Clear Catalyzed Conversion Varnish

- Used on kitchen cabinets, furniture and flooring
- Resin System:
  - Coconut alkyd: Beckosol® 12035-E2 (65% NV in 32/4 TBAC/A100)
  - Polyol: SAA-100 (100% NV)
  - Crosslinker: Cymel U80 (98% NV)
- Solvents used:
  - TBAC, n-butanol, MAK
  - Small amounts of Aromatic 100 and Isopropanol
- Varnish formulation
  - 209 grams VOC/L
  - 50wt% solids
  - Viscosity = 75 Cps
- Varnish applied to unprimed oak boards

White Alkyd Enamel Paint*

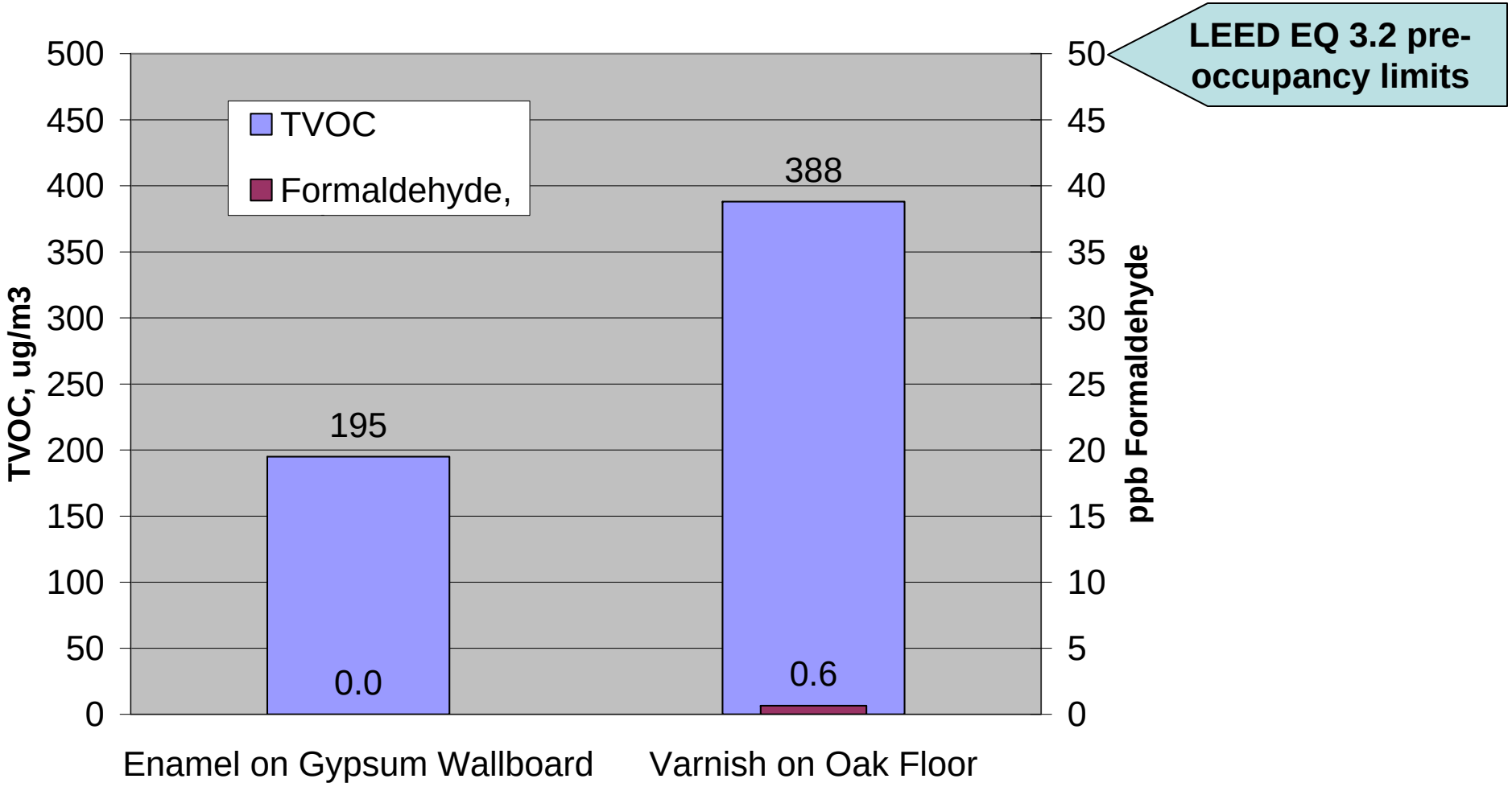
- Used on wood trim, cabinets, walls
- Resin System:
  - Soy alkyd: Beckosol® 11081-E2 (70% NV in 26/4 TBAC/A100)
- White pigment: TiO_2
- Solvents used:
  - TBAC/mineral spirits 26/10, 2% methanol
- Enamel properties
  - 250 grams VOC/L
  - 62 wt% solids
  - Viscosity = 68 KU
  - PVC: 21%
  - Pigment to binder weight ratio: 0.93
- Enamel applied to unprimed gypsum wallboard

***Enamel paint prepared by Jeff Danneman, Reichhold Chemical.**

TBAC Indoor Air Concentrations After Painting

- Model classroom parameters:
  - Room volume 231 m3
  - Area painted: walls = 94.6 m2; flooring = 89.2 m2
  - Air exchange rate = 0.9 hr-1
- Conversion varnish on floor (960 sf)
  - TBAC concentration safe (below acute RfC) after 24 hours
  - TBAC below odor detection threshold after 200 hours (8.3 days)
- White enamel on walls (1,018 sf)
  - TBAC concentration safe (below acute RfC) after 5 hours
  - TBAC below odor detection threshold within a week

TVOCs and Formaldehyde in Classroom @14 Days



- Both paints qualify for LEED credits EQ 3.2 and EQ 4.2

Conclusions

- Coating VOC regulations are spreading and becoming stricter
- VOC-exempt solvents like TBAC are useful formulating tools for cost-effective, high performance coatings
- TBAC is suitable for a wide range of coating technologies
- Solvent-based coatings require less energy to produce, apply, and cure than other low-VOC coatings
- Solvent-based coatings with TBAC can meet stringent VOC-content limits as well as qualify for green building environmental credits

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supersedes 3385-V1-0908